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# Retention and multiphase transformation of selenium oxyanions during the formation of magnetite via ferrous hydroxide and green rust

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## Abstract

Environmental and health hazards of the trace element Se are mainly related to the presence of highly mobile Se oxyanion species (oxidation states +4 and +6). In this study, we investigate the immobilization of dissolved Se oxyanions during the formation process of magnetite by the progressive oxidation of an alkaline, anoxic Fe<sup>2+</sup> system (pH 9.2). Up to initial concentrations of  $c(\text{Se})_0 = 10^{-3}$  mol/L (m/V ratio = 3.4 g/L), logRd values of xxxx demonstrate a strong retention of Se oxyanions during this mineral formation process. This Se immobilization is due to the reduction of Se(IV) or Se(VI), resulting in the precipitation of sparingly soluble Se compounds. By XRD analysis, these Se compounds were identified as crystalline elemental Se(0) that occurred in all coprecipitation products after the completed magnetite formation. The time-resolved analysis of the Se retention during the magnetite formation and detailed spectroscopic analyses (XPS, XAS) of the involved solid phases showed that the reduction takes place under the anoxic conditions in the early phase of the coprecipitation process by the interaction with iron(II) hydroxide and green rust. Both minerals represent the primary Fe(II)-containing precipitation products in the aquatic Fe<sup>2+</sup> system and the precursor phases of the later formed magnetite. Spectroscopic and electron microscopic analysis prove that this early Se interaction leads to the formation of a nanoparticulate iron selenide phase [FeSe], which is oxidized and transformed into trigonal gray elemental Se during the progressive oxidation of the system. Regarding the retention behavior of Se, it is irrelevant whether the oxidation of the

35 meta-stable iron oxide phases leads to the formation of magnetite only or also to other iron  
36 oxide phases like goethite. This reductive precipitation of Se induced by an interaction with  
37 metastable Fe(II)-containing iron oxide minerals should affect the mobility of Se oxyanions in  
38 contaminated environments, including the behavior of <sup>79</sup>Se in the near-field of HLW  
39 repositories.

## 40 1 Introduction

41 The trace element selenium (Se) is of special concern because of the extremely fine line between  
42 its opposing properties: At low concentrations, it is an essential nutrient for many organisms,  
43 at slightly higher quantities, however, it becomes a toxic contaminant (Lenz and Lens, 2009).  
44 In addition, Se occurs in high-level nuclear waste (HLW) in the form of the long-lived, harmful  
45 radionuclide <sup>79</sup>Se, which may play a crucial role for the long-term safety assessments of deep  
46 geological repositories (De Cannière et al., 2010; Jörg et al., 2010).

47 In nature, Se occurs in five different oxidation states (-II, -I, 0, IV, VI). Of particular relevance  
48 are the two higher oxidations states, where Se forms the oxyanions selenite [Se(IV)] and  
49 selenate [Se(VI)]. In aquatic systems, both Se oxyanions occur in the form of well soluble  
50 species, which are generally highly mobile due to their limited interaction with geological  
51 materials (Grambow, 2008; Fernández-Martínez and Charlet, 2009). By contrast, Se species of  
52 the oxidation states Se(-II), Se(-I) and Se(0) are characterized by forming sparingly soluble  
53 compounds like metal selenides or elemental Se (Séby et al., 2001). The oxidation state is  
54 therefore the key factor determining the biochemical behavior of Se, since parameters such as  
55 solubility, mobility, bioavailability and toxicity mainly depend on the occurrence of dissolved  
56 Se species (Dhillon and Dhillon, 2003; Winkel et al., 2015; Nothstein et al., 2016). For this  
57 reason, environmental health and safety hazards of Se are primarily associated with the presence  
58 or absence of Se oxyanions.

59 Regarding the oxidation state of Se in HLW, recent research has demonstrated that Se occurs  
60 as Se(-II) in spent nuclear fuel (Curti et al., 2014; Curti et al., 2015). The formation of mobile  
61 Se species is therefore rather unlikely given the predicted reducing conditions of most HLW  
62 repositories. The expected predominant Se oxidation state in vitrified HLW arising from  
63 nuclear fuel reprocessing plants, however, is Se(IV) in the form of selenite groups (Bingham et  
64 al., 2011). Moreover, it cannot be fully excluded that oxidation processes induced by long-term  
65 irradiation could also lead to a transformation to Se(VI) or selenate, respectively (Bingham et  
66 al., 2011). The oxidation state of Se and the associated dominant Se species in HLW is therefore  
67 dependent on the waste form.

68 The iron oxide magnetite [Fe<sub>3</sub>O<sub>4</sub>] is widespread in nature and a common mineral in sediments  
69 and soils. Furthermore, magnetite is the most likely corrosion product of the steel canisters  
70 (technical barrier) under the expected alkaline, anoxic conditions in the near-field of a HLW  
71 repository (Smailos et al., 1992; Miller et al., 2000; Wersin et al., 2003; Smart et al., 2008). The  
72 corrosion of elemental iron to magnetite is, however, not a single reaction, but involves an  
73 intermediate stage, which is associated with the presence of precursor phases such as iron(II)  
74 hydroxide or green rust (Cornell and Schwertmann, 2003). Due to the relevance of magnetite  
75 and its precursors for various environments, their influence on the behavior of dissolved Se  
76 oxyanions has been investigated in previous studies. It was found that mineral phases that  
77 contained a reduced iron species are basically able to reduce Se oxyanions under anoxic  
78 conditions. Besides magnetite (Scheinost and Charlet, 2008), this includes the minerals iron(II)  
79 hydroxide (Murphy, 1988; Zingaro et al., 1997), green rust (Myneni et al., 1997; Johnson and  
80 Bullen, 2003; Scheidegger et al., 2003) as well as elemental iron (Olegario et al., 2010; Yoon  
81 et al., 2011; Liang et al., 2013), iron(II) sulfides (Bruggeman et al., 2005; Scheinost et al., 2008)  
82 or Fe<sup>2+</sup> adsorbed on clay minerals (Charlet et al., 2007). Since reduction of Se oxyanions causes  
83 the formation of sparingly soluble compounds, this interaction generally results in the  
84 immobilization of Se. These Se compounds are either elemental Se or iron selenides, whereby  
85 the nature of the products varies depending on the involved iron phases, the hydrochemical  
86 conditions, and the reduction kinetics. Especially the latter seems to be the main cause why the  
87 majority of the above-mentioned studies identified elemental Se (Murphy, 1988; Myneni et al.,  
88 1997; Zingaro et al., 1997; Scheidegger et al., 2003; Bruggeman et al., 2005; Charlet et al.,  
89 2007; Chen et al., 2009) whereas only a few studies proved the occurrence of iron selenides  
90 (Scheinost et al., 2008; Scheinost and Charlet, 2008; Olegario et al., 2010). This can be  
91 attributed to the fact that a reduction to Se(-II) and formation of iron selenides is limited to a  
92 rapid reduction of Se oxyanions (Scheinost et al., 2008).

93 However, retention of Se oxyanions during the magnetite formation process has never been  
94 investigated in detail, although it is probable that both also interact at this stage. This applies,  
95 for instance, to the formation of magnetite due to the corrosion of elemental iron, which  
96 represents an important process in the above-mentioned surroundings of geological  
97 repositories. Another example is the formation of magnetite caused by biologically or  
98 abiotically induced transformation of unstable iron minerals in natural environments like  
99 sediments or soils (Kämpf et al., 2011; Blume et al., 2016). Such mineral formation processes  
100 may affect the immobilization of Se oxyanions, which has been demonstrated for the formation  
101 of hematite via ferrihydrite (Börsig et al., 2017).

102 In this study, we examined the interaction processes that lead to an immobilization of Se(IV)  
103 or Se(VI) during the formation and growth of magnetite or its precursor phases. Aim of this  
104 work was to identify and to characterize the Se retention mechanisms and to assess retention  
105 capacity and stability. To achieve this, we performed coprecipitation experiments with  
106 magnetite and Se oxyanions at alkaline pH, which is especially relevant for the near-field of  
107 HLW repositories. Furthermore, another key aspect was to investigate in which way a change  
108 of the redox conditions affects the Se retention. For this reason, the redox conditions were  
109 changed from initial anoxic to later oxic conditions during the experiments. With the help of  
110 hydrochemical data and a detailed analysis of the precipitation products by spectroscopic and  
111 electron microscopic methods, we were able to prove that two main redox processes were  
112 involved in the Se immobilization.

## 113 2 Materials and Methods

### 114 2.1 Synthesis of magnetite

115 Magnetite (Mt) was synthesized in the laboratory by using a modified method of Schwertmann  
116 and Cornell (2000). This method was originally designed for the preparation of goethite (Gt)  
117 and based on the progressive oxidation of an anoxic aquatic  $\text{Fe}^{2+}$  system. By increasing the  
118 solution pH from neutral to alkaline conditions, it was possible to inhibit the formation of  
119 goethite and to produce pure magnetite. One advantage of this method is that the preparation of  
120 magnetite by oxidizing an initially aquatic  $\text{Fe}^{2+}$  system is more suitable to simulate the  
121 formation of magnetite in nature than a preparation based on the mixing of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$   
122 solutions. For the synthesis of magnetite 5 g of  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$  were dissolved in 500 ml  $\text{N}_2$ -  
123 degassed Milli-Q water (~pH 3.5). After the addition of 55 ml 1 M KOH and the immediate  
124 precipitation of a bluish green compound (~pH 8), the suspension was titrated and buffered with  
125 25 ml of 1 M  $\text{NaHCO}_3$  solution, which led to a pH value of ~8.5. All solutions were made of  
126 analytically pure grade chemicals and de-ionized,  $\text{N}_2$ -degassed Milli-Q water ( $18.2 \text{ M}\Omega\text{cm}^{-1}$ ).  
127 Continuous stirring during and after the mixing resulted in a progressive oxidation of the anoxic  
128  $\text{Fe}^{2+}$  system by atmospheric oxygen. Within the total reaction time of 48 hours, this input of  
129 oxygen caused the transformation of the bluish green precipitate in a magnetic black mineral  
130 phase. In order to analyze the initially formed precipitation products, the synthesis process was  
131 terminated after 30 minutes and 3 hours, respectively. With about 2 g precipitated iron oxide  
132 forming, the mass to volume ratio (m/V) between magnetite and the aqueous solution was  
133 approx. 3.4 g/L in these batch experiments. At the end of the 48 hour reaction time, the black  
134 precipitates were decanted and centrifuged. While a sample of the solutions was taken for the

135 analysis of the Fe concentration and pH, a part of the solids were washed three times with  
136 Milli-Q water to remove  $\text{Cl}^-$  and  $\text{HCO}_3^-$  impurities. The washed magnetite samples were then  
137 dried at  $40^\circ\text{C}$ . The remaining part of the solid sample was dried without prior washing with  
138 Milli-Q water in order to preserve the surface characteristics of the sample. After drying, the  
139 aggregated particles were ground with an agate mortar and stored until analysis. In case of the  
140 initial precipitation products (magnetite precursor), the samples were not washed or dried after  
141 the respective reaction time but were stored in their original synthesis solution. This was done  
142 to avoid further oxidation and crystallization processes after the terminated reaction with  
143 oxygen.

## 144 2.2 Coprecipitation experiments

145 The general procedure as well as the subsequent sample preparation of the coprecipitation  
146 experiments were almost identical to those of the magnetite synthesis described above. To  
147 investigate the behavior of Se(IV) or Se(VI) during the coprecipitation with magnetite, various  
148 volumes of Se stock solutions were added to the dissolved  $\text{Fe}^{2+}$  prior to the mineral  
149 precipitation. Se stock solutions were prepared by dissolving defined quantities of  $\text{Na}_2\text{SeO}_3$  or  
150  $\text{Na}_2\text{SeO}_4 \cdot 10 \text{H}_2\text{O}$  in  $\text{N}_2$ -degassed Milli-Q water to receive total Se(IV) or Se(VI)  
151 concentrations of 0.1 mol/L and 1.0 mol/L. Se stock solution was added to obtain initial Se  
152 concentrations of  $10^{-4}$  -  $10^{-2}$  mol/L after the mixing of all solutions (m/V ratio = 3.4 g/L). These  
153 relatively high Se concentrations were necessary to obtain sufficiently high Se concentrations  
154 in the solid samples for the subsequent solid state analyses. After the completed mineral  
155 formation, the residual Se concentration in solution was analyzed to calculate the amount of  
156 removed Se(IV) or Se(VI). The maximum reaction time of the coprecipitation studies was also  
157 48 hours. For the time-resolved investigation of the Se(IV) and Se(VI) retention behavior,  
158 however, precipitates and solutions were collected and analyzed also after reaction times of 30  
159 minutes and 3 hours.

## 160 2.3 Analytical techniques

161 The Se and Fe concentrations in the aqueous phase were determined by ICP-OES (Varian  
162 715ES) or ICP-MS (X-Series 2; Thermo Fisher Scientific Inc.) depending on the solution  
163 concentrations. X-Ray Diffraction (XRD) was used for analysis of the purity and mineral  
164 composition of the synthesized solid materials and was performed on a Bruker D8 Advance X-  
165 ray diffractometer ( $\text{Cu K}\alpha$ ). In order to calculate the specific surface areas (SSA) of magnetite  
166 and its precursor phase, BET measurements were performed using a Quantachrome Autosorb  
167 1-MP. The total Se content of the solid phases was determined by polarized Energy Dispersive

168 X-ray Fluorescence Spectroscopy (pEDXRF) using an Epsilon 5 (PANalytical). Electron  
169 microscopy with energy dispersive X-ray spectroscopy was used to characterize the  
170 morphology, the particle size, and the detailed chemical composition of the solid phases. Images  
171 were recorded using a LEO 1530 (Zeiss Inc.) SEM with a NORAN System SIX (Thermo  
172 Electron Corp.) EDX-System or alternatively via a FEI Talos F200X analytical S/TEM  
173 equipped with an integrated ChemiSTEM EDX system with four windowless silicon drift  
174 detectors. To examine the Se oxidation state and to identify elemental composition of the  
175 surface area, X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a  
176 PHI 5000 VersaProbe II (ULVAC-PHI Inc.). Detailed information about measurement  
177 parameters and sample preparation are described in the Supporting Information.

178 X-ray Absorption Spectroscopy (XAS) analysis was carried out on selected Se-bearing samples  
179 to identify the Se oxidation state as well as the nature of the molecular Se structure. Se K-edge  
180 X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine-  
181 Structure (EXAFS) spectra were collected at the Rossendorf Beamline (ROBL) at ESRF  
182 (Grenoble, France). Measurement parameters and sample preparation are described in detail in  
183 the Supporting Information. The XAS data reduction, including dead time correction of the  
184 fluorescence signal, energy calibration and the averaging of single scans were performed with  
185 the software package SixPack (Webb xxxx). Normalization, transformation from energy into k  
186 space, and subtraction of a spline background was performed with WinXAS using routine  
187 procedures (Ressler, 1998). The  $k^3$ -weighted EXAFS data were fit in R space with WinXAS  
188 using theoretical back-scattering amplitudes and phase shifts calculated with FEFF 8.2  
189 (Ankudinov and Rehr, 1997). Statistical analysis of spectra was performed with the ITFA  
190 program package (Rossberg et al., 2003). Spectra of Se reference samples (Se(IV) solution as  
191 well as crystalline achavalite, ferroselite, and gray elemental Se) were taken from Scheinost  
192 and Charlet (2008).

### 193 3 Results and Discussion

#### 194 3.1 Characterization of synthesized magnetite and its precursor phases

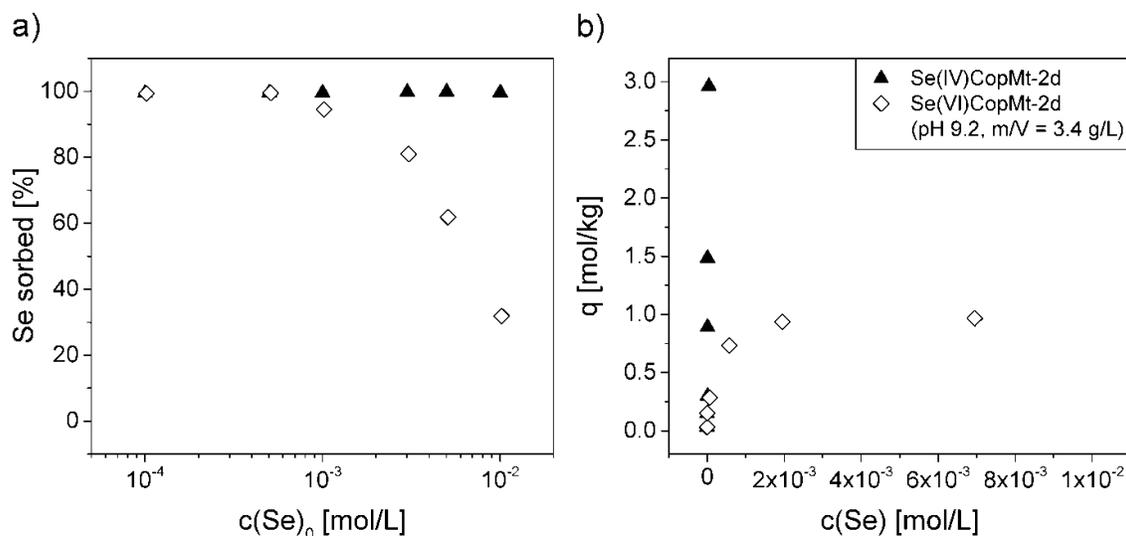
195 XRD patterns of synthesized magnetite after the total reaction of 48 h showed that pure  
196 magnetite [Fe<sub>3</sub>O<sub>4</sub>] was formed without any evidence of goethite contaminations. For the  
197 magnetite precursor phases (reaction time 30 min or 3 h), the XRD analysis revealed that these  
198 samples consist of a mixture of different mineral phases (SI Fig. A.1). The XRD patterns are  
199 dominated by a broad peak, which can be attributed to the presence of an amorphous or poorly  
200 crystalline mineral phase. In their description of the synthesis method, Schwertmann & Cornell

201 (2000) point out that the oxidation of the anoxic aquatic  $\text{Fe}^{2+}$  system takes place with the  
202 participation of iron(II) hydroxide phases. These phases are the immediate precipitation  
203 products after the first increase of the solution pH and also represent the unstable precursors of  
204 the subsequently forming (meta-) stable Fe (hydr)oxides. The occurrence of larger amounts of  
205 amorphous or poorly crystalline iron oxides in these samples is hence quite conceivable.  
206 Furthermore, one can identify peaks that are associated with the presence of small amounts of  
207 crystalline iron oxide phases such as magnetite and green rust, whereby the early magnetite  
208 formation is probably due to small quantities of dissolved oxygen in the synthesis solution.  
209 Besides that, small amounts of (hydrogen)carbonate salts occur in these unwashed samples  
210 (precipitated background electrolyte). BET measurements gave specific surface areas (SSA) of  
211  $32 \text{ m}^2/\text{g}$  for magnetite and  $264 \text{ m}^2/\text{g}$  for its precursor phase after a reaction time of 30 min. The  
212 determined SSA of magnetite is consistent with published values in the literature. It is known  
213 that the SSA of synthesized magnetite can vary widely depending on its formation pathway and  
214 that, in particular, magnetite precipitation from solution can lead to very small particles with a  
215 SSA of up to  $100 \text{ m}^2/\text{g}$  (Cornell and Schwertmann, 2003). The microscopic characterization  
216 (SEM) revealed that the pure magnetite consists of aggregated bulky particles with a size of  
217 about  $50 \text{ nm}$  (SI Fig. A.2). In case of the magnetite precursor phase, the high SSA of  $264 \text{ m}^2/\text{g}$   
218 is in good agreement with the XRD results suggesting a poorly crystalline mineral phase.  
219 However, one has to consider that the magnetite precursor might consist of several mineral  
220 phases and that the required sample drying before the BET analysis might have changed the  
221 characteristics of this sample type. By means of XPS analysis, it was possible to identify low  
222 amounts of Cl, K, and Na beside Fe and O in the near-surface region of an unwashed magnetite  
223 phase (SI Table A.1). This chemical composition is likely caused by adsorption of dissolved  
224 ionic species onto the magnetite surface. XPS analysis also enabled the determination of the  
225  $\text{Fe(II)}/\text{Fe}_{\text{total}}$  ratio (here defined as  $x_{\text{Fe(II)}}$ ) on the mineral surface. The used evaluation method is  
226 described in Huber et al. (2012) and is based on a comparison between the Fe 2p spectra of a  
227 sample and the Fe 2p spectra of references with known  $x_{\text{Fe(II)}}$  values. Hematite and a freshly  
228 prepared magnetite were used as references, hence this method can only be applied to iron  
229 oxides but not to iron hydroxides or oxyhydroxides. With a determined  $x_{\text{Fe(II)}}$  value of 0.14 the  
230 results indicate that the synthesized magnetite is partially oxidized to maghemite [ $\gamma\text{-Fe}_2\text{O}_3$ ] at  
231 the end of synthesis process. Maghemite ( $x_{\text{Fe(II)}} = 0$ ) is an oxidation product of magnetite ( $x_{\text{Fe(II)}}$   
232  $= 0.33$ ) after the contact with atmospheric oxygen, and both minerals represent the end members  
233 of a solid solution series (Schwertmann and Cornell, 2000; Tang et al., 2003). However, since  
234 the XRD analysis showed no indication for the presence of maghemite, one can assume that

235 mainly the surface region is affected by oxidation, but not the bulk phase. This assumption is  
 236 supported by the fact that oxidation of magnetite in maghemite on the surface of magnetite  
 237 particles can inhibit further oxidation processes (Rebodos and Vikesland, 2010).

### 238 3.2 Removal of Se(IV) and Se(VI) by coprecipitation

239 The analysis of the residual Se concentration allowed the determination of the Se(IV) or Se(VI)  
 240 amount that was removed during the coprecipitation with magnetite. Figure 1 shows the  
 241 quantities of Se associated with the solid phase as a function of the Se concentration at pH 9.2.  
 242 Both data sets, the percentage of removed Se depending on the initial Se concentration (Fig. 1a)  
 243 as well as the Se uptake depending on the Se equilibrium concentration (Fig. 1b), indicate that  
 244 coprecipitation represents a highly efficient process to immobilize dissolved Se oxyanions.  
 245 However, the results also demonstrate that the Se retention is affected by the speciation. For  
 246 Se(VI), the uptake by coprecipitation decreases with higher initial Se concentrations and the  
 247 Se(VI) sorption reaches an upper limit at ~1 mol/kg. By contrast, retention of Se(IV) is not  
 248 influenced by higher initial Se amounts and even at concentrations of  $10^{-2}$  mol/L all available  
 249 Se is removed. The same applies to the total Se(IV) sorption, which rises to values of up to  
 250 ~3 mol/kg and shows no indication of a sorption limit in the tested concentration range.



251

252 **Fig. 1. Retention of Se(IV) and Se(VI) during the coprecipitation (Cop) with magnetite (Mt). (a) Se sorption**  
 253 **as a function of the initial Se concentration, (b) Se uptake as a function of the Se equilibrium concentration.**

### 254 3.3 Development of the coprecipitation products within the Fe-Se-H<sub>2</sub>O system

255 Table 1 compiles the main properties of samples from coprecipitation experiments, which were  
 256 conducted at different initial Se concentrations. Besides detailed hydrochemical data and the  
 257 calculated Se uptake represented as both the sorbed Se percentage and the distribution

258 coefficient ( $\log K_d$ ), the table contains a summarized overview of solids analysis. Regarding  
 259 EDXRF results, one can observe a correlation between the total Se content of the solid phases  
 260 and the initial Se concentration respectively the sorbed Se percentage. Increasing concentrations  
 261 of dissolved Se(IV) or Se(VI) increase also the Se contents of the coprecipitation products, with  
 262 Se(IV) causing a stronger effect than Se(VI).

263 **Table 1. Equilibrium concentrations of Fe and Se, Se removal (in % and  $\log K_d$ ) and the mineral composition**  
 264 **(Mt: magnetite, Gt: goethite, Se(0): elemental Se) of selected samples of coprecipitation experiments with**  
 265 **different initial amounts of Se;  $^{\circ}c(\text{Se})_0 = "X" \cdot 10^{-3} \text{ mol/L}$ .**

| #  | Se species | Sample                     | Mineral(s) <sup>a</sup> | Se <sup>b</sup><br>[ppm] | pH <sup>c</sup> | c(Fe)<br>[mol/L] | c(Se) <sub>0</sub><br>[mol/L] | c(Se)<br>[mol/L] | Se sorbed<br>[%] | log K <sub>d</sub><br>[L/kg] |
|----|------------|----------------------------|-------------------------|--------------------------|-----------------|------------------|-------------------------------|------------------|------------------|------------------------------|
| 1  | ---        | Mt (pure)                  | Mt                      | bdl                      | 8.9             | 7.96E-07         | 0.00E+00                      | bdl              | -                | -                            |
| 2  | Se(VI)     | Se(VI)CopMt <sup>0.1</sup> | Mt                      | 1700                     | 9.2             | 6.45E-08         | 1.02E-04                      | 5.71E-07         | 99.4             | 4.72                         |
| 3  | "          | Se(VI)CopMt <sup>0.5</sup> | Mt + Se(0)              | 9900                     | 9.1             | 4.16E-07         | 5.11E-04                      | 2.73E-06         | 99.5             | 4.74                         |
| 4  | "          | Se(VI)CopMt <sup>1</sup>   | Mt + Se(0)              | 16000                    | 9.2             | 4.51E-07         | 1.02E-03                      | 5.66E-05         | 94.5             | 3.70                         |
| 5  | "          | Se(VI)CopMt <sup>3</sup>   | Mt + Se(0)              | 40000                    | 9.0             | 1.69E-06         | 3.07E-03                      | 5.84E-04         | 81.0             | 3.10                         |
| 6  | "          | Se(VI)CopMt <sup>5</sup>   | Mt + Se(0)              | 58000                    | 9.3             | 3.47E-07         | 5.11E-03                      | 1.95E-03         | 61.9             | 2.68                         |
| 7  | "          | Se(VI)CopMt <sup>10</sup>  | Mt + Gt + Se(0)         | 120000                   | 9.1             | 3.28E-06         | 1.02E-02                      | 6.95E-03         | 32.0             | 2.14                         |
| 8  | Se(IV)     | Se(IV)CopMt <sup>0.1</sup> | Mt                      | 1700                     | 9.2             | 5.23E-08         | 1.00E-04                      | 5.84E-07         | 99.4             | 4.70                         |
| 9  | "          | Se(IV)CopMt <sup>0.5</sup> | Mt + Se(0)              | 8600                     | 9.2             | 6.41E-08         | 5.02E-04                      | 2.25E-06         | 99.6             | 4.82                         |
| 10 | "          | Se(IV)CopMt <sup>1</sup>   | Mt + Se(0)              | 17000                    | 9.1             | 2.53E-07         | 1.00E-03                      | 5.10E-06         | 99.5             | 4.76                         |
| 11 | "          | Se(IV)CopMt <sup>3</sup>   | Mt + Se(0)              | 48000                    | 9.0             | 2.80E-07         | 3.01E-03                      | 8.61E-06         | 99.7             | 5.01                         |
| 12 | "          | Se(IV)CopMt <sup>5</sup>   | Mt + Se(0)              | 74000                    | 9.3             | 6.56E-06         | 5.02E-03                      | 1.02E-05         | 99.8             | 5.16                         |
| 13 | "          | Se(IV)CopMt <sup>10</sup>  | Mt + Gt + Se(0)         | 140000                   | 9.5             | 1.04E-06         | 1.00E-02                      | 4.30E-05         | 99.6             | 4.84                         |

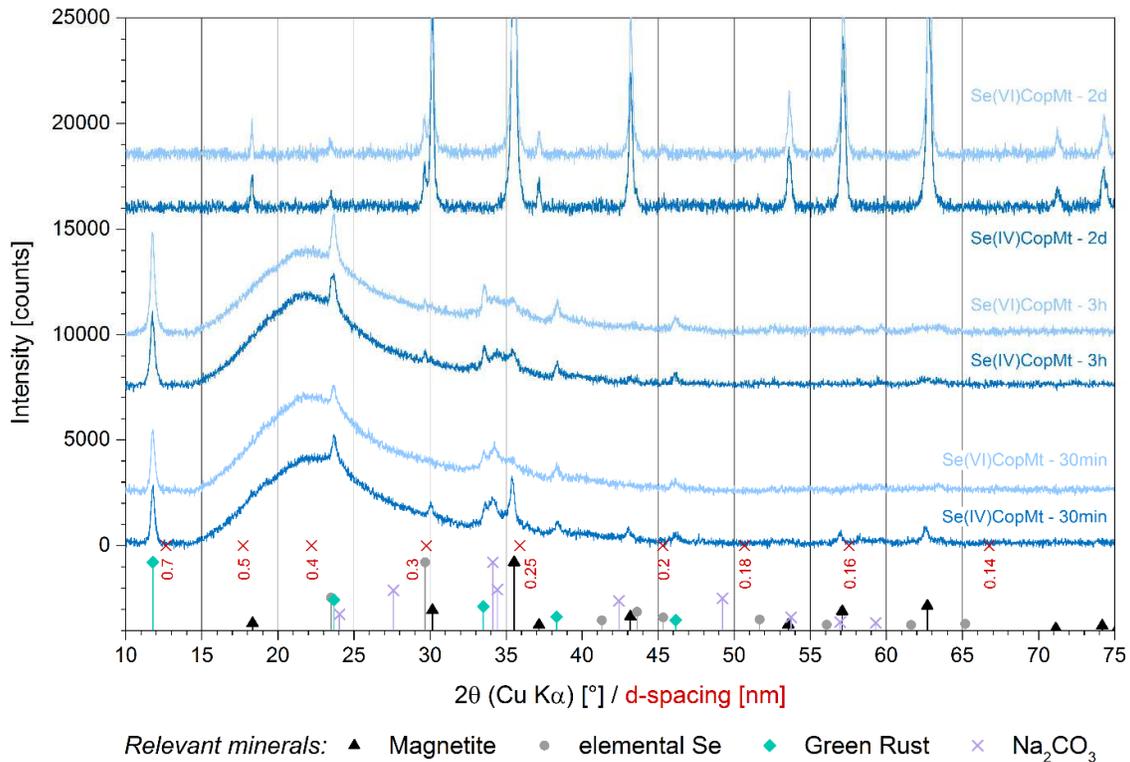
<sup>a</sup> Mineral composition (XRD analysis). <sup>b</sup> Se content of the solid phase (EDXRF analysis). <sup>c</sup> pH after synthesis/coprecipitation

266 Furthermore, the analysis of the mineral composition demonstrated that, following the  
 267 coprecipitation process, almost all samples contained crystalline elemental Se [Se(0)]. Se(0)  
 268 could be identified by means of its characteristic peaks, which occurred in the XRD plots of all  
 269 samples with higher Se contents beside the peaks of magnetite (SI Fig. A.3). Only the samples,  
 270 whose total Se concentrations were too low to successfully detect the presence of Se(0) by XRD  
 271 showed no signs for mineral phases other than magnetite. This indicates that the share of Se in  
 272 the precipitation products is due to the presence of crystalline elemental Se. The coprecipitation  
 273 of Se oxyanions and magnetite thus leads to the reduction of Se(IV) or Se(VI), resulting in the  
 274 precipitation of sparingly soluble Se(0). This reductive precipitation of Se(0) does, however,  
 275 not have much influence on the iron oxide formation process as neither the final pH nor the  
 276 residual Fe concentration or the nature of the formed iron oxide are affected by high Se  
 277 concentrations (Table 1). Solely the formation of pure magnetite is no longer possible in the  
 278 case of extremely high initial Se concentrations, which instead cause the formation of  
 279 magnetite-goethite mixed phases. Furthermore, samples of unsuccessful Se-magnetite  
 280 coprecipitation experiments showed that the precipitation of elemental Se is not affected by the

281 nature of the final iron oxide product. Regardless of whether the coprecipitation process leads  
282 to the formation of pure magnetite or iron(III) oxyhydroxides like goethite and lepidocrocite,  
283 formation of elemental Se can be observed (Fig. A.4).

284 Evaluation of the Fe(II)/Fe<sub>total</sub> ratio of the final coprecipitation products yielded similar results  
285 ( $x_{\text{Fe(II)}} = 0.09 - 0.13$ ) as those obtained for Se-free magnetite (SI Table A.1). Although the  
286 coprecipitated magnetite is affected by a partial oxidation in maghemite (cf. chapter 3.1), the  
287 oxidation process is not enhanced by the presence of dissolved Se oxyanions. Just like the Se-  
288 free magnetite, the near-surface region of the unwashed final coprecipitation products contain,  
289 besides Fe and O, certain variable amounts of C, Cl, K and Na, which indicate adsorption of  
290 dissolved ionic species or precipitation of salt phases. In addition, the final precipitates also  
291 consist of small shares of Se (~0.7 at%) resulting from the presence of elemental Se.

292 In order to investigate the temporal development of the coprecipitation processes within the Fe-  
293 Se-H<sub>2</sub>O system, we analyzed samples representing different stages of the coprecipitation  
294 process. This examination included a detailed characterization of the precipitation products by  
295 XRD (Fig. 2). The results show that, at the end of the progressive oxidation (reaction time 48  
296 hour), the coprecipitation products of both Se systems contain magnetite and elemental Se only  
297 (cf. Table 1 & SI Fig. A.3). In contrast, and as already been shown in 3.1, the precipitates that  
298 represent the early anoxic or suboxic stage of the magnetite formation process (reaction time  
299 30 min or 3 h) consist of a number of different crystalline mineral phases. This includes iron  
300 oxides such as magnetite and green rust, (hydrogen)carbonate salts (precipitated background  
301 electrolyte) as well as elemental Se. Since the hydrochemical system contains mainly the anions  
302 chloride and (hydrogen)carbonate, it can be assumed that the green rust phase [GR] is primarily  
303 chloride green rust [GR(Cl<sup>-</sup>)] or carbonate green rust [GR(CO<sub>3</sub><sup>2-</sup>)] (Drissi et al., 1994; Refait et  
304 al., 1998). Formation of selenite or selenate green rust (Refait et al., 2000), however, can be  
305 excluded (cf. 3.4.2).



306

307 **Fig. 2. Time-resolved XRD analysis of the magnetite formation pathway: At an early stage unstable green**  
 308 **rust (GR) is present beside Mt. During the progressive oxidation, GR is completely transformed into Mt and**  
 309 **elemental Se occurs as a separate mineral phase.**

310 The short-term samples presumably also contain amorphous or poorly crystalline iron(II)  
 311 hydroxide, which might be responsible for the broad peak in the XRD plot. That the short-term  
 312 coprecipitation samples mainly consist of iron hydroxides rather than iron oxides could be  
 313 confirmed by the analysis of the O 1s spectra. Based on the comparison of the measured O 1s  
 314 binding energies with references, the dominance of hydroxide (OH<sup>-</sup>) over oxide (O<sup>2-</sup>)  
 315 compounds could be illustrated (SI Fig. A.5). Due to this dominance of iron hydroxides, it was,  
 316 however, not possible to apply the previous described evaluation procedure for the  
 317 determination of  $x_{\text{Fe(II)}}$  (cf. chapter 3.1). In order to estimate the Fe(II)/Fe<sub>total</sub> ratio, the Fe 2p  
 318 spectra of the analyzed coprecipitation samples were therefore directly compared with the  
 319 published Fe 2p spectra of stoichiometric GR(CO<sub>3</sub><sup>2-</sup>) [Fe<sup>II</sup><sub>4</sub>Fe<sup>III</sup><sub>2</sub>(OH)<sub>12</sub>CO<sub>3</sub> · 3 H<sub>2</sub>O;  
 320  $x_{\text{Fe(II)}} = 0.67$ ] (Mullet et al., 2008). Since the Fe 2p spectra are almost identical (SI Fig. A.5),  
 321 one can assume that the proportion of Fe(II) lies also in the range of  $x_{\text{Fe(II)}} = \sim 0.67$   
 322 (SI Table A.1).

323 Regarding the mineral composition as well as the relative proportions of the minerals (estimated  
 324 from peak intensities), there is hardly any difference between reaction times of 30 min or 3 h.  
 325 The only exceptions are elemental Se, which can only be identified in the samples with a

326 reaction time of 3 hours, and the GR phase, whose fraction seems to increase (Fig. 2). The  
327 relatively large proportion of green rust in the short-term coprecipitation samples (30 min and  
328 3 h) is particularly noticeable in comparison to the equivalent samples of the Se-free system,  
329 which show scarcely any evidence of GR (cf. SI Fig. A.1). Precipitation of GR therefore  
330 appears to be associated with the presence of dissolved Se oxyanions.

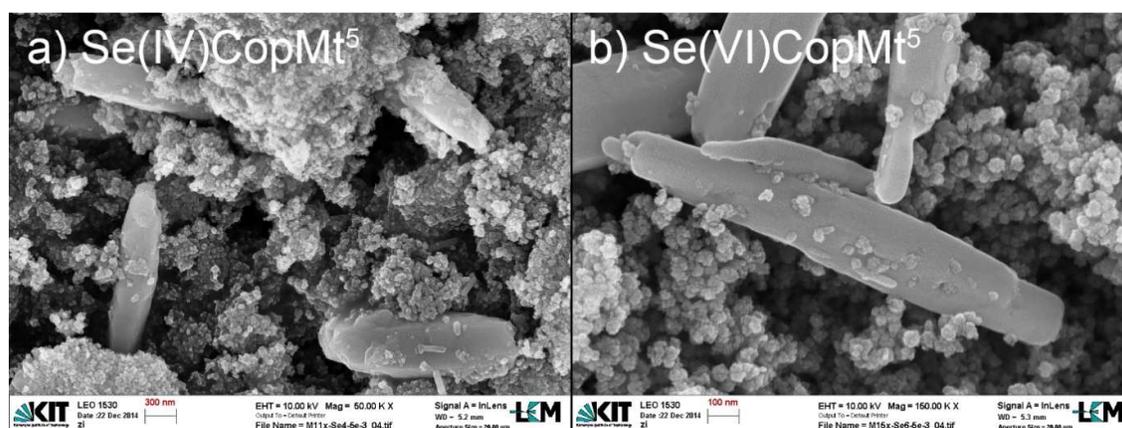
331 Furthermore, since the proportion of magnetite does not increase within the first 3 hours, one  
332 can conclude that the magnetite formation requires a certain period of time. This is also  
333 confirmed by the macroscopic observation that the color change of the precipitate from bluish  
334 green to black lasts several hours. Formation of magnetite is thus the result of the progressive  
335 oxidation of the system, which causes the complete transformation of the primarily formed  
336 Fe(II)-rich iron oxide phases into magnetite. It is known that both iron(II) hydroxide and GR  
337 are only stable under anoxic conditions and are oxidized to magnetite or iron(III) oxyhydroxides  
338 like goethite or lepidocrocite in contact with air or dissolved oxygen, respectively (Drissi et al.,  
339 1994; Schwertmann and Fechter, 1994). The nature of the oxidation product thereby depends  
340 on the general hydrochemical conditions, whereby low oxidation rates as well as an alkaline  
341 pH favor the formation of magnetite (Drissi et al., 1994; Perez et al., 1998; Refait et al., 1998;  
342 Perez and Umetsu, 2000; Sumoondur et al., 2008).

#### 343 3.4 Reductive precipitation of Se oxyanions

344 Precipitation of elemental Se could also be verified by SEM/EDX and XPS results. SEM images  
345 of two analyzed samples from each Se system – Se(IV) or Se(VI) – are shown in Figure 3 and  
346 SI Figure A.6 & A.7, respectively. These samples were selected because of their high Se content  
347 (6 - 7 wt%), arising from initial Se(IV) or Se(VI) concentrations of  $5 \cdot 10^{-3}$  mol/L. The images  
348 of both samples indicate the formation of elongated (1 - 2  $\mu\text{m}$ ) euhedral Se(0) crystals  
349 (identified via EDX; SI Fig. A.6 or A.7) that are embedded in the magnetite matrix. Although  
350 the Se(0) crystals vary in size, they are all significantly larger than the magnetite particles with  
351 average sizes of 25 - 50 nm. Moreover, the XPS analysis prove that, at the end of the 48-hour  
352 reaction time [SeCopMt], Se is present in the oxidation state Se(0) (SI Table A.1). This  
353 confirms the previous findings, according to which the coprecipitation of Se(IV) or Se(VI) with  
354 magnetite ends in the formation of elemental Se.

355 That interaction between reduced Fe minerals and Se oxyanions can cause a reductive Se  
356 precipitation and hence a Se immobilization was also observed in previous publications.  
357 Formation of Se(0) was demonstrated by studies regarding Se(IV) or Se(VI) reduction by ZVI  
358 (Liang et al., 2013; Tang et al., 2014) or Fe(II)-bearing mineral phases like iron(II) hydroxide

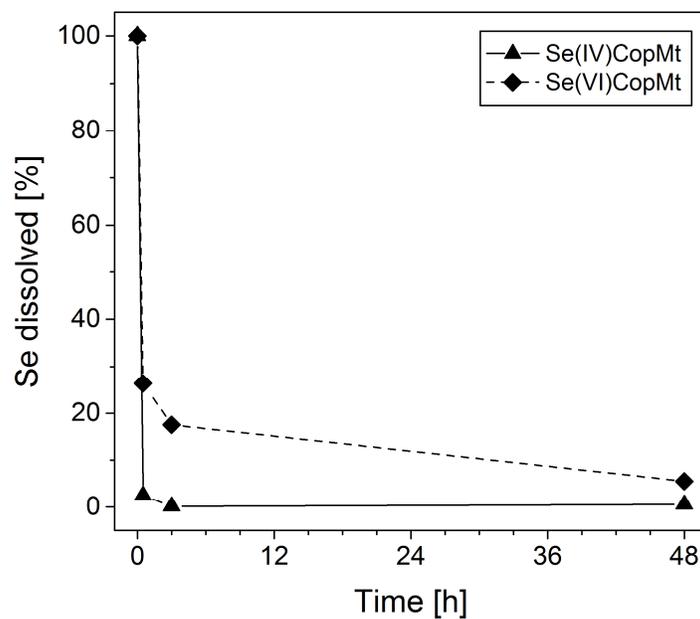
359 (Murphy, 1988; Zingaro et al., 1997; Chen et al., 2009) and green rust (Myneni et al., 1997;  
360 Johnson and Bullen, 2003; Scheidegger et al., 2003). By contrast, sorption studies on magnetite  
361 (Scheinost et al., 2008; Scheinost and Charlet, 2008) showed that reduction processes can also  
362 lead to the formation of various iron selenide compounds. This also applies to an interaction of  
363 Se(VI) with nanoparticulate ZVI (Olegario et al., 2010). However, even under consistently  
364 anoxic conditions, interaction of Se oxyanions with reduced Fe phases does not always cause a  
365 reductive Se precipitation, which was confirmed in several sorption studies (Loyo et al., 2008;  
366 Jordan et al., 2009; Missana et al., 2009). Concerning the Se reduction process, this suggests  
367 that the formation pathway of magnetite and the other involved iron oxide phases plays a crucial  
368 role.



370 **Fig. 3. SEM images of coprecipitation products consisting of large, lath-shaped elemental Se crystals in**  
371 **the matrix of magnetite aggregates. (a) Se(IV)-magnetite coprecipitation; (b) Se(VI)-magnetite**  
372 **coprecipitation.  $c(\text{Se})_0 = 5 \cdot 10^{-3}$  mol/L.**

373 In addition, the time-resolved analysis of the coprecipitation process shows that elemental Se  
374 occurs for the first time after 3 hours and that the intensity of the Se(0) peaks and hence the  
375 relative Se(0) content increases in the subsequent period (Fig. 3). The formation of Se(0),  
376 therefore, does not take place in the very beginning of the coprecipitation process, but only at  
377 a later stage. Indications for the presence of crystalline Se-bearing minerals other than Se(0) are  
378 not visible.

379 The results of the development of the residual Se concentrations, however, clearly demonstrate  
380 that most of the initial Se(IV) or Se(VI) content is already removed from solution after reaction  
381 times of 30 min (Fig. 4). This is confirmed by the XPS results of the respective solid samples  
382 [SeCopMt-30min], whose chemical composition show significant shares of Se. The analysis of  
383 the dissolved Se concentration also illustrates that no Se is released during the Se(0) formation,  
384 or during the transformation of the iron hydroxides into magnetite.



385

386 **Fig. 4. Evolution of the Se(IV) or Se(VI) concentration during the coprecipitation process.**

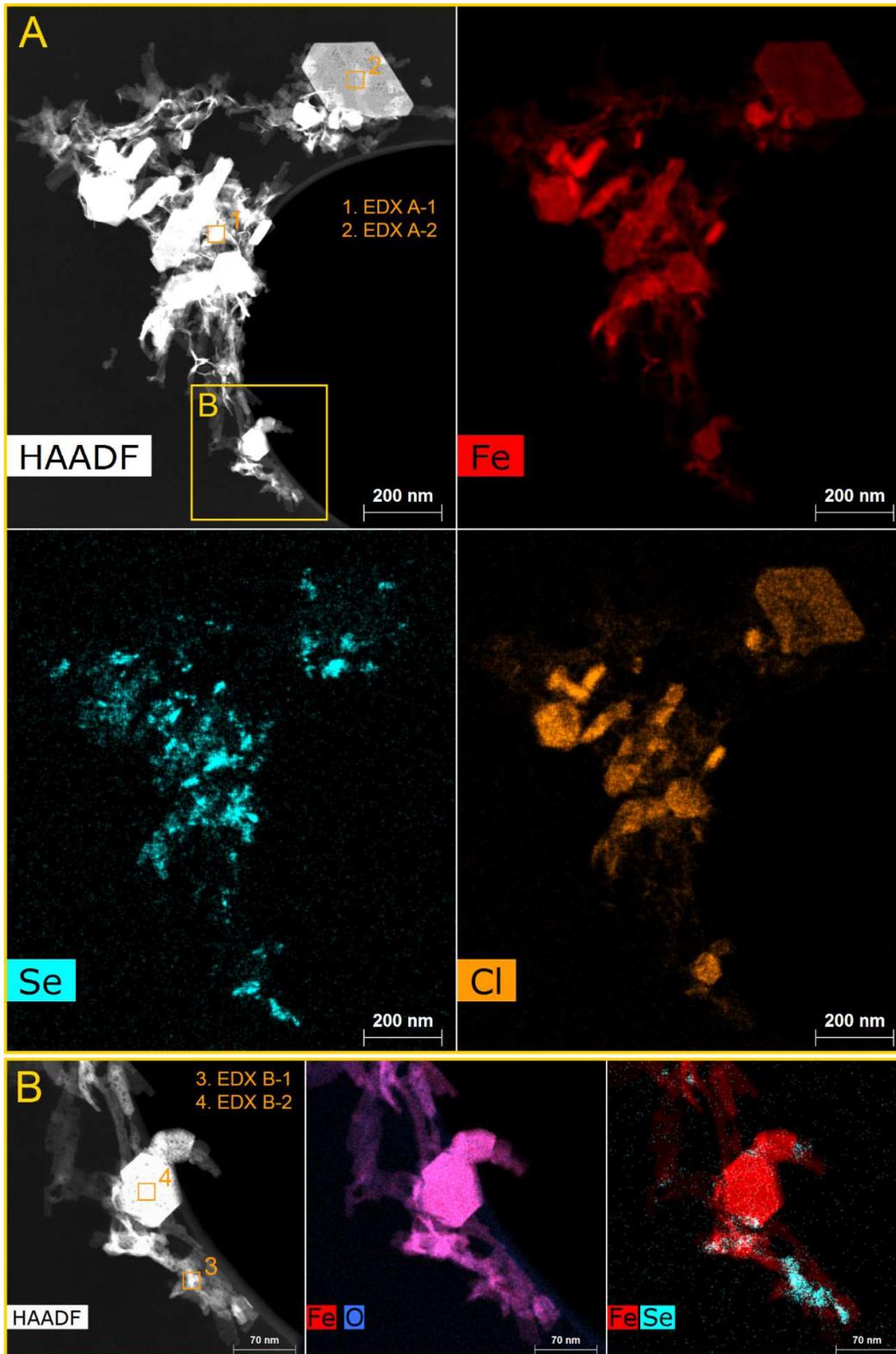
387 In order to find out what retention mechanism causes the immobilization of Se(IV) or Se(VI)  
 388 in the early stage of the coprecipitation process, the fate of Se after reaction times of 30 min  
 389 was characterized in detail. This included, among other things, an analysis of the Se oxidation  
 390 state by the determination of the Se binding energies via XPS (SI Table A.1). The results prove  
 391 that the precipitates representing the early coprecipitation stage [SeCopMt-30min] contain Se  
 392 in the oxidation stage Se(-II). Reduction of Se(IV) and Se(VI) thus takes place within the first  
 393 minutes of the coprecipitation, in a period in which the dissolved Se oxyanions are in contact  
 394 with the Fe(II)-rich precursor phases of magnetite under anoxic conditions.

395 In addition, the absence of Se(IV) or Se(VI) demonstrates that the retention is not due to  
 396 adsorption processes, which means, that the fast removal of Se oxyanions is not associated with  
 397 the rapid adsorption kinetic of Se oxyanions on iron oxide minerals (Rovira et al., 2008; Loyo  
 398 et al., 2008; Missana et al., 2009; Mitchell et al., 2013). The same also applies to Se  
 399 immobilization due to the formation of selenite or selenate GR or the incorporation of Se  
 400 oxyanions in magnetite or its precursor phases. That the coprecipitation between magnetite and  
 401 dissolved oxyanions can generally lead to an incorporation was demonstrated by Wang et al.  
 402 (2011) for the oxyanion As(V). Up to now, however, there is no evidence that comparable  
 403 processes could also be relevant for the Se(IV)-magnetite or Se(VI)-magnetite system.

404 S/TEM in combination with EDX analyses enabled a spatially resolved optical and chemical  
 405 characterization of a Se(-II)-bearing coprecipitation sample [Se(IV)CopMt-30min]. Figure 5  
 406 shows a HAADF image together with relevant elemental mappings.

407 Regarding the mineral composition, the TEM/EDX analysis confirms the previous results,  
408 according to which the primary precipitation products consist of different mineral phases. These  
409 are primarily iron minerals and, in particular, iron oxides. The analyzed sample contains  
410 crystalline as well as amorphous or poorly crystalline phases, whereby the relatively large GR  
411 particles are particularly striking. GR crystals can be identified by their distinctive hexagonal  
412 crystal shape (Legrand et al., 2004; Génin et al., 2006). Since they are characterized by higher  
413 levels of chloride, it is also possible to identify GR particles that are positioned vertically. The  
414 higher chloride contents suggest that the GR phase is primarily GR(Cl). In this context, one  
415 has however to consider that the analysis of carbon and therefore the detection of GR(CO<sub>3</sub><sup>2-</sup>)  
416 was not possible via EDX due to the C-containing TEM grid. Elements such as Na and K show  
417 a homogeneous distribution and their occurrence is not connected with particular mineral  
418 phases. This indicates that the major part of Na and K is adsorbed on the surface of iron oxide  
419 minerals.

420 Unlike Na und K, the distribution of Se is extremely heterogeneous. There are no signs that  
421 spots with high Se concentrations are associated with certain iron oxide minerals. EDX spectra  
422 of Se-rich spots are characterized by high Se and Fe contents, while their proportion of O tends  
423 to be lower than for Se-free spots. The latter can be seen in SI Fig. A.8, which includes a  
424 comparison between the EDX spectrum of an isolated Se-rich spot and the spectrum of the  
425 center of a GR particle, containing mainly Fe, O, and small amounts of Cl. Therefore, higher  
426 Se concentrations are likely associated with the occurrence of iron selenide compounds. These  
427 compounds are present in the iron oxide matrix in the form of heterogeneously distributed  
428 independent mineral phases. Moreover, with sizes below 100 nm, these iron selenide particles  
429 are also rather small.



430

431

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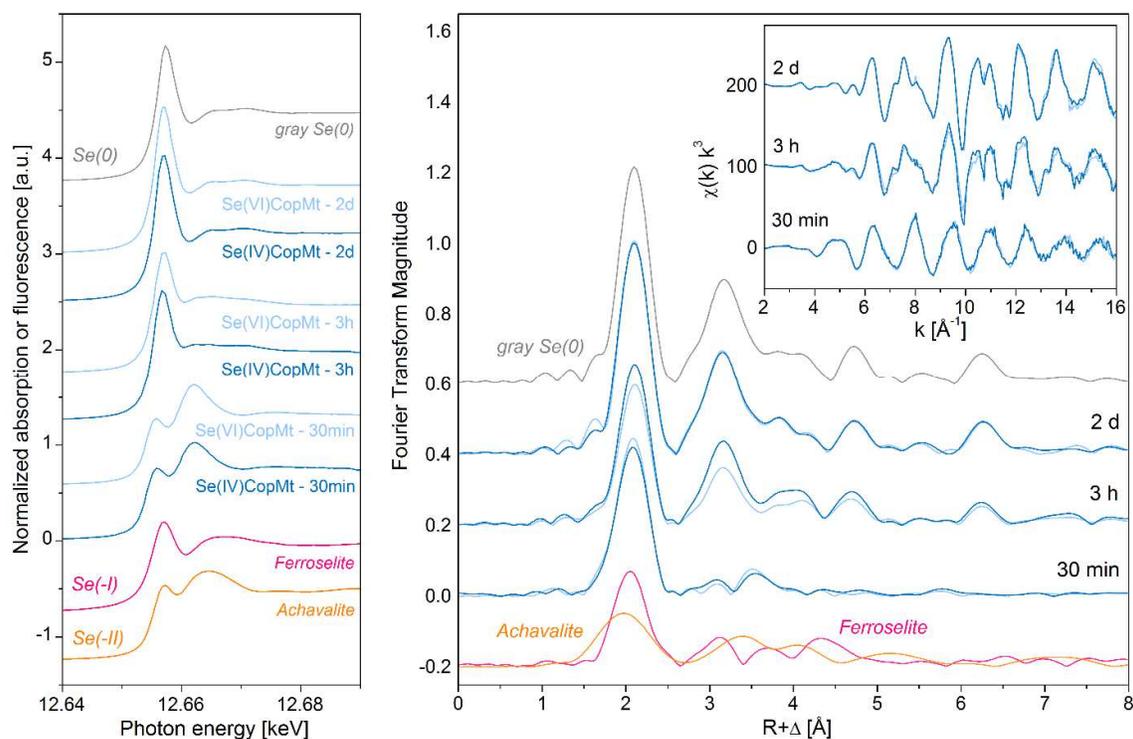
433

Fig. 5. HAADF images and elemental mappings of a Se(IV)-magnetite coprecipitation product after a reaction time of 30 min. EDX spectra of the marked spots are shown in Fig. A.8.

434 3.5 Temporal evolution of the Se speciation

435 Results of Se K-edge XAS analyses were used to characterize the Se oxidation state (XANES)  
436 as well as the nature of the local Se structure (EXAFS) during the coprecipitation process. For  
437 this purpose, coprecipitation products of both Se systems were analyzed after reaction times of  
438 30 min, 3 h and 48 h (cf. samples Fig 2).

439 Figure 6 shows the Se K-edge XANES spectra of the analyzed samples together with reference  
440 spectra of the minerals ferroselite [FeSe<sub>2</sub>], achavalite [FeSe], and, gray elemental Se [Se(0)]. A  
441 comparison of the reference spectra illustrates that the oxidation states Se(0), Se(-I), and Se(-II)  
442 are difficult to differentiate based on the very similar position of their absorption edge  
443 (12.6553 - 12.6560 keV). However, they can be easily distinguished based on the characteristic  
444 shape of the white line. While the white line of gray Se(0) is dominated by one significant peak,  
445 the white line of ferroselite and achavalite is of lower intensity and, in case of achavalite, also  
446 characterized by two maxima. Just like achavalite, the samples with reaction times of 30 min  
447 [SeCopMt-30min] show white lines of relatively low intensities and two maxima, confirming  
448 that Se is indeed present in the form of Se(-II). These XANES data are thus in line with the  
449 previous findings of the XPS analysis after which dissolved Se(IV) and Se(VI) oxyanions are  
450 reduced to Se(-II) in the early stage of the coprecipitation process.

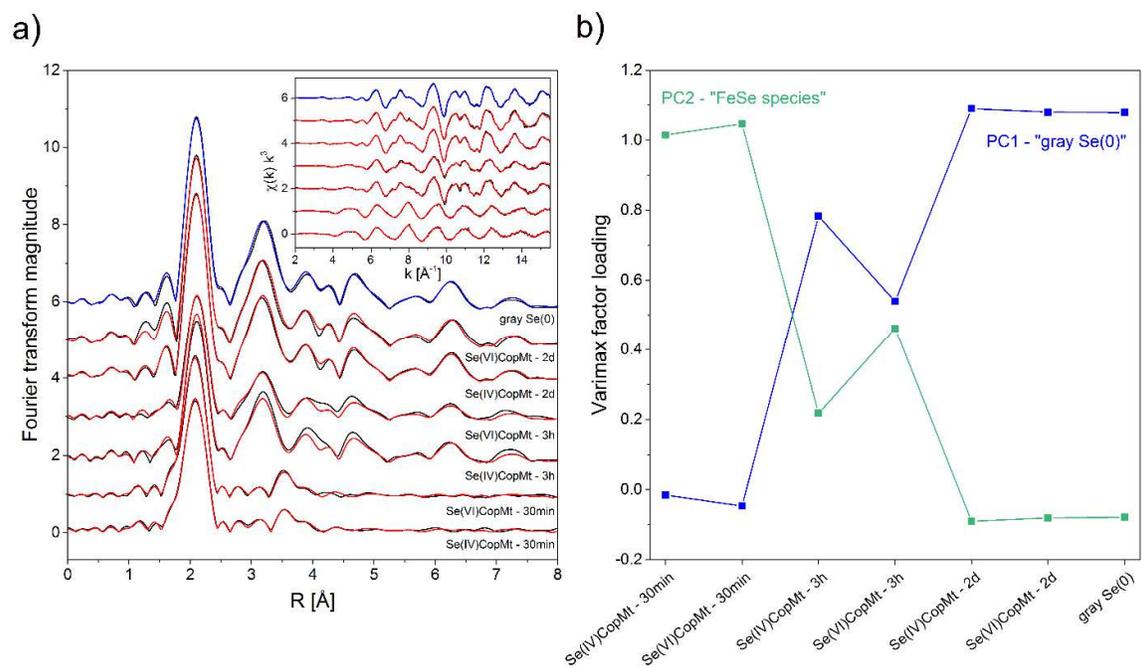


451

452 Fig. 6. Se K-edge XANES and EXAFS spectra of Se-magnetite coprecipitation products of different  
453 reaction times and various Se references.

454 However, during the oxidation of the system, these Se(-II) species are afterwards transformed  
455 to elemental Se, as can be seen from the high similarity between the white lines of gray Se and  
456 the coprecipitation samples with reaction times of 3 hours [SeCopMt-3h] and 2 days  
457 [SeCopMt-2d]. In this form, the Se stays stable, although Se(0) does not represent the  
458 thermodynamically most stable oxidation state under oxic conditions. Furthermore, there is no  
459 difference between samples of the Se(IV) and Se(VI) system, indicating that at no time of the  
460 oxidation process the Se solid state speciation is influenced by the initial aqueous speciation.

461 Regarding the Se binding structure, a comparison of the EXAFS Fourier transforms (FT)  
462 illustrates that spectra of the Se(0)-bearing samples are identical to the gray Se reference,  
463 whereas the EXAFS FT magnitude of the Se(-II) species is clearly different from reference  
464 spectra of achavalite or ferroselite (Fig 6). In order to check whether the samples with reaction  
465 times of 3 hours represent a spectral mixture of Se(-II) and Se(0) species, a statistical analysis  
466 was performed using Iterative Transformation Factor Analysis (ITFA) (Rossberg et al., 2003;  
467 Scheinost and Charlet, 2008). This ITFA included the EXAFS spectra of all coprecipitation  
468 samples as well as the spectrum of gray Se, since the previous results showed that the  
469 immobilized Se should be present as gray Se at the end of the coprecipitation process. Fig. 7a  
470 shows the excellent match between the experimental spectra (black lines) and their  
471 reconstructions (red or blue lines) by two principal components (PC). The Varimax factor  
472 loadings (Fig 7b) demonstrate that the gray Se reference as well as the final coprecipitation  
473 products [SeCopMt-2d] are solely dominated by PC 1, without any influence of PC 2. PC 1  
474 therefore represents the occurrence of elemental gray Se. By contrast, samples of the early stage  
475 [SeCopMt-30min] are characterized only by PC 2, epitomizing the the Se(-II) phase. In  
476 addition, as the samples of the intermediate stage [SeCopMt-3h] are described by both principal  
477 components, one can conclude that these samples contain indeed both different types of Se  
478 species. Due to the limited radial resolution of EXAFS, only the samples representing the Se(0)  
479 and Se(-II) endmembers were fitted (Table 2).



480

481 **Fig. 7. (a) Se K-edge EXAFS spectra of Se-magnetite coprecipitation products of different reaction times**  
 482 **and of a gray Se(0) reference. Experimental spectra are shown as black lines, their reconstruction by two**  
 483 **factors as red or blue lines. (b) Varimax loadings of the two factors.**

484 For the Se(-II)-bearing samples, the  $k^3$ -weighted  $\chi$  spectra were fit with a FEFF 8.2 file  
 485 generated with the crystallographic structure of tetragonal iron(II) selenide (FeSe, CIF 26889).  
 486 The EXAFS FT magnitude of these samples is dominated by a strong peak at 2.1 Å (uncorrected  
 487 for phase shift). This peak could be well fitted with a single scattering Se-Fe path, resulting in  
 488 iron coordination numbers (CN) of 2.7 - 2.8 and atomic distances of 2.40 Å. The use of a Se-  
 489 Se path, in contrast, led to poor fit results, hence can be excluded. In case of the structural  
 490 features in the EXAFS FT range between 3.1 - 3.5 Å (uncorrected for phase shift), three  
 491 individual single scattering Se-Fe and Se-Se paths had to be used to achieve a good fitting. This  
 492 resulted in further shells of approximately 1 Se atom at 3.39 Å, 5 - 6 Se atoms at 3.90 Å and  
 493 2 - 3 Fe atoms at 4.12 Å (Table 2). A comparison with the known crystal structures of the iron  
 494 selenides dzharkenite, ferroselite, achavalite, tetragonal FeSe, Fe<sub>3</sub>Se<sub>4</sub> or Fe<sub>7</sub>Se<sub>8</sub> (Scheinost et  
 495 al., 2008) demonstrates that none of these minerals match the observed atomic distances of the  
 496 Se(-II) species within the reduced samples. The highest similarity shows tetragonal FeSe, which  
 497 is characterized by a Fe coordination shell at 2.37 Å and neighboring Se atoms in a distance of  
 498 3.91 Å. However, while unlike tetragonal FeSe, the reduced samples show no Se shell at  
 499 approximately 3.77 Å, the documented Se and Fe shells at 3.38 Å and 4.12 Å, respectively, are  
 500 missing in case of tetragonal FeSe (Scheinost and Charlet, 2008).

501 The general observation that the structure of a Se reduction product, resulting from an  
502 interaction with reduced iron, shows similarities with tetragonal FeSe was also observed in  
503 EXAFS studies by other authors (Scheinost et al., 2008; Scheinost and Charlet, 2008; Loyo et  
504 al., 2008; Olegario et al., 2010). Like in our study, the fit results of reduction products showed  
505 a Fe coordination shell in a distance of 2.34 - 2.42 Å and Se neighbors at 3.87 - 4.02 Å  
506 (Scheinost et al., 2008; Loyo et al., 2008; Olegario et al., 2010). Moreover, some of these  
507 authors also found additional Se and Fe shells similar to the observed Se shell at 3.38 Å  
508 (Scheinost and Charlet, 2008; Loyo et al., 2008) or Fe shell at 4.12 Å (Scheinost et al., 2008),  
509 which are missing in the case of tetragonal FeSe. In addition, all EXAFS results have in  
510 common that the coordination numbers of the Fe and Se shells are much smaller than the ones  
511 of crystalline iron selenide minerals. This suggests that the reductive precipitation of Se  
512 oxyanions leads to the formation of an iron selenide phase [FeSe] with particle sizes in the  
513 nanometer range (Scheinost et al., 2008; Scheinost and Charlet, 2008; Loyo et al., 2008;  
514 Olegario et al., 2010). Even though these FeSe nanoparticles are characterized by a short-range  
515 structure, their binding structure is different from that of macrocrystalline FeSe minerals like  
516 achavalite or tetragonal FeSe. The theory of the formation of nanoparticulate FeSe is also  
517 strongly supported by the TEM results, providing the first direct evidence that the FeSe particles  
518 are smaller than 100 nm. Furthermore, the presence of poorly crystalline FeSe nanoparticles  
519 would explain why the FeSe phase could not be detected by XRD.

520 **Table. 2 Se-K XANES edge energies and EXAFS fit results of Se-magnetite coprecipitation products of**  
521 **different reaction times ( $S_0^2 = 0.9$ ).**

| Sample                          | $E_0$ [keV] | Coordination shell |                    |   | Further shells |                |                              | $\Delta E_0$ [eV] | $\chi^2_{res}$ [%] |     |
|---------------------------------|-------------|--------------------|--------------------|---|----------------|----------------|------------------------------|-------------------|--------------------|-----|
|                                 |             | CN <sup>a</sup>    | R [Å] <sup>b</sup> | $\sigma^2$ [Å <sup>2</sup> ] <sup>c</sup> | CN             | R [Å]          | $\sigma^2$ [Å <sup>2</sup> ] |                   |                    |     |
| Se(IV)CopMt <sup>1</sup> -30min | 12.6541     | 2.7                | Fe                 | 2.40                                      | 0.0037         | 1.0            | Se                           | 3.39              | 12.7               | 4.3 |
|                                 |             |                    |                    |   |                | 5.3            | Se                           | 3.89              |                    |     |
|                                 |             |                    |                    |   |                | 2.4            | Fe                           | 4.11              |                    |     |
| Se(VI)CopMt <sup>1</sup> -30min | 12.6540     | 2.8                | Fe                 | 2.40                                      | 0.0036         | 0.5            | Se                           | 3.38              | 12.9               | 3.6 |
|                                 |             |                    |                    |   |                | 6.1            | Se                           | 3.90              |                    |     |
|                                 |             |                    |                    |   |                | 2.6            | Fe                           | 4.13              |                    |     |
| Se(IV)CopMt <sup>1</sup> -2d    | 12.6556     | 2 <sup>f</sup>     | Se                 | 2.38                                      | 0.0015         | 4 <sup>f</sup> | Se                           | 3.38              | 10.6               | 3.8 |
|                                 |             |                    |                    |   |                | 2 <sup>f</sup> | Se                           | 3.74              |                    |     |
|                                 |             |                    |                    |   |                | 6 <sup>f</sup> | Se                           | 4.32              |                    |     |
|                                 |             |                    |                    |   |                | 4 <sup>f</sup> | Se                           | 4.46              |                    |     |
|                                 |             |                    |                    |   |                | 4 <sup>f</sup> | Se                           | 4.94              |                    |     |
| Se(VI)CopMt <sup>1</sup> -2d    | 12.6556     | 2 <sup>f</sup>     | Se                 | 2.38                                      | 0.0015         | 4 <sup>f</sup> | Se                           | 3.38              | 10.9               | 4.2 |
|                                 |             |                    |                    |   |                | 2 <sup>f</sup> | Se                           | 3.74              |                    |     |
|                                 |             |                    |                    |   |                | 6 <sup>f</sup> | Se                           | 4.31              |                    |     |
|                                 |             |                    |                    |   |                | 4 <sup>f</sup> | Se                           | 4.45              |                    |     |
|                                 |             |                    |                    |   |                | 4 <sup>f</sup> | Se                           | 4.94              |                    |     |

<sup>a</sup> CN: coordination number, error  $\pm 25\%$ . <sup>b</sup> R: Radial distance, error  $\pm 0.01$  Å. <sup>c</sup>  $\sigma^2$ : Debye-Waller factor, error  $\pm 0.0005$  Å<sup>2</sup>.

<sup>f</sup> fixed coordination numbers. <sup>§</sup> Upper  $\sigma^2$  limit reached. <sup>™</sup>  $c(\text{Se})_0 = "X" \cdot 10^{-3}$  mol/L.

522 The fit of  $\chi$  spectra of the Se(0)-bearing samples was performed with a FEFF 8.2 file generated  
523 with the crystallographic structure of gray Se (Se trigonal, CIF 22251). As the previous results  
524 have already shown that Se is most likely present as gray Se in these samples, we used the first  
525 6 single scattering Se-Se paths of this Se reference with fixed coordination numbers for the  
526 fitting (Table 2). The perfect fit and the corresponding interatomic Se distances clearly show  
527 that the Se species in these samples is indeed crystalline gray Se.

528 That reduction of Se oxyanions by reduced iron can result in the formation of trigonal, gray Se  
529 was also demonstrated in studies with iron(II) hydroxide (Zingaro et al., 1997), siderite  
530 (Scheinost et al., 2008), or ferrous iron sorbed on clay minerals (Charlet et al., 2007). Other  
531 publications, however, reported the formation of amorphous elemental Se. This includes studies  
532 about the reduction potential of green rust minerals (Myneni et al., 1997; Scheidegger et al.,  
533 2003). In addition, Scheinost and Charlet (2008) showed that reduction of Se(IV) by  
534 mackinawite caused the formation of nanoparticulate red Se.

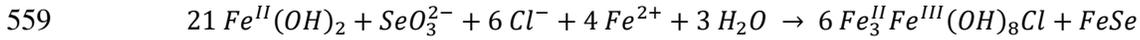
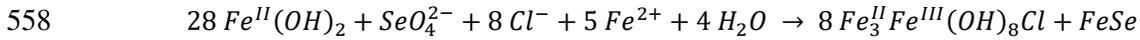
### 535 3.6 Conceptual model of the Se retention during the magnetite formation

536 The results of this study prove that the immobilization of Se oxyanions during the aerial  
537 oxidation of an anoxic Fe-Se-H<sub>2</sub>O system, which results in the formation of magnetite, is due  
538 to two redox processes.

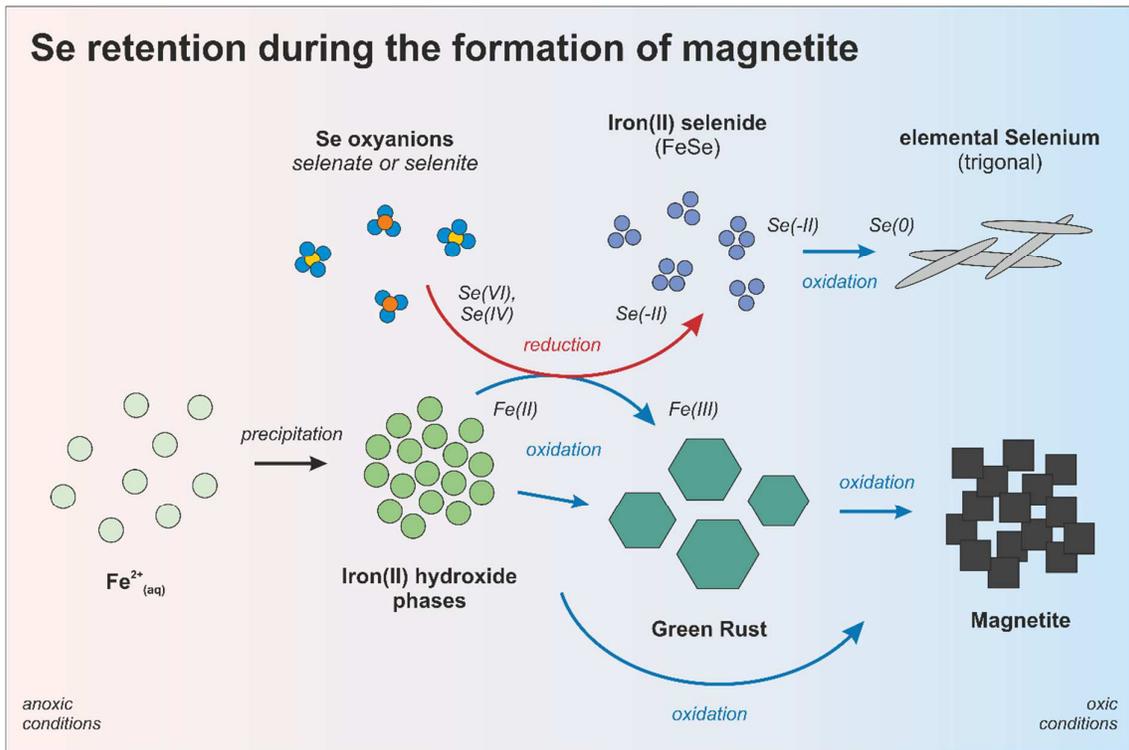
539 The first redox process takes place under reducing conditions in the early stage of the magnetite  
540 formation, where dissolved Se oxyanions interact with primarily Fe(II)-rich precipitation  
541 products of the aquatic Fe<sup>2+</sup> system. These products are mainly iron(II) hydroxide and green  
542 rust, which represent the unstable precursor phases of the later formed magnetite. This  
543 interaction leads to a reduction of Se(IV) or Se(VI) to Se(-II) and causes the formation of  
544 nanoparticulate iron selenide (FeSe) phase. At the same time, the involved iron(II) hydroxide  
545 phases are transformed to Fe(III)-rich minerals, due to the corresponding oxidation of Fe(II) to  
546 Fe(III) during this reductive Se precipitation (Fig. 8).

547 It is known that the reduction of dissolved Se oxyanions by Fe(II) requires the presence of Fe(II)  
548 mineral phases and the reaction with their active mineral surfaces (Chen et al., 2009). Although  
549 the presence of dissolved Fe<sup>2+</sup> generally favors the Se reduction process (Tang et al., 2014), a  
550 reduction only by dissolved Fe<sup>2+</sup> is not possible due to the difference in reduction potentials of  
551 the redox couples (Chakraborty et al., 2010). Responsible for the Se reduction is most likely  
552 the interaction with iron(II) hydroxide and its subsequent oxidation to green rust, since the  
553 occurrence of larger amounts of green rust is directly related to the presence of dissolved Se  
554 oxyanions. Thus, only the reductive Se precipitation by iron(II) hydroxide and the associated

555 production of Fe(III) makes the formation of an iron(II,III) mineral like green rust possible  
 556 under the prevailing anoxic condition. Regarding the formation of GR(Cl), the corresponding  
 557 redox reaction would be:



560 As can be seen from these equations, the quantity of available iron(II) hydroxide determines  
 561 the total amount of immobilized Se(IV) or Se(VI). Since the reduction of Se(VI) to FeSe  
 562 requires more iron(II) hydroxide than the reduction of Se(IV), the amount of reduced Se(IV) is  
 563 always higher at a specific Se/Fe<sup>2+</sup> ratio. However, the amount of immobilized Se also depends  
 564 on the reduction kinetics, whereby particularly the reduction step of Se(VI) to Se(VI) is  
 565 kinetically hindered (Séby et al., 1998; De Cannière et al., 2010).



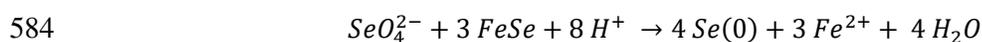
566

567 **Fig. 8. Schematic representation of the retention of Se oxyanions during the formation of magnetite.**

568 Concerning the question why the reduction of Se oxyanions sometimes causes the formation of  
 569 FeSe and sometimes of elemental Se, Scheinost et al. (2008) postulated a theory according to  
 570 which the type of precipitation product is linked to the reduction kinetics. While formation of  
 571 iron selenides is only possible in case of fast reduction kinetics, a slow Se reduction favors the  
 572 precipitation of elemental Se. In general, the reduction kinetics is directly related to the particle  
 573 sizes and morphology of the interacting Fe(II)-bearing mineral phases. A fast Se reduction is

574 therefore only possible in case of relatively small particles with high specific surface areas  
575 (Scheinost et al., 2008; Scheinost and Charlet, 2008). Since the Se reduction process mainly  
576 takes place within the first 30 minutes and through the interaction with iron(II) hydroxide and  
577 green rust, which are both characterized by small particle sizes and/or high specific surface  
578 areas, the results of this study are consistent with the theory that the reduction kinetics defines  
579 the Se precipitation product.

580 Moreover, Kang et al. (2013) found that the total amount of Se oxyanions plays an important  
581 role in this context. This is due to the fact that shares of remaining non-reduced Se oxyanions  
582 prevent the precipitation of FeSe and support the formation of elemental Se:



585 However, because of the alkaline pH as well as the relatively large amount of Fe(II) mineral  
586 phases, resulting in a small amount of remaining Se oxyanions, one can assume that this  
587 reaction is prevented in our studies.

588 The second important Se redox reaction takes place during the progressive oxidation of the  
589 aquatic system due to the contact with atmospheric oxygen. This process leads to further  
590 oxidation of Fe(II) to Fe(III) and thereby to the complete transformation of iron(II) hydroxide  
591 and green rust into magnetite. Besides that, however, oxygen also causes the oxidation of Se(-  
592 II) to Se(0). As a consequence, the nanoparticulate FeSe oxidizes to gray elemental Se that  
593 occurs in form of euhedral crystals with sizes of 1 - 2  $\mu\text{m}$  within the magnetite matrix (Fig. 8).  
594 The oxidation of FeSe in elemental Se can generally be described by the following two-part  
595 dissolution-precipitation reaction:



598 As can be derived from this reaction, formation of microcrystalline gray Se from  
599 nanoparticulate FeSe should only be possible when  $O_2$  reacts primarily with the iron hydroxide  
600 phases and not with FeSe. Otherwise it is hard to explain how the  $HSe^-$  remains stable long  
601 enough to form Se(0) particles of larger sizes. However, if the entry of  $O_2$  causes the oxidation  
602 of the iron hydroxides, this would result in a buffering of the system and in the preservation of  
603 the initial anoxic conditions. Kurokawa and Senna (1999) reported a self-stabilization effect of  
604 green rust against aerial oxidation by adsorption of dissolved  $Fe^{2+}$ . This oxidation process  
605 would then inevitably lead to a consumption of  $Fe^{2+}$ , which in turn would cause the dissolution

606 of the most unstable Fe(II) mineral phases. In this context, dissolution of the nanoparticulate  
607 FeSe comes into question, since FeSe has a relatively high solubility compared to other iron  
608 selenides or iron(II) hydroxides (Kang et al., 2013). Furthermore, it is known that the solubility  
609 of nanoparticulate phases can be significantly higher than for crystalline particles of larger sizes  
610 (Fernández-Martínez and Charlet, 2009). Due to the still prevailing anoxic conditions, the  
611 hereby formed  $\text{HSe}^-$  species would be stable for a longer time. This would allow a more  
612 controlled and slower Se(-II) oxidation and thus the formation of elemental Se with larger  
613 particle sizes.

614 It must also be noted that elemental Se is still the dominant Se phase at the end of the  
615 coprecipitation process, even though Se(0) is not the thermodynamically favored oxidation state  
616 under alkaline, oxic conditions. This is probably influenced by the relatively large size of the  
617 elemental Se crystals that inhibits further oxidation of Se(0). Since the progressive oxidation is  
618 not accompanied by remobilization of Se and there is also no indication of a further Se  
619 oxidation, the stability of the Se immobilization seems to be mainly determined by the previous  
620 transformation of unstable FeSe into elemental Se. Interestingly, the Se retention mechanism is  
621 also not affected by the nature of the final iron oxide precipitation product (Fig. A.4). Dissolved  
622 Se oxyanions are initially reduced to FeSe and then oxidized to elemental gray Se, regardless  
623 of whether the oxidation of iron(II) hydroxide and green rust leads to the formation of magnetite  
624 or iron(III) oxyhydroxides like goethite and lepidocrocite.

## 625 4 Conclusion

626 The results of this study demonstrate that the formation pathway of magnetite is more crucial  
627 for the immobilization of dissolved Se oxyanions than the interaction processes after the  
628 completed mineral formation. Key factor is the contact and interaction of Se oxyanions with  
629 metastable Fe(II)-rich intermediates, which causes a reductive Se precipitation and defines the  
630 retention capacity. Also of great importance are the prevailing hydrochemical conditions,  
631 including pH and redox, since those parameters primarily determine the iron oxide formation  
632 and transformation pathway as well as the nature and stability of the Se precipitation products.  
633 In case of the here investigated conditions, this behavior led to the initial reduction of Se(IV)  
634 or Se(VI) to FeSe, which was afterwards oxidized to elemental gray Se during the progressive  
635 aerial oxidation process.

636 Regarding the behavior of Se in the geosphere, the study showed that reductive Se precipitation  
637 represents an efficient and comparatively durable mechanism to immobilize dissolved Se  
638 oxyanions. Processes like these should be considered in safety assessments of HLW disposal

639 sites, as they may affect the migration of the radionuclide  $^{79}\text{Se}$  (interaction of  $^{79}\text{Se}$  with  
640 secondary iron oxides in the near-field). Moreover, one could imagine that this mechanisms are  
641 used actively to reduce the appearance of mobile Se species. An intended manipulation of the  
642 redox-dependent Se solubility due to the entry of reduced iron could, for example, be applied  
643 in the treatment of Se contaminated wastewaters.

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