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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 Fe²⁺ 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 Fe²⁺ 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 ⁷⁹Se 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 ⁷⁹Se, 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 [Fe₃O₄] 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 Fe²⁺ 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 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 Fe^{2+} system is more suitable to simulate the
121 formation of magnetite in nature than a preparation based on the mixing of Fe^{2+} and 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 N_2 -
123 degassed Milli-Q water ($\sim\text{pH}$ 3.5). After the addition of 55 ml 1 M KOH and the immediate
124 precipitation of a bluish green compound ($\sim\text{pH}$ 8), the suspension was titrated and buffered with
125 25 ml of 1 M 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, 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 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 Cl^- and HCO_3^- impurities. The washed magnetite samples were then
137 dried at 40°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 Fe^{2+} prior to the mineral
149 precipitation. Se stock solutions were prepared by dissolving defined quantities of Na_2SeO_3 or
150 $\text{Na}_2\text{SeO}_4 \cdot 10 \text{H}_2\text{O}$ in 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

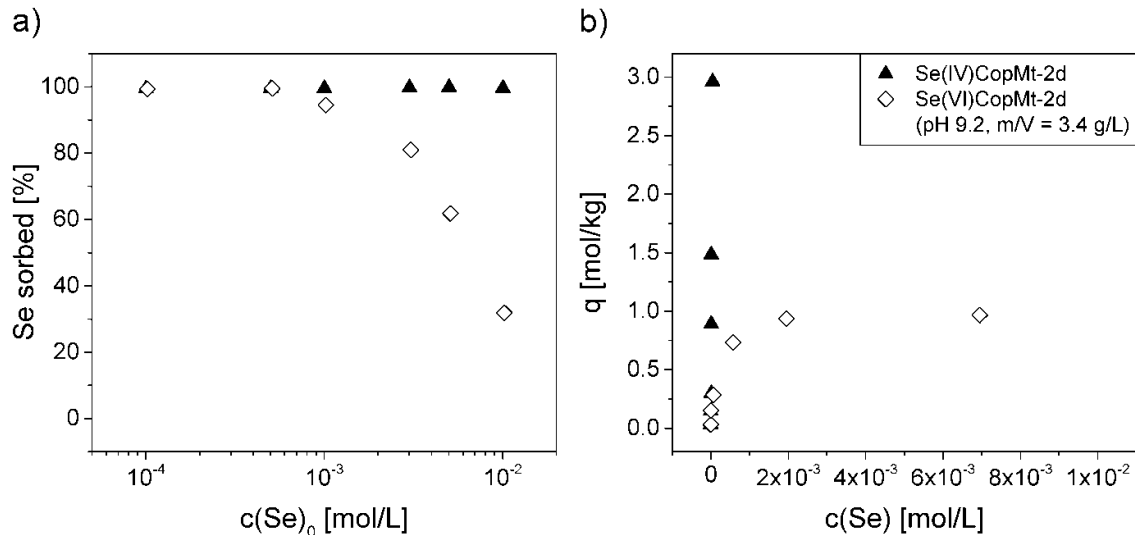
195 XRD patterns of synthesized magnetite after the total reaction of 48 h showed that pure
196 magnetite [Fe₃O₄] was formed without any evidence of goethite contaminations. For the
197 magnetite precursor phases (reaction time 30 min or 3 h), the XRD analysis revealed that these
198 samples consist 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 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 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-H₂O 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) ^a	Se ^b [ppm]	pH ^c	c(Fe) [mol/L]	c(Se) ₀ [mol/L]	c(Se) [mol/L]	Se sorbed [%]	log K _d [L/kg]
1	---	Mt (pure)	Mt	bdl	8.9	7.96E-07	0.00E+00	bdl	-	-
2	Se(VI)	Se(VI)CopMt ^{0.1}	Mt	1700	9.2	6.45E-08	1.02E-04	5.71E-07	99.4	4.72
3	"	Se(VI)CopMt ^{0.5}	Mt + Se(0)	9900	9.1	4.16E-07	5.11E-04	2.73E-06	99.5	4.74
4	"	Se(VI)CopMt ¹	Mt + Se(0)	16000	9.2	4.51E-07	1.02E-03	5.66E-05	94.5	3.70
5	"	Se(VI)CopMt ³	Mt + Se(0)	40000	9.0	1.69E-06	3.07E-03	5.84E-04	81.0	3.10
6	"	Se(VI)CopMt ⁵	Mt + Se(0)	58000	9.3	3.47E-07	5.11E-03	1.95E-03	61.9	2.68
7	"	Se(VI)CopMt ¹⁰	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 ^{0.1}	Mt	1700	9.2	5.23E-08	1.00E-04	5.84E-07	99.4	4.70
9	"	Se(IV)CopMt ^{0.5}	Mt + Se(0)	8600	9.2	6.41E-08	5.02E-04	2.25E-06	99.6	4.82
10	"	Se(IV)CopMt ¹	Mt + Se(0)	17000	9.1	2.53E-07	1.00E-03	5.10E-06	99.5	4.76
11	"	Se(IV)CopMt ³	Mt + Se(0)	48000	9.0	2.80E-07	3.01E-03	8.61E-06	99.7	5.01
12	"	Se(IV)CopMt ⁵	Mt + Se(0)	74000	9.3	6.56E-06	5.02E-03	1.02E-05	99.8	5.16
13	"	Se(IV)CopMt ¹⁰	Mt + Gt + Se(0)	140000	9.5	1.04E-06	1.00E-02	4.30E-05	99.6	4.84

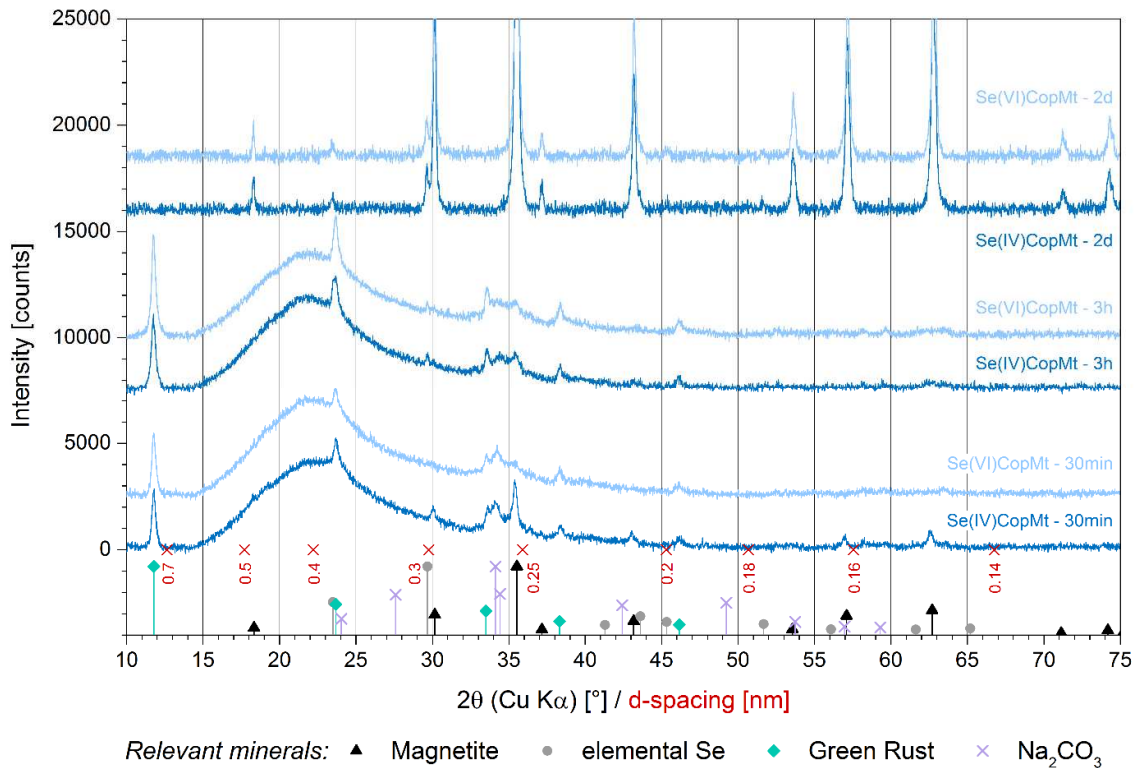
^a Mineral composition (XRD analysis). ^b Se content of the solid phase (EDXRF analysis). ^c pH after synthesis/coprecipitation

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_{total} 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-H₂O 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⁻)] or carbonate green rust [GR(CO₃²⁻)] (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⁻) over oxide (O²⁻)
 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_{total} 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(CO₃²⁻) [Fe^{II}₄Fe^{III}₂(OH)₁₂CO₃ · 3 H₂O;
 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.

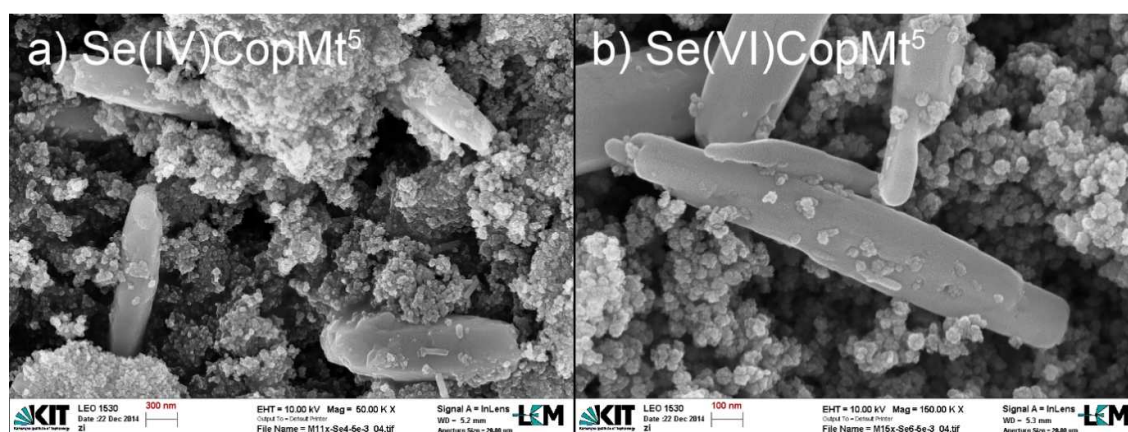
331 Furthermore, since the proportion of magnetite does not increase within the first 3 hours, one
332 can conclude that the magnetite formation requires a certain period of time. This is also
333 confirmed by the macroscopic observation that the color change of the precipitate from bluish
334 green 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 μm) 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

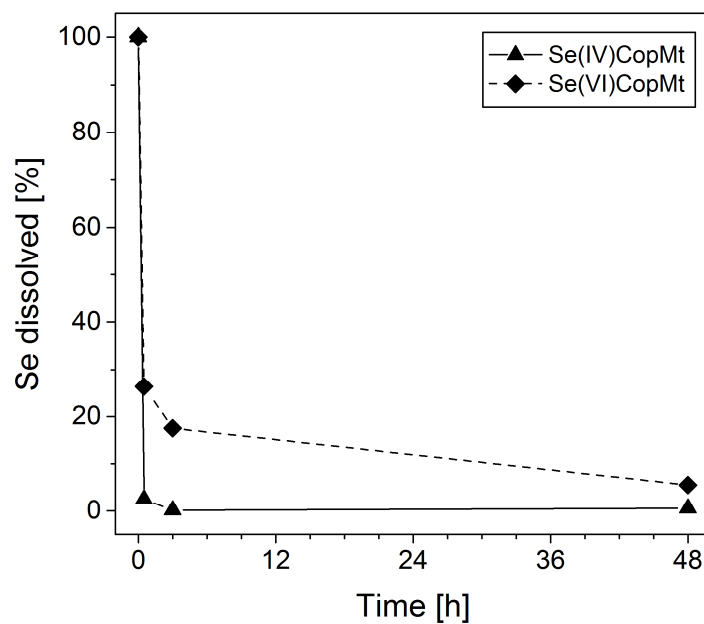
359 (Murphy, 1988; Zingaro et al., 1997; Chen et al., 2009) and green rust (Myneni et al., 1997;
360 Johnson and Bullen, 2003; Scheidegger et al., 2003). By contrast, sorption studies on magnetite
361 (Scheinost et al., 2008; Scheinost and Charlet, 2008) showed that reduction processes can also
362 lead 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.**

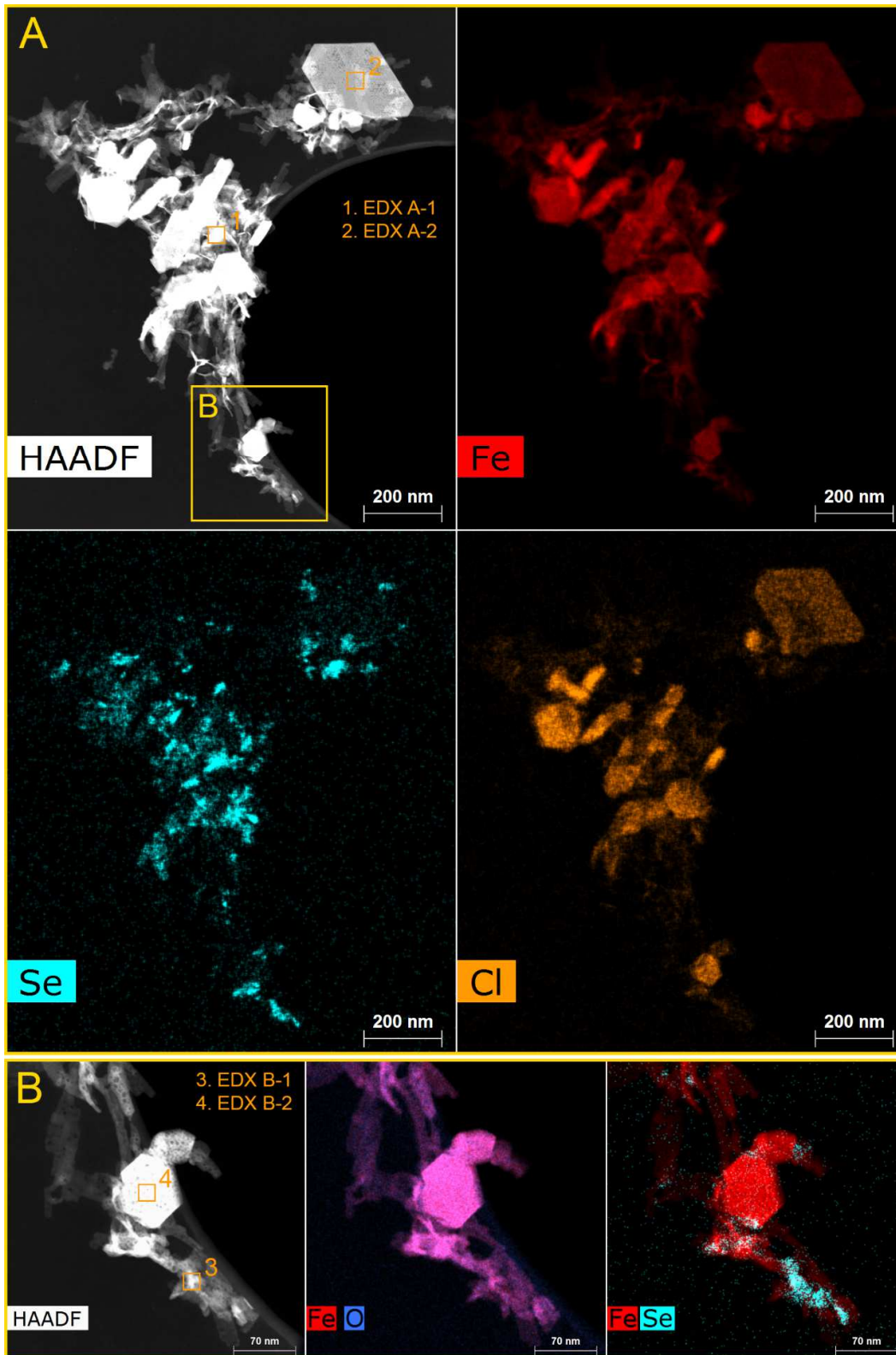
387 In order to find out what retention mechanism causes the immobilization of Se(IV) or Se(VI)
 388 in the early stage of the coprecipitation process, the fate of Se after reaction times of 30 min
 389 was characterized in detail. This included, among other things, an analysis of the Se oxidation
 390 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(CO₃²⁻)
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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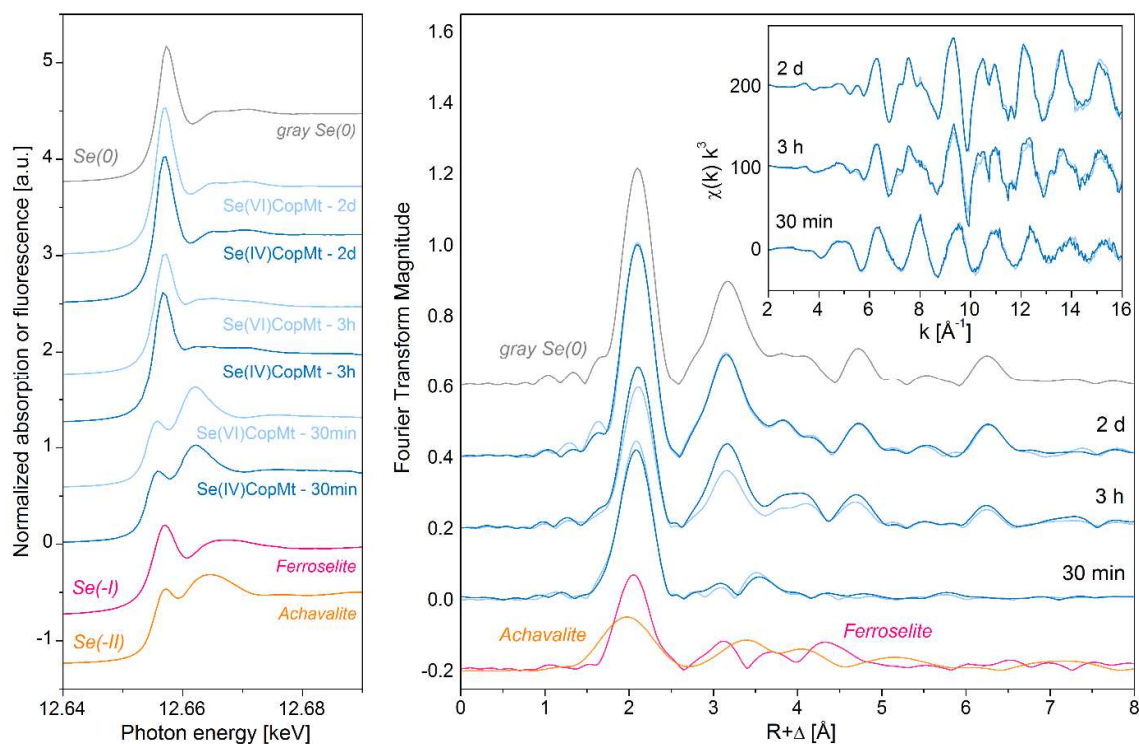
433

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 [FeSe₂], 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.

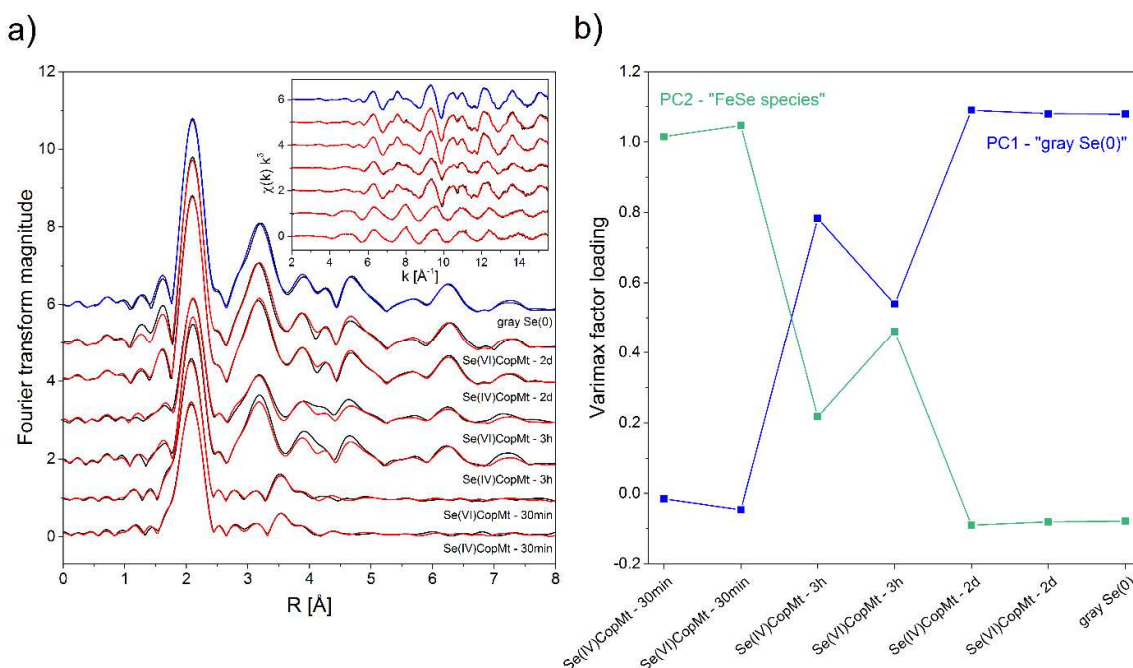


451

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 χ 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, Fe₃Se₄ or Fe₇Se₈ (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			ΔE_0 [eV]	χ^2_{res} [%]			
		CN ^a	R [Å] ^b	σ^2 [Å ²] ^c	CN	R [Å]	σ^2 [Å ²]					
Se(IV)CopMt ¹ -30min	12.6541	2.7	Fe	2.40	0.0037	1.0	Se	3.39	0.0066	12.7	4.3	
						5.3	Se	3.89	0.0100			§
						2.4	Fe	4.11	0.0074			
Se(VI)CopMt ¹ -30min	12.6540	2.8	Fe	2.40	0.0036	0.5	Se	3.38	0.0052	12.9	3.6	
						6.1	Se	3.90	0.0100			§
						2.6	Fe	4.13	0.0070			
Se(IV)CopMt ¹ -2d	12.6556	2 ^f	Se	2.38	0.0015	4 ^f	Se	3.38	0.0047	10.6	3.8	
						2 ^f	Se	3.74	0.0034			
						6 ^f	Se	4.32	0.0058			
						4 ^f	Se	4.46	0.0046			
						4 ^f	Se	4.94	0.0048			
Se(VI)CopMt ¹ -2d	12.6556	2 ^f	Se	2.38	0.0015	4 ^f	Se	3.38	0.0046	10.9	4.2	
						2 ^f	Se	3.74	0.0036			
						6 ^f	Se	4.31	0.0061			
						4 ^f	Se	4.45	0.0049			
						4 ^f	Se	4.94	0.0050			

^a CN: coordination number, error $\pm 25\%$. ^b R: Radial distance, error ± 0.01 Å. ^c σ^2 : Debye-Waller factor, error ± 0.0005 Å².

^f fixed coordination numbers. [§] Upper σ^2 limit reached. ^x $c(\text{Se})_0 = "X" \cdot 10^{-3}$ mol/L.

522 The fit of χ 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.

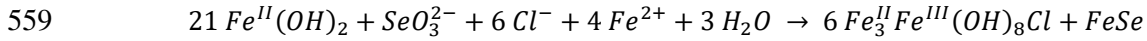
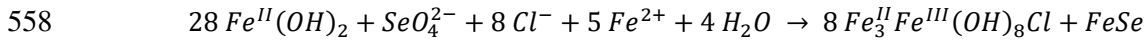
535 3.6 Conceptual model of the Se retention during the magnetite formation

536 The results of this study prove that the immobilization of Se oxyanions during the aerial
537 oxidation of an anoxic Fe-Se-H₂O system, which results in the formation of magnetite, is due
538 to two redox processes.

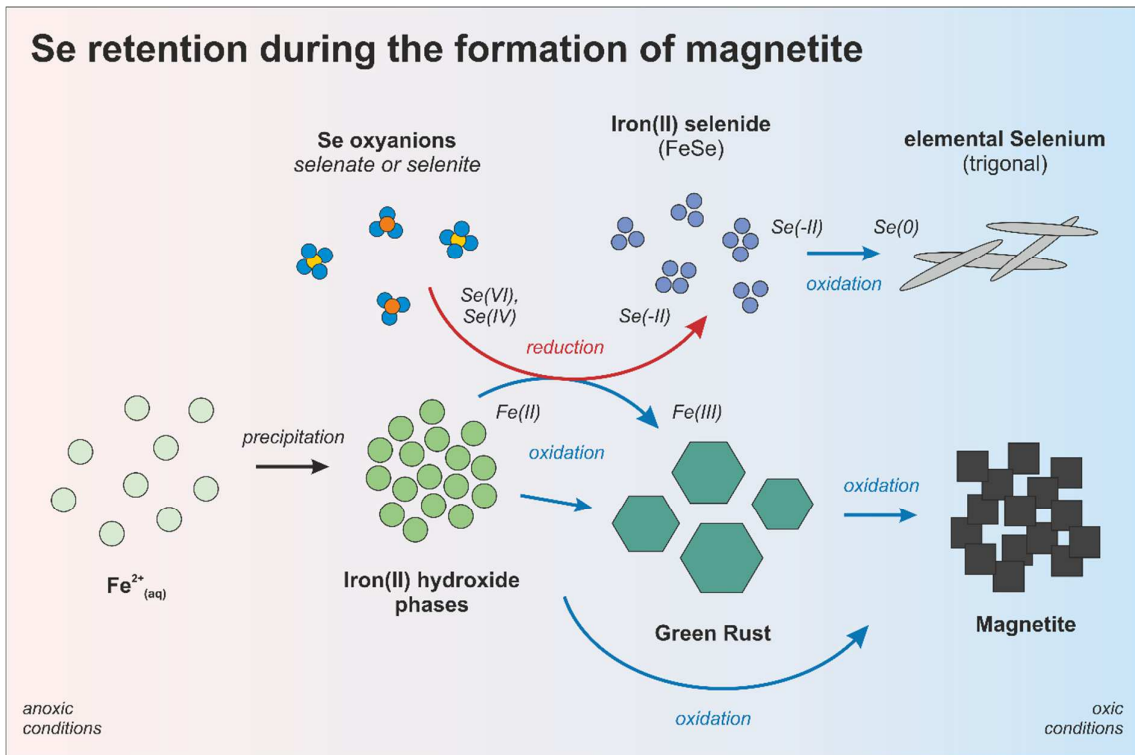
539 The first redox process takes place under reducing conditions in the early stage of the magnetite
540 formation, where dissolved Se oxyanions interact with primarily Fe(II)-rich precipitation
541 products of the aquatic Fe²⁺ system. These products are mainly iron(II) hydroxide and green
542 rust, 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 Fe²⁺ generally favors the Se reduction process (Tang et al., 2014), a
550 reduction only by dissolved Fe²⁺ 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/Fe²⁺ 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).



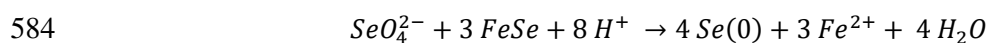
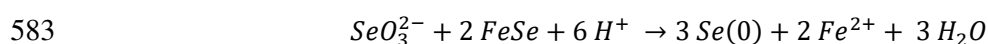
566

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 μm 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 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}Se (interaction of ^{79}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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653 References

- 654 Ankudinov A. L. and Rehr J. J. (1997) Relativistic calculations of spin-dependent x-ray-absorption
655 spectra. *Phys. Rev. B* **56**, 1712–1715.
- 656 Bingham P. A., Connelly A. J., Cassingham N. J. and Hyatt N. C. (2011) Oxidation state and local
657 environment of selenium in alkali borosilicate glasses for radioactive waste immobilisation. *J. Non.*
658 *Cryst. Solids* **357**, 2726–2734.
- 659 Blume H.-P., Brümmer G. W., Fleige H., Horn R., Kandeler E., Kögel-Knabner I., Kretzschmar R.,
660 Stahr K. and Wilke B.-M. (2016) *Scheffer/Schachtschabel - Soil Science*. 16th ed., Springer,
661 Heidelberg, Germany.
- 662 Börsig N., Scheinost A. C., Shaw S., Schild D. and Neumann T. (2017) Uptake mechanisms of selenium
663 oxyanions during the ferrihydrite-hematite recrystallization. *Geochim. Cosmochim. Acta* **206**,
664 236–253.
- 665 Bruggeman C., Maes A., Vancluysen J. and Vandemussele P. (2005) Selenite reduction in Boom clay:
666 Effect of FeS_2 , clay minerals and dissolved organic matter. *Environ. Pollut.* **137**, 209–21.
- 667 De Cannière P., Maes A., Williams S., Bruggeman C., Beauwens T., Maes N. and Cowper M. (2010)
668 *Behaviour of Selenium in Boom Clay. External Report of the Belgian Nuclear Research Centre.,*
669 *SCK•CEN-ER-120*, Mol, BEL.
- 670 Chakraborty S., Bardelli F. and Charlet L. (2010) Reactivities of Fe(II) on Calcite : Selenium Reduction.
671 *Environ. Sci. Technol.* **44**, 1288–1294.
- 672 Charlet L., Scheinost A. C., Tournassat C., Greneche J. M., Géhin A., Fernández-Martínez A., Coudert
673 S., Tisserand D. and Brendle J. (2007) Electron transfer at the mineral/water interface: Selenium
674 reduction by ferrous iron sorbed on clay. *Geochim. Cosmochim. Acta* **71**, 5731–5749.
- 675 Chen Y.-W., Truong H.-Y. T. and Belzile N. (2009) Abiotic formation of elemental selenium and role
676 of iron oxide surfaces. *Chemosphere* **74**, 1079–1084.
- 677 Cornell R. M. and Schwertmann U. (2003) *The iron oxydes: Structure, Properties, Reactions,*

- 678 *Occurrences and Uses*. 2nd ed., Wiley-VCH, Weinheim, Germany.
- 679 Curti E., Froideval-Zumbiehl A., Günther-Leopold I., Martin M., Bullemer A., Linder H., Borca C. N.
680 and Grolimund D. (2014) Selenium redox speciation and coordination in high-burnup UO₂ fuel:
681 Consequences for the release of ⁷⁹Se in a deep underground repository. *J. Nucl. Mater.* **453**, 98–
682 106.
- 683 Curti E., Puranen A., Grolimund D., Jädernas D., Sheptyakov D. and Mesbah A. (2015) Characterization
684 of selenium in UO₂ spent nuclear fuel by micro X-ray absorption spectroscopy and its
685 thermodynamic stability. *Environ. Sci. Process. Impacts* **17**, 1760–1768.
- 686 Dhillon K. S. and Dhillon S. K. (2003) Distribution and management of seleniferous soils. *Adv. Agron.*
687 **79**, 119–184.
- 688 Drissi H., Refait P. and Génin J.-M. R. (1994) The oxidation of Fe(OH)₂ in the presence of carbonate
689 ions : Structure of carbonate green rust one. *Hyperfine Interact.* **90**, 395–400.
- 690 Fernández-Martínez A. and Charlet L. (2009) Selenium environmental cycling and bioavailability: A
691 structural chemist point of view. *Rev. Environ. Sci. Biotechnol.* **8**, 81–110.
- 692 Génin J.-M. R., Ruby C., Géhin A. and Refait P. (2006) Synthesis of green rusts by oxidation of
693 Fe(OH)₂, their products of oxidation and reduction of ferric oxyhydroxides; Eh-pH Pourbaix
694 diagrams. *Comptes Rendus Geosci.* **338**, 433–446.
- 695 Grambow B. (2008) Mobile fission and activation products in nuclear waste disposal. *J. Contam.*
696 *Hydrol.* **102**, 180–186.
- 697 Huber F., Schild D., Vitova T., Rothe J., Kirsch R. and Schäfer T. (2012) U(VI) removal kinetics in
698 presence of synthetic magnetite nanoparticles. *Geochim. Cosmochim. Acta* **96**, 154–173.
- 699 Johnson T. M. and Bullen T. D. (2003) Selenium isotope fractionation during reduction by Fe(II)-Fe(III)
700 hydroxide-sulfate (green rust). *Geochim. Cosmochim. Acta* **67**, 413–419.
- 701 Jordan N., Lomenech C., Marmier N., Giffaut E. and Ehrhardt J.-J. (2009) Sorption of selenium(IV)
702 onto magnetite in the presence of silicic acid. *J. Colloid Interface Sci.* **329**, 17–23.
- 703 Jörg G., Bühnenmann R., Hollas S., Kivel N., Kossert K., Van Winckel S. and Lierse v. Gostomski C.
704 (2010) Preparation of radiochemically pure ⁷⁹Se and highly precise determination of its half-life.
705 *Appl. Radiat. Isot.* **68**, 2339–2351.
- 706 Kämpf N., Scheinost A. C. and Schulze D. G. (2011) Oxide Minerals in Soils. In *Handbook of Soil*
707 *Sciences: Properties and Processes* (eds. P. M. Huang, Y. Li, and M. E. Sumner). CRC Press,
708 Boca Raton, USA. p. 1442.
- 709 Kang M., Ma B., Bardelli F., Chen F., Liu C., Zheng Z., Wu S. and Charlet L. (2013) Interaction of
710 aqueous Se(IV)/Se(VI) with FeSe/FeSe₂: Implication to Se redox process. *J. Hazard. Mater.* **248**–
711 **249**, 20–28.
- 712 Kurokawa H. and Senna M. (1999) Self-stabilization of green rust (II) as a precursor of acicular goethite
713 particles with highest possible aspect ratio. *Powder Technol.*, 71–79.
- 714 Legrand L., Mazerolles L. and Chaussé A. (2004) The oxidation of carbonate green rust into ferric
715 phases: Solid-state reaction or transformation via solution. *Geochim. Cosmochim. Acta* **68**, 3497–
716 3507.
- 717 Lenz M. and Lens P. N. L. (2009) The essential toxin: The changing perception of selenium in
718 environmental sciences. *Sci. Total Environ.* **407**, 3620–3633.
- 719 Liang L., Yang W., Guan X., Li J., Xu Z., Wu J., Huang Y. and Zhang X. (2013) Kinetics and
720 mechanisms of pH-dependent selenite removal by zero valent iron. *Water Res.* **47**, 5846–5855.
- 721 Loyo R. L. de A., Nikitenko S. I., Scheinost A. C. and Simonoff M. (2008) Immobilization of selenite
722 on Fe₃O₄ and Fe/Fe₃C ultrasmall particles. *Environ. Sci. Technol.* **42**, 2451–2456.
- 723 Miller W., Alexander R., Chapman N., McKinley J. C. and Smellie J. A. T. (2000) *Geological Disposal*

- 724 *of Radioactive Wastes and Natural Analogues.*, Elsevier Science.
- 725 Missana T., Alonso U., Scheinost A. C., Granizo N. and García-Gutiérrez M. (2009) Selenite retention
726 by nanocrystalline magnetite: Role of adsorption, reduction and dissolution/co-precipitation
727 processes. *Geochim. Cosmochim. Acta* **73**, 6205–6217.
- 728 Mitchell K., Couture R.-M., Johnson T. M., Mason P. R. D. and Van Cappellen P. (2013) Selenium
729 sorption and isotope fractionation: Iron(III) oxides versus iron(II) sulfides. *Chem. Geol.* **342**, 21–
730 28.
- 731 Mullet M., Guillemin Y. and Ruby C. (2008) Oxidation and deprotonation of synthetic Fe^{II}-Fe^{III}
732 (oxy)hydroxycarbonate Green Rust: An X-ray photoelectron study. *J. Solid State Chem.* **181**, 81–
733 89.
- 734 Murphy A. P. (1988) Removal of selenate from water by chemical reduction. *Ind. Eng. Chem. Res.* **27**,
735 187–191.
- 736 Myneni S. C. B., Tokunaga T. K., Brown Jr., G. E. (1997) Abiotic Selenium Redox Transformations in
737 the Presence of Fe(II,III) Oxides. *Science* . **278**, 1106–1109.
- 738 Nothstein A. K., Eiche E., Riemann M., Nick P., Winkel L. H. E., Göttlicher J., Steininger R., Brendel
739 R., Von Brasch M., Konrad G. and Neumann T. (2016) Tracking Se Assimilation and Speciation
740 through the Rice Plant - Nutrient Competition, Toxicity and Distribution. *PLoS One* **11**.
- 741 Olegario J. T., Yee N., Miller M., Sczepaniak J. and Manning B. (2010) Reduction of Se(VI) to Se(-II)
742 by zerovalent iron nanoparticle suspensions. *J. Nanoparticle Res.* **12**, 2057–2068.
- 743 Perez O. P. and Umetsu Y. (2000) ORP-monitored magnetite formation from aqueous solutions at low
744 temperatures. *Hydrometallurgy* **55**, 35–56.
- 745 Perez O. P., Umetsu Y. and Sasaki H. (1998) Precipitation and densification of magnetic iron
746 compounds from aqueous solutions at room temperature. *Hydrometallurgy* **50**, 223–242.
- 747 Rebodos R. L. and Vikesland P. J. (2010) Effects of oxidation on the magnetization of nanoparticulate
748 magnetite. *Langmuir* **26**, 16745–16753.
- 749 Refait P., Abdelmoula M. and Génin J.-M. R. (1998) Mechanisms of formation and structure of green
750 rust one in aqueous corrosion of iron in the presence of chloride ions. *Corros. Sci.* **40**, 1547–1560.
- 751 Refait P., Simon L. and Génin J.-M. R. (2000) Reduction of SeO₄²⁻ Anions and Anoxic Formation of
752 Iron (II) - Iron (III) Hydroxy-Selenate Green Rust. *Environ. Sci. Technol.* **34**, 819–825.
- 753 Ressler T. (1998) WinXAS: a program for X-ray absorption spectroscopy data analysis under MS-
754 Windows. *J. Synchrotron Radiat.* **5**, 118–122.
- 755 Rossberg A., Reich T. and Bernhard G. (2003) Complexation of uranium(VI) with protocatechuic acid-
756 application of iterative transformation factor analysis to EXAFS spectroscopy. *Anal. Bioanal.*
757 *Chem.* **376**, 631–638.
- 758 Rovira M., Giménez J., Martínez M., Martínez-Lladó X., de Pablo J., Martí V. and Duro L. (2008)
759 Sorption of selenium(IV) and selenium(VI) onto natural iron oxides: Goethite and hematite. *J.*
760 *Hazard. Mater.* **150**, 279–284.
- 761 Scheidegger A. M., Grolimund D., Cui D., Devoy J., Spahiu K., Wersin P., Bonhoure I. and Janousch
762 M. (2003) Reduction of selenite on iron surfaces: A microspectroscopic study. *J. Phys. IV* **104**,
763 417–420.
- 764 Scheinost A. C. and Charlet L. (2008) Selenite reduction by mackinawite, magnetite and siderite: XAS
765 characterization of nanosized redox products. *Environ. Sci. Technol.* **42**, 1984–1989.
- 766 Scheinost A. C., Kirsch R., Banerjee D., Fernandez-Martinez A., Zaenker H., Funke H. and Charlet L.
767 (2008) X-ray absorption and photoelectron spectroscopy investigation of selenite reduction by
768 FeII-bearing minerals. *J. Contam. Hydrol.* **102**, 228–245.
- 769 Schwertmann U. and Cornell R. M. (2000) *Iron oxides in the laboratory: Preparation and*

- 770 *characterization*. 2nd ed., Wiley-VCH, Weinheim, Germany.
- 771 Schwertmann U. and Fechter H. (1994) The formation of green rust and its transformation to
772 lepidocrocite. *Clay Miner.* **29**, 87–92.
- 773 Séby F., Potin-Gautier M., Giffaut E., Borge G. and Donard O. F. X. (2001) A critical review of
774 thermodynamic data for selenium species at 25°C. *Chem. Geol.* **171**, 173–194.
- 775 Séby F., Potin-Gautier M., Giffaut E. and Donard O. F. X. (1998) Review Assessing the speciation and
776 the biogeochemical processes affecting the mobility of selenium from a geological repository of
777 radioactive wastes to the biosphere. *Analisis* **26**, 193–198.
- 778 Smailos E., Schwarzkopf W., Kienzler B. and Köster R. (1992) Corrosion of carbon-steel container for
779 heat-generating nuclear waste in brine environment relevant for a rock-salt repository. *MRS Proc.*
780 **257**, 299–406.
- 781 Smart N. R., Rance A. P. and Werme L. O. (2008) The effect of radiation on the anaerobic corrosion of
782 steel. *J. Nucl. Mater.* **379**, 97–104.
- 783 Sumoondur A., Shaw S., Ahmed I. and Benning L. G. (2008) Green rust as a precursor for magnetite:
784 an in situ synchrotron based study. *Mineral. Mag.* **72**, 201–204.
- 785 Tang C., Huang Y. H., Zeng H. and Zhang Z. (2014) Reductive removal of selenate by zero-valent iron:
786 The roles of aqueous Fe²⁺ and corrosion products, and selenate removal mechanisms. *Water Res.*
787 **67**, 166–174.
- 788 Tang J., Myers M., Bosnick K. a and Brus L. E. (2003) Magnetite Fe₃O₄ Nanocrystals: Spectroscopic
789 Observation of Aqueous Oxidation Kinetics. *J. Phys. Chem. B* **107**, 7501–7506.
- 790 Wang Y., Morin G., Ona-Nguema G., Juillot F., Calas G. and Brown G. E. (2011) Distinctive arsenic(V)
791 trapping modes by magnetite nanoparticles induced by different sorption processes. *Environ. Sci.*
792 *Technol.* **45**, 7258–7266.
- 793 Wersin P., Johnson L. H., Schwyn B., Berner U. and Curti E. (2003) *Redox Conditions in the Near Field*
794 *of a Repository for SF/HLW and ILW in Opalinus Clay. NAGRA Technical Report 02-13.*,
795 Wettingen, CH.
- 796 Winkel L. H. E., Vriens B., Jones G. D., Schneider L. S., Pilon-Smits E. and Bañuelos G. S. (2015)
797 Selenium Cycling Across Soil-Plant-Atmosphere Interfaces: A Critical Review. *Nutrients* **7**, 4199–
798 4239.
- 799 Yoon I.-H., Kim K.-W., Bang S. and Kim M. G. (2011) Reduction and adsorption mechanisms of
800 selenate by zero-valent iron and related iron corrosion. *Appl. Catal. B Environ.* **104**, 185–192.
- 801 Zingaro R. A., Dufner D. C., Murphy A. P. and Moody C. D. (1997) Reduction of oxoselenium anions
802 by iron(II) hydroxide. *Environ. Int.* **23**, 299–304.
- 803