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 Coláiste na hOllscoile Corcaigh

1 Enrichment processes of arsenic in oxidic sedimentary rocks – from geochemical and genetic  
2 characterization to potential mobility

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13  
14 Abstract

15 Sedimentary marine iron ores of Jurassic age and Tertiary marine sandy sediments containing iron  
16 hydroxides concretions have been sampled from boreholes and outcrops in two study areas in  
17 Germany to examine iron and arsenic accumulation processes. Samples were analyzed for bulk rock  
18 geochemistry (INAA/ICP-OES), quantitative mineralogy (XRD with Rietveld analysis), element  
19 distribution (electron microprobe) and arsenic fractionation (sequential extraction). Bulk Jurassic ores  
20 contain an average arsenic content of  $123 \mu\text{g g}^{-1}$  hosted in mainly goethite ooids which slowly formed  
21 in times of condensed sedimentation. Enrichment occurred syndepositionally and is therefore  
22 characterized as primary. Iron concretions in Tertiary sediments mainly consist of goethite and yield  
23 arsenic up to  $1860 \mu\text{g g}^{-1}$ . The accumulation process is secondary as it took place in the course of  
24 oxidation of the originally reduced marine sediments under terrestrial conditions, leading to element  
25 redistribution and local enrichment in the near-surface part. The scale of enrichment was assessed

26 calculating Enrichment Factors, indicating that arsenic accumulation was favoured over other potential  
27 contaminants. In spite of higher bulk arsenic contents in the oxidic rocks, the mainly pyrite-hosted As  
28 pool within the reduced deeper part of the Tertiary sediments is shown to have a higher potential for  
29 remobilization and creation of elevated arsenic concentrations in groundwater.

30

31 Keywords

32 arsenic, accumulation process, iron mineral, enrichment factor, redox conditions, mobilization

33

34

35 1 Introduction

36 1.1 Background and objectives

37 During the past two decades, the intensity of arsenic (As) research has increased substantially.

38 Reasons for that are the recognition of As toxicity and its initially underestimated impact on human

39 health on a global scale, focussing on large problem areas, especially in Southeast Asia (e.g.

40 Ravenscroft et al. 2005, Zahid et al. 2009). Consequently, drinking water threshold values were

41 broadly lowered in the 1990ies, mostly down to  $10 \mu\text{g L}^{-1}$ . This confronted water suppliers with the

42 problem of an increased need to process raw water in order to match drinking water requirements. In

43 recent years, it was also found that in the large majority of cases, naturally occurring As is responsible

44 for elevated groundwater concentrations. Thereby, mobilization from As-enriched minerals is the

45 dominating process (e.g. Lowers et al. 2007, Armienta et al. 2001). Showing characteristics of both

46 chalcophile and siderophile behaviour, arsenic tends to be preferably hosted by sulphide minerals like

47 pyrite or (hydr)oxidic Fe phases like goethite, both of which can contain As up to several wt.%

48 (Smedley and Kinniburgh 2002). In spite of its low average abundance in the upper earth's crust ( $1.5\text{-}2$

49  $\mu\text{g g}^{-1}$ ; Matschullat 1999), arsenic can accumulate in rocks to concentrations several orders of

50 magnitude higher than this value. The fate of As in the environment is controlled by the prevailing

51 physico-chemical conditions and the presence of other ions. Redox potential, pH and ionic

52 competition are crucial parameters governing As behaviour (adsorption, desorption, transport, redox

53 transformation). Reducing conditions can lead to As mobilization from oxides while oxidizing  
54 conditions may mobilize As bound to sulphides. High groundwater pH constrains As adsorption to  
55 mineral surfaces and may therefore be responsible for elevated concentrations in solution. Ions  
56 competing with As species for surface binding sites, especially phosphate, can lead to the same result  
57 (Stollenwerk 2002, Smedley and Kinniburgh 2002).

58 The basis to understand geogenic As cycling and the impact of water-rock-interaction leading to  
59 groundwater contamination is the comprehension of the mechanisms that led to those accumulations,  
60 i.e. arsenic enrichment processes. These often took place millions of years ago, but still have a major  
61 influence on the recent occurrence and thus, hydrogeochemical behaviour, of As and other potential  
62 groundwater contaminants.

63 While As accumulation in Southeast Asia is subject to extensive research and ongoing lively  
64 discussions (e.g. Acharyya et al. 2000, Stanger 2005), little is known about the origin and development  
65 of geogenic As accumulations in Germany which have been studied sporadically and on a rather local  
66 to regional scale (e.g. Bayer 1997, Heinrichs and Udluft 1999, Rude and Königskötter 2009, Banning  
67 et al. 2009), although elevated As concentrations have been detected in many parts of the country, an  
68 overview is given by Heinrichs and Udluft (1996).

69 In this study, we analyzed and compared As-bearing sedimentary rocks in two study areas in Germany  
70 and deduced the relevant accumulation processes, taking hydrogeochemical, mineralogical and  
71 paleogeographical information into account, evaluating the scale of enrichment and estimating the  
72 consequences for potential As remobilization and output into groundwater.

73

## 74 1.2 Study areas

75 Two investigation areas in Germany were selected for rock sampling in the Upper Rhine Graben and  
76 in the Lower Rhine Embayment, respectively (Fig. 1).

77

78 Figure 1 Location of study areas in Germany (right side) and geological overview maps with sampling locations  
79 in the Lower Rhine Embayment (LRE; upper left side) and the Upper Rhine Graben (URG; lower left  
80 side).

81

### 82 1.2.1 Upper Rhine Graben (URG)

83 The URG is an approximately NE-SW-striking rift structure in the border area between Germany and  
84 France. It is situated in between the crystalline basement areas of the Black Forest (Germany) and the  
85 Vosges mountains (France) and mainly filled with sediments of Tertiary age (Fig. 1). Along the  
86 fringes, within the contact zone between crystalline basement and basin filling, shallow marine  
87 Jurassic rocks crop out hosting several horizons of sedimentary-marine ooidic Fe ores which can be  
88 found for ~150 km along the basin margin (Sauer and Simon 1975). During the break-in of the URG,  
89 starting in the early Tertiary and being active to date, steep marginal faults developed and the Jurassic  
90 sediments disrupted and today represent the base rock of the Cenozoic graben filling. In the better  
91 accessible marginal part, the sedimentary Fe ores, deposited in the middle Jurassic (Aalenian), were  
92 mined until the 1960ies. One former location of surface Fe ore mining, the Kahlenberg (~30 km north  
93 of Freiburg, mined until 1969 and today serving as a waste disposal site, Fig. 1), offers a nearly  
94 complete succession of sedimentary rocks from the middle Jurassic (Fig. 2) and was therefore chosen  
95 for sampling.

96

### 97 1.2.2 Lower Rhine Embayment (LRE)

98 The LRE is part of the northwest European Tertiary basin which ranges from the British Isles to  
99 Poland. Similar to, and in continuance of, the URG, it represents a rift structure starting its break-in in  
100 middle Tertiary. It is mainly filled with Tertiary marine sediments deriving from the uplift and  
101 subsequent erosion of the surrounding Rhenish Massif. The basin strikes NNW-SSE (Fig. 1). The  
102 graben filling comprises a relatively complete succession of Oligocene, Miocene and Pliocene  
103 sediments which have variable thicknesses due to extensional fault tectonics and the crust breaking  
104 apart into several blocks. The Grafenberg-layers of the Upper Oligocene ( Chattian) are very  
105 widespread within the LRE. They represent marine fine sands with a significant thickness of several  
106 hundred meters due to a high sea level and a quite rapid basin floor subsidence during the Chattian  
107 (GLA NRW 1988, Hiss et al. 2005). The primary calcareous and glauconitic Grafenberg-layers

108 underwent deep terrestrial weathering in the Late Tertiary. This way, they were altered to a depth of  
109 several decametres in terms of losing their calcitic cement and having their Fe(II) mineral phases  
110 oxidized. Iron was mobilized and accumulated as Fe(III) hydroxides in the oxidized upper part. The  
111 redox boundary is not observable in outcrops nowadays, but was described from former quarries and  
112 boreholes by Quaas (1917). He documented it mainly between 20 and 30 m, in one outcrop in only  
113 6 m depth below ground surface. The geological development and present situation is similar to the  
114 one described for the southwestern Münsterland Cretaceous Basin (Banning et al. 2009). The reduced  
115 lower part of the Grafenberg-layers was sampled from boreholes near Willich and Hamminkeln, the  
116 oxidized upper part from two outcrops of these sediments near Stüchteln (Fig. 1).

117

## 118 2 Material and methods

### 119 2.1 Material

120 From the Jurassic sedimentary profile at the Kahlenberg, 32 rock samples were obtained, covering a  
121 sediment thickness of ~34 m and crossing the stratigraphical boundary between Aalenian (Dogger  $\beta$ )  
122 and Bajocian (Dogger  $\gamma$ ) (Fig. 2). Out of these samples, 11 are from the main Fe ore body  
123 (*murchinsonae* ore horizon) and 7 from two thinner Fe ore layers. In the following, the sampled profile  
124 is shortly described. The stratigraphical terms are mainly from Bayer (1970), derived from biozone  
125 classification by ammonites.

126 The profile starts at the bottom with clays (*opalinus* clay) and calcareous sandstones (lowest  
127 Aalenian), both of which were not accessible for sampling. Subsequently, the main ore body  
128 (“Haupterzlager” – HEL) follows with a thickness of ~11 m. The ore consists of Fe phase ooids in  
129 mainly calcitic cement. It is very fossiliferous, especially containing echinoderm remains.

130 Sedimentological studies showed that Fe ooid formation occurred in a shallow marine environment  
131 with long-term relatively stable flow velocities in a facies transition zone between rather carbonate-  
132 dominated and more sandy sediments. The latter can be found some kilometres north of the  
133 Kahlenberg outcrop, arguing for higher flow velocities, lower water depths and proximity to the  
134 coastline (Aldinger 1957; Urban 1966). Clastic and Fe input into the system are estimated to derive

135 from terrestrial weathering of the Rhenisch-Ardennic Shield in the north (Sauer and Simon 1975). The  
136 *staufensis* zone, containing the *murchinsonae* ore, is followed by the *concava* zone composed of  
137 marlstones (“Gryphitenmergel” – GM; ~2 m), sandstones (“Wedelsandstein” – WS; ~6.5 m) and the  
138 lower ore layer (LOL; ~0.7 m). The latter comprises Fe ooids in carbonatic matrix again, and thus  
139 indicates the return of favourable conditions for Fe accumulation. An omission surface on top of this  
140 layer contains the Aalenian-Bajocian stratigraphic boundary. Above that, clayey marlstone (~1.5 m;  
141 not sampled), the upper ore layer (UOL; ~0.7 m; macroscopically similar to the lower one), a  
142 mudstone (“Rimsinger Ton” – RT; ~6 m) and limestone layer (“Hangende Kalke” – HK; ~2.5 m)  
143 belong to the *hyperlioceras* and the *sowerby* zone. The Jurassic rocks in the area are covered by  
144 Pleistocene loess with a thickness of up to 10 m.

145 From the range of the Grafenberg-layers in the LRE, a total number of 36 sediment samples were  
146 taken, 16 of which stem from the reduced lower part and were sampled from cores of up to 182 m  
147 deep boreholes (in addition, one sample of the Quaternary cover sediment – coarse sand – was taken  
148 for comparison). All borehole samples were sealed in gastight bags and stored at 4° C. The remaining  
149 19 samples were obtained from two outcrops of the oxidized upper part of the Grafenberg-layers.

150 The reduced lower facies of the Grafenberg-layers comprises a quite homogenous marine fine sand of  
151 greyish to greenish colours with a total thickness of up to ~300 m in the study area (Nickel 2003).

152 They are little consolidated and contain calcite, glauconite and abundant mollusc shells. Sediment  
153 habit hardly changes on a length of ~140 m in the sampled core (with an important exception in the  
154 uppermost section of the strata which is discussed later on), documenting relatively stable shallow  
155 marine depositional conditions during the Chattian. Clastic input into the basin derived from the  
156 weathering of Variscan mainlands to the east of the LRE.

157 Resulting from the paleo-redox process mentioned in the previous chapter, the oxidized upper facies  
158 of the Grafenberg-layers is composed of yellowish to orange fine sands. They are unconsolidated due  
159 to the loss of their carbonatic cement. Iron mobilized from reduced phases during the late Tertiary  
160 weathering precipitated in the upper part, forming Fe(III) hydroxide coatings around quartz grains. In  
161 outcrops, Fe(III)-concretions are observable which are orange to dark red in colour and significantly

162 more consolidated than the ambient sands. Special attention was paid to these concretions during  
163 sampling.

164

## 165 2.2 Methods

166 Bulk rock geochemistry (55 elements) was assessed for all (68) samples using either Instrumental  
167 Neutron Activation Analysis (INAA; thermal neutron flux:  $7 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ ; Ge detector: resolution  
168 better than 1.7 keV for the 1332 keV,  $^{60}\text{Co}$  photopeak) or total digestion ( $\text{HClO}_4\text{-HNO}_3\text{-HCl-HF}$  at  
169  $240^\circ\text{C}$ ) followed by analysis with ICP-OES (Varian 735ES).

170 Seventeen selected samples (five Jurassic ore samples, five samples from the reduced part of the  
171 Grafenberg-layers, seven from the respective oxidized part) were ground to powder grain size in a  
172 corundum mill and their mineralogical composition was determined using a Bruker AXS D8 Advance  
173 X-ray diffractometer (XRD; operational adjustments: 40 kV, 40 mA;  $2\theta=2\text{-}92^\circ$ ). Quantitative mineral  
174 phase analysis was accomplished applying Rietveld analysis with the software BGMN, version 4.2.3.

175 Thin sections were produced from five Fe ore samples (three from the main ore body – lower, middle  
176 and upper part – and one from the lower and upper ore layer, respectively). These were studied and  
177 photographed using a reflected-light microscope (Leica MZ75). Additionally, two thin sections (upper  
178 and lower part of the main ore body) were analyzed for element distribution with an electron  
179 microprobe (EMP, JEOL JXA-8900R, equipped with energy-dispersive and wavelength-dispersive  
180 spectrometers, and operated at 15 kV and 23 nA with a beam diameter of 1.6  $\mu\text{m}$ ). Qualitative  
181 chemical mapping was performed for Si, Ca, Fe, Mn and As to characterize element distribution  
182 between the main rock components (ooids, matrix, clastic grains). Moreover, a traverse of quantitative  
183 single spot measurements was produced to assess chemical distribution in the single ooid grain scale,  
184 i.e. in the nucleus and the cortex.

185 Arsenic fractionation and mobilization potential were examined applying a sequential extraction  
186 procedure (SEP), designed for As by Wenzel et al. (2001). It was modified accounting for sample  
187 composition, i.e. two additional steps, targeting for As bound on Mn (hydr)oxides and sulphides,  
188 respectively, were implemented for samples with significant Mn or S (as pyrite) content, see chapter



189 3.1. Altogether, the applied procedure consisted of six steps (Tab. 1). A total of 20 samples were  
190 involved in the sequence (eight from the Jurassic sedimentary profile, four from the reduced Tertiary  
191 sediments, eight from their oxidized facies). The pulverized (agate mortar) solid sample (2 g) was  
192 placed in centrifugation tubes. Successively, 50 mL of each extraction reagent was added and the  
193 respective extraction procedure for each step was carried out. The tube was then centrifuged at 3000  
194 rpm for 15 minutes and subsequently, the supernatant solution was filtered through 0.45 µm cellulose  
195 acetate filters. The remaining solid material was then used for the next extraction step. Analysis of  
196 dissolved As was performed using AAS (Perkin Elmer AAnalyst 800, THGA furnace).

197

198 Table 1: Sequential Extraction Procedure.

199

## 200 3 Results

201 Obtained results are presented in this chapter, distinguishing between Jurassic and Tertiary sediments  
202 in the subsections.

### 203 3.1 Bulk rock geochemistry and mineralogy

#### 204 3.1.1 Jurassic sediments

205 Contents of elements relevant for this study in the sampled Jurassic rocks as determined from  
206 INAA/TD-ICP analysis as well as MUNSELL sample colour characterization are shown in Table 2.  
207 Figure 2 illustrates the development of Fe and As as well as Fe phase fractionation in the sediment  
208 profile at the Kahlenberg.

209

210 Table 2: Whole rock geochemical results of selected elements from the Jurassic samples (DL: detection limit;  
211 HK: Hangende Kalke, limestone; RT: Rimsinger Ton, mudstone; UOL: upper ore layer, LOL: lower ore  
212 layer; WS: Wedelsandstein, sandstone; GM: Gryhitenmergel, marlstone; HEL: Haupterzlager, main Fe  
213 ore body). Samples marked with grey background were analyzed with XRD, see also Table 3.

214

215 Iron overall average content for the ore layers is  $17.8 \pm 7.0$  wt.% while the non-ore sediments show an  
216 average of  $2.2 \pm 1.1$  wt.%. The three different ore horizons contain  $14.1 \pm 3.0$  wt.% (UOL),  $11.6 \pm 1.2$

217 wt.% (LOL) and  $21.3 \pm 6.9$  wt.% (HEL), respectively. Arsenic in all ore samples is present at  $123 \pm$   
218  $48.5 \mu\text{g g}^{-1}$  (UOL:  $131 \pm 21 \mu\text{g g}^{-1}$ ; LOL:  $97 \pm 11 \mu\text{g g}^{-1}$ ; HEL:  $133 \pm 59 \mu\text{g g}^{-1}$ ), in the remaining  
219 sediments at  $18.0 \pm 7.8 \mu\text{g g}^{-1}$ . Iron and As development with depths exhibit a close positive  
220 correlation (Fig. 2). Trace metals contents in single samples and average values for the different  
221 stratigraphical layers are shown in Table 2.

222

223 Figure 2: Lithological profile, Fe and As contents development and Fe phase fractionation of the sampled  
224 Jurassic sediments, former quarry Kahlenberg.

225

226 The mineralogical composition of the ooidic Fe ores, calculated from X-ray diffractograms using  
227 Rietveld analysis is summarized in Table 3. Iron phase fractionation is additionally indicated in  
228 Figure 2. Goethite ( $\alpha\text{-FeOOH}$ ) is the most important Fe host mineral in the ore layers, accounting for  
229  $67 \pm 9$  % of the present Fe phases, whereby the proportion is slightly higher in the ore layers,  
230 compared to the main ore body. Other Fe phases, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ;  $23.8 \pm 16$  %) and the Fe silicate  
231 mineral chamosite ( $(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$ ;  $8.8 \pm 10$  %), show much higher variabilities.  
232 Hematite is more abundant in the main ore body, while chamosite reaches significant amounts in the  
233 ore layers only (Fig. 2). Besides Fe host minerals, bulk ore samples contain calcite ( $\text{CaCO}_3$ ) as the  
234 main matrix mineral, detrital quartz ( $\text{SiO}_2$ ) and minor amounts of muscovite ( $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$ )  
235 and microcline ( $\text{KAlSi}_3\text{O}_8$ ). Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) is partly detectable, pyrite ( $\text{FeS}_2$ ) is present in  
236 trace amounts in the two thinner ore layers only.

237

238 Table 3: Mineralogical composition of Jurassic Fe ore samples, see Tab. 2 for stratigraphical allocation (n.d. –  
239 not detectable).

240

241 In all Fe ore thin sections, oval to nearly round ooid grains of brownish to reddish colour in a mainly  
242 greyish calcitic matrix were observed. In some parts, the latter is of yellowish-orange colour,  
243 indicating matrix areas with elevated Fe. Sub-rounded detrital quartz grains and bioclasts are further  
244 components. Among the fossils found in the samples, echinoderms, especially crinoids, are most  
245 abundant. Additionally, gastropoda, bivalvia, bryozoa, foraminifera and one calcite-filled belemnite

246 rostrum were found. Some Fe grains exhibit characteristics of broken and regenerated ooids. It can be  
247 assumed that during ooid formation, the milieu underwent multiple synsedimentary reworking and  
248 redeposition as also indicated by ooids forming the nucleus of the next ooid generation (Flügel 2004).  
249 Bioclasts serve as further nucleus material. Despite their abundance in the ores, silicate (mainly  
250 quartz) grains were not found as nuclei, which is in agreement with Jurassic ooidic Fe ores from the  
251 Swiss Jura mountains (Burkhalter 1995). Thin section analyses indicate that the samples are rather  
252 matrix-supported (matrix/component ratios range from ~80/20 to 50/50, with HEL ores showing a  
253 higher component proportion). The carbonatic matrix is micritic in UOL and LOL, whereas it is rather  
254 sparitic in HEL, arguing for a higher degree of cementation. This is supported by a lower amount of  
255 bioclasts and a higher proportion of hematite, possibly formed through dehydration of primary  
256 goethite or its precursor phases (Maynard 1983, Schwertmann et al. 1999), compared to the thinner ore  
257 layers.

258

### 259 3.1.2 Tertiary sediments

260 Table 4 shows the geochemical composition of sediments from the Grafenberg-layers. A concentration  
261 profile indicates geochemical development of some elements and Fe phase fractionation dependent  
262 upon depth in the borehole (Fig. 3).

263

264 Table 4: Whole rock geochemical results of selected elements from the Tertiary sediments (DL: detection limit;  
265 Ox\_G: oxidized Grafenberg-layers; QC\_G: Quarternary cover sediment; Red\_G: reduced Grafenberg-  
266 layers; Red\_H: Reduced Grafenberg-layers from the borehole in Hamminkeln). Samples marked with  
267 grey background were analyzed with XRD, see also Table 5.

268

269 The reduced lower part of the Grafenberg-layers contains relatively homogenous Fe and As of  $1.84 \pm$   
270  $0.57$  wt.% and  $11.6 \pm 3.6 \mu\text{g g}^{-1}$ , respectively. Sulphur content is  $0.22 \pm 0.09$  wt.% on average, it  
271 correlates well with As for a large part of the profile (Fig. 3).

272

273 Figure 3: Stratigraphical profile, Fe, As and S contents development and Fe phase fractionation of the  
274 Grafenberg-layers sampled from a borehole near Willich.

275

276 Bulk sediment mineralogical results can be found in Table 5. Moreover, Figure 3 contains Fe phase  
277 fractionation in borehole samples. XRD analysis identified several reduced Fe minerals, wherein  
278 glauconite ((K,Na)(Fe,Al,Mg)<sub>2</sub>[(OH)<sub>2</sub>[(Si,Al)<sub>4</sub>O<sub>10</sub>]]) is dominant (60 % of all Fe phases on average),  
279 followed by pyrite (FeS<sub>2</sub>) and siderite (FeCO<sub>3</sub>). Greenish glauconite and framboidal pyrite grains were  
280 observable in the sediments under the microscope. One layer at the bottom of the borehole contains a  
281 high glauconite proportion of 11.1 % of the bulk sample. Goethite (FeOOH) was identified in the  
282 uppermost Tertiary sample (GW\_0201) only, coexisting with siderite, glauconite and pyrite and thus  
283 indicating a zone of redox transition. The calcite content here (0.09 %) is depleted, compared to the  
284 deeper sediments (1.82 ± 0.79 %); on the other hand, Fe and As are enriched by factor 3 and 2,  
285 respectively. The discordantly following Quarternary cover sediments yield significantly lower  
286 contents of Fe and As (Fig. 3). Besides quartz as the dominant mineral phase, calcite and the  
287 mentioned Fe phases (Tab. 5), the samples contain minor amounts of muscovite, clay minerals and  
288 feldspar.

289

290 Table 5: Mineralogical composition of Grafenberg-layers samples, see Tab. 4 for facies allocation (n.d. – not  
291 detectable).

292

293 In contrary to the deep sediments, the upper oxidized facies of the Grafenberg-layers shows a very  
294 heterogenous distribution of Fe, As and other trace elements, so mean values are not given in Table 4.  
295 Iron content averages 3.93 ± 2.2 wt.% in the unconsolidated sands, but can be as high as 23.4 wt.% in  
296 concretions. All samples contain goethite whose proportion ranges from 1.04 to 34.51 %.  
297 Lepidocrocite (γ-FeOOH) as a second Fe hydroxide was identified in two samples. XRD analysis of  
298 one sample in the grain fraction <0.63 μm (GG\_0102f; obtained through wet sieving) indicated that Fe  
299 hydroxides are preferably occurring in the fine-grained sediment proportion. Calcite is not detectable  
300 in any sample (Tab. 5).

301 Arsenic contents average 20.3 ± 11.8 μg g<sup>-1</sup> in sands, but yield a peak value of 1860 μg g<sup>-1</sup> As in one  
302 Fe concretion, thus underlining the pronounced heterogeneity of element distribution in the oxidized  
303 facies, even at very close range (Fig. 4).

304

305 Figure 4: Example of heterogeneous Fe and As distribution in the oxidized part of the Grafenberg-layers. The  
306 inset (upper left corner) shows Fe concretions found in the darker (orange) layer on the left side.

307

308 In the example shown in figure 4, Fe and As levels increase erratically from hardly coloured (right  
309 side) via bright orange sands (left side) to the very hard, dark reddish Fe concretions (inset) found  
310 within the latter. Approximate relational factors in these three sediment zones for Fe are 1-2-17, for As  
311 1-5-207. The different scales of enrichment, also for other trace elements, are discussed in chapter 4.2.

312

### 313 3.2 EMP results in Fe ores

314 Results of the chemical mapping of an ooid grain from the upper part of the main ore body conducted  
315 with energy-dispersive microprobe analysis are shown in Figure 5a. The general detection limit for  
316 this method is approximately 0.5 wt.%. The mapping area was chosen to contain all important  
317 sediment components (Fe ooids, carbonate matrix, clastic grains). For As, the resulting map was  
318 homogenous, thus not showing any differences in As distribution. This suggests that As is present in  
319 contents <0.5 wt.% in all rock compounds. To assess As contents in the ooid grains, a traverse of  
320 quantitative wavelength-dispersive single spot measurements was carried out (Fig. 5b). Detection limit  
321 for As in this procedure was calculated to be  $117 \mu\text{g g}^{-1}$ .

322

323 Figure 5: a: elemental mapping of an Fe ooid in calcitic matrix (qualitative), b: traverse (indicated in  
324 backscattered light image) of single spot chemical measurements through cortex and nucleus of an Fe  
325 ooid.

326

327 Element distribution maps (Fig. 5a) show a well-defined oval Fe ooid (Fe map) from the HEL,  
328 together with matrix material and margins of two silicate grains (Si map). Calcium is present in the  
329 matrix only. Besides the detrital grains, Si occurs in smaller amounts in some areas within the ooid.  
330 The distribution of Mn indicates its preferential presence in the matrix rather than in the ooid. Iron  
331 distribution within the ooid is not even, differences correspond to different layers of the cortex, the  
332 ooid rim seems to be particularly enriched. In the case of Figure 5a, the nucleus is Fe-rich (although it

333 seems to contain less Fe than the average cortex), thus probably representing an ooid fragment of a  
334 previous generation. A profile of point measurements, shown for another Fe ooid in Figure 5b  
335 (backscattered light), supports these findings. Iron is enriched in the “lighter” parts (areas of higher  
336 electron density) of the cortex and in the nucleus, exceeding 50 wt.%, while the “darker” layers  
337 contain around 40 wt.% Fe. On the contrary, Al and Si are more abundant in the darker parts. Unlike  
338 in the “macroscopic” outcrop scale (Fig. 2), arsenic contents do not necessarily follow Fe in the grain  
339 scale. While, independent from Fe, arsenic content is around 1000  $\mu\text{g g}^{-1}$  in the cortex layers, it drops  
340 to below 500  $\mu\text{g g}^{-1}$  in the nucleus.

341

### 342 3.3 SEP results

343 Sequential extraction procedures base on using increasingly stronger solvents, each targeting a specific  
344 host mineral fraction (Tab. 1) which allows us to subdivide the bulk trace element (in this case As)  
345 content of a sample into proportions of different extractabilities. This enables an estimation of the  
346 potential mobility of As and is thus more valuable for ecological considerations than the bulk content.

347

#### 348 3.3.1 Jurassic sediments

349 Results of As fractionation determined by SEP are shown in Figure 6a. An average proportion of  $3.64$   
350  $\pm 1.9\%$   $\text{As}_{\text{tot}}$  is surface-bound (i.e.  $\text{NH}_4\text{H}_2\text{PO}_4$ -soluble and thus quite readily available through pH  
351 changes or P addition, Wenzel et al. 2001) in Fe ore layers, corresponding to more variable absolute  
352 amounts of 1.9-10.3  $\mu\text{g g}^{-1}$ . Mudstone (RT) and sandstone (WS) from the Jurassic sediment profile  
353 both show comparable relative proportions of 3.7 %, but absolute As amounts of only 0.8-1.5  $\mu\text{g g}^{-1}$   
354 soluble in step 1. Arsenic bound to Mn (hydr)oxides, targeted with  $\text{NH}_2\text{OH-HCl}$  (step 2), is of minor  
355 importance ( $0.69 \pm 0.4\%$  in ore layers).  $\text{NH}_4$ -oxalate-soluble As (step 3) is most important in RT  
356 mudstone (27 %), fresh Fe hydroxide striation was observable in the sampled sediments. The As  
357 proportion dissolved in this step is higher in UOL and LOL (~13 %) than in HEL (~7 %, decreasing  
358 towards the lower part). Arsenic fractions of lower extractability (step 4 and step 6) are dominant in all  
359 ore layers. Within HEL, residual As increases with depth. Step 5-soluble As is negligible except for

360 RT (8.5 %). Assuming a change in redox conditions from presently oxidizing to rather reducing  
361 conditions, the potentially short- to medium-term mobilizable As amount corresponds to steps 1-3  
362 soluble As (Banning et al. 2009). This proportion is higher for the thinner ore layers (~18 %) than for  
363 HEL (~11 %), nevertheless, corresponding maximum absolute values are comparable (Fig. 6a).

364

365 Figure 6: Sequential extraction results of samples from the Jurassic profile (a) (RT: Rimsinger Ton, mudstone;  
366 UOL: upper ore layer, LOL: lower ore layer; WS: Wedelsandstein, sandstone; HEL: Haupterzlager,  
367 main Fe ore body) and selected Tertiary sediment samples (b), ordered by redox facies.

368

### 369 3.3.2 Tertiary sediments

370 Sequential extraction results for samples from the range of the Grafenberg-layers are illustrated in  
371 Figure 6b. The reduced lower part of the Grafenberg-layers comprises a relatively homogenous As  
372 fractionation. Arsenic soluble in step 1 is  $7.30 \pm 0.4$  %,  $31.89 \pm 2.1$  % in step 3,  $28.76 \pm 5.2$  % in step  
373 4 and  $27.47 \pm 5.6$  % in step 5. In the redox transition zone,  $H_2O_2$ -soluble As decreases to 16 %.  
374 Potential mobilizability is similar in all samples ( $38.57 \pm 2.3$  %  $A_{S_{tot}}$ ), but higher absolute amounts are  
375 found in the transition zone (Fig. 6b).

376 Arsenic extractability in the oxidized facies is more heterogenous. Fractions of steps 4 and 6 are  
377 dominant in all samples, but proportions of higher extractability (steps 1-3) vary heavily in  
378 unconsolidated sands (5.9-33.1 %) as well as in harder concretions (3.4-39.1 %). Corresponding  
379 potentially mobile As varies between 1.3 and  $62.6 \mu\text{g g}^{-1}$  with a peak value for Fe concretion  
380 GG\_0103 (Fig. 6b).

381

## 382 4 Discussion

383 The Discussion chapter distinguishes between Jurassic and Tertiary sediments in the three subsections  
384 4.1-4.3, before a comparison is drawn in the Conclusions chapter 5.

### 385 4.1 Geochemical characterization and timing of As accumulation

#### 386 4.1.1 Jurassic sediments

387 The studied Fe ores from the former quarry Kahlenberg represent a significant As sink with a  
388 maximum content of 223  $\mu\text{g g}^{-1}$  at 32.2 wt.% Fe in HEL. The overall average of the ore samples (123  
389  $\mu\text{g g}^{-1}$ ) is elevated by ~factor 7, compared to the non-ore sediments of the profile. Lithologically and  
390 facially similar Jurassic ooidic Fe ores from Luxemburg and France (so called Minette Fe ores) are  
391 known to be potential As hosts: Siehl and Thein (1978) detected maximum As contents of 435  $\mu\text{g g}^{-1}$   
392 at 50 wt.% Fe in one profile (with As and Fe correlating well), thus showing conditions comparable to  
393 the ooid ores studied in this work. The scale of As (and other elements) enrichment is discussed in  
394 more detail in chapter 4.2.1.

395 Statistical analysis of ore samples from the main ore body (HEL) was conducted using the software  
396 SPSS Statistics 17.0. A matrix of Pearson element correlations is presented in Figure 7a.

397

398 Figure 7: Pearson element correlation matrices for samples from the HEL (a) and the oxidized facies of the  
399 Grafenberg-layers (b).

400

401 Arsenic occurrence and behaviour is controlled by Fe oxides and hydroxides, as suggested by  
402 mineralogical and sequential extraction results, as well as element correlation analysis (Fig. 7a).  
403 Goethite was found to be the most important Fe host phase, which is in agreement with previous  
404 studies about these ores (Aldinger 1957, Sauer and Simon 1975). This is also valid for similar ooidic  
405 Fe accumulations of Aalenian/Bajocian age from Switzerland described by Burkhalter (1995). In that  
406 study, also chamositic ooids were found, forming a complete transition series with goethite ooids.  
407 Varying degrees of the chamosite compound in predominantly goethite ooids might explain the  
408 occurrence of elevated Si in some areas of the ooid studied with EMP (Fig. 5a), Al and Si enrichment  
409 in the “darker” layers of the cortex (Fig. 5b) as well as a positive Fe-Al correlation (Fig. 7a). Another  
410 similarity is a comparably high P content in the Fe ore layers (0.3 wt.% on average in this study),  
411 attributable to apatite admixtures in the ooids on a submicroscopic scale (Burkhalter 1995). This is  
412 supported by a very significant positive correlation between Fe and P (Fig. 7a), indicating that P is  
413 hosted by Fe ooids. However, apatite was not detectable in XRD, making it more likely that P is  
414 present on the Fe (hydr)oxide surfaces as it was described for Jurassic Fe ooids in Bavaria (Halbach



415 1968). Most probably, it was adsorbed as  $\text{PO}_4^{3-}$  from sea water during the precipitation of positively  
416 charged  $\text{Fe}(\text{OH})_3$  particles.

417 In contrast to P-Fe, Ca correlation with Fe is significantly negative. Calcium is present in the calcitic  
418 matrix only, while Fe is broadly limited to ooid grains (although microscopy of thin sections revealed  
419 some areas of visible Fe contribution to the matrix material). The only studied element with a positive  
420 relationship towards Ca, and therefore most probably hosted predominantly in the matrix, is Mn. It  
421 correlates significantly negative with all other metals, As and P and thus indicates its absence in the Fe  
422 ooids. These findings are supported by elemental mapping in EMP (Fig. 5a) and the lack of As bound  
423 to Mn (hydr)oxides as suggested by SEP (Fig. 6a). Consequently, although Mn mineral phases can  
424 yield a major influence on As behaviour (Smedley and Kinniburgh 2002), they do not do so in the case  
425 of the studied ores. An explanation for this phenomenon might be the formation of weakly reducing  
426 microenvironments caused by bacterial decomposition of organic matter in the sediments. This may  
427 lead to Mn release from the solid phase to solution and subsequent uptake by the calcite matrix, while  
428  $\text{Fe}^{2+}$  remained in the form of chamosite (the presence of chamosite is interpreted as a proxy for mildly  
429 reducing conditions during diagenesis, Berner 1981). A mechanism like that is proposed for Tertiary  
430 Fe ooids in Egypt (Salama et al. 2008). During the latest period of Fe ooid formation in the studied  
431 profile (i.e., in the UOL), stronger reducing conditions seem to have been prevailing, indicated by  
432 trace amounts of pyrite and a high proportion of chamosite among Fe phases (Fig. 2).

433 In contrary to Mn, Pb, Zn, Co, Cd, Cr and Ni correlate positively with Fe and As, and with each other,  
434 and negatively with Ca and Mn, clearly indicating that these heavy metals are hosted by Fe ooids, and  
435 hardly appear in the matrix. The correlation of Fe and As is weaker at the grain scale as deviated by  
436 single ooid measurements (Fig. 5b). This suggests that conditions for As accumulation varied before  
437 (ooid nuclei), during (ooid cortices) and after (matrix) Fe ooid formation.

438 Element and mineral distribution in the studied sediments argue for a primary, i.e. syndepositional  
439 accumulation of As in Fe ooids from the middle Jurassic. Shallow marine origin of the ores under  
440 tropical climatic conditions is evident from the fossil record (chapter 3.1.1; Urban 1966). Iron (and As)  
441 accumulation in the present form occurred in times of non-deposition (concerning clastic input, i.e. in  
442 condensed horizons) in at least temporarily agitated water, which are prerequisites for Fe ooid

443 formation (Burkhalter 1995). Under these conditions, Fe together with As and trace metals, was  
444 transported in solution or colloidal form from the weathering mainland towards shallow marine  
445 environments. There, it was able to accumulate, before conditions changed once more and the calcitic  
446 matrix settled. During the slow process of Fe ooid formation, reactive surfaces were available for a  
447 long time for  $\text{AsO}_4^{3-}$  adsorption on hydroxides as described above for the geochemically very similar  
448  $\text{PO}_4^{3-}$ . Additionally, these surfaces were renewed through rhythmic formation of ooid cortices and  
449 periodical reworking of the sediments. This way, syndepositional As enrichment potential in Fe ooids  
450 is obvious. After the main accumulation (HEL), a sedimentary milieu favouring Fe and As enrichment  
451 returned twice as documented by LOL and UOL.

452

#### 453 4.1.2 Tertiary sediment

454 The oxidized upper part of the Grafenberg-layers, compared to the reduced lower part, is enriched in  
455 As by ~factor 2, considering average values. However, due to the extremely heterogenous element  
456 distribution, the scale of enrichment has to be analysed in more detail (chapter 4.2.2). Like for the  
457 Jurassic samples described in chapter 4.1.1, statistical analysis for the oxidized near-surface facies of  
458 the Grafenberg-layers was conducted using SPSS software. The Pearson element correlation matrix is  
459 shown in figure 7b. Due to its partly extremely high concentrations, especially for Fe and As,  
460 concretion GG\_0103 was not included in the calculations. Like in the Fe ooids, a striking positive  
461 correlation ( $R^2=0.93$ ) between Fe and P is observable – again, P is bound to Fe hydroxides (goethite  
462 and, less abundant, lepidocrocite), ubiquitarily available in the oxidized sediments. Iron correlations  
463 with metals are variable. While Cd ( $R^2=0.96$ ), Zn ( $R^2=0.80$ ) and, less distinct, Cr ( $R^2=0.60$ ) show a  
464 clear positive relation towards Fe, regression is much weaker for Ce ( $R^2=0.39$ ), Mn ( $R^2=0.37$ ), Co  
465 ( $R^2=0.37$ ), Pb ( $R^2=0.31$ ), As ( $R^2=0.30$ ) and Ni ( $R^2=0.21$ ) and is not detectable for Cu and Al. From the  
466 second group, Mn, Co, Ni and Ce provide positive interrelations ( $R^2=0.63-0.97$ ) arguing for a common  
467 occurrence, while Cu, Al and As do not yield any significant correlation with the other metals. These  
468 results underline the extreme heterogenous element distribution. Nevertheless, the lack of As-Al  
469 correlation and SEP results indicate that no clay minerals or other silicates but rather Fe hydroxides act  
470 as As sinks, albeit with large variations in adsorbed As amounts. The by far highest As content has

471 been measured in the most Fe-rich sample (Fig. 4). In a similar geological environment showing  
472 pronounced post paleo-redox elemental redistribution, Banning et al. (2009) found As being  
473 accumulated in Fe hydroxide concretions without yielding any correlation with bulk Fe.

474 The source of near-surface Fe (and As) is believed to be the reduced Fe phases from the deeper  
475 sediments, i.e. the primary depositional facies, nowadays only accessible in boreholes. Several  
476 “candidate” minerals were identified by XRD: glauconite, pyrite and siderite, additionally goethite  
477 was detected in the uppermost Tertiary sample GW\_0201, indicating a redox transition zone (chapter  
478 3.1.2). The potential role of the reduced Fe phases for As behaviour in the Tertiary sediments will be  
479 discussed in the course of a short literature overview in the following.

480 Glauconite has the highest proportion in Fe phases in the fully reduced sediments, whereas siderite  
481 seems to be more abundant in the oxidation cap (Fig. 3). Greensands containing significant amounts of  
482 glauconite are known to have a potential for As accumulation. Dooley (1998) found As contents in  
483 New Jersey greensand one order of magnitude higher than in average soils of the area. Barringer et al.  
484 (2009) consider these glauconites as one source of elevated As concentrations in groundwater. In a  
485 creek near Brussels, Belgium, Cappuyns et al. (2002) detected As accumulations in soil Fe hydroxides  
486 and attributed them to mobilization from As-rich glauconites in the subsurface. Patyk-Kara et al.  
487 (2008) found “abnormally high As” contents in glauconite samples from central Russia. Conducting  
488 SEM analysis of single grains, they measured up to 72 wt.% (!) As in glauconite surface coatings and  
489 attributed that to the mineral’s high sorption capacity. This is supported by Spoljaric and Crawford  
490 (1978) who found a nearly quantitative As retention from basic solution when filtering it through  
491 greensand containing 80 % glauconite. Hence, the mineral has the potential to act as As sink and  
492 source, as was suspected in an earlier study (Banning 2008). Nevertheless, to the authors’ knowledge  
493 and despite all these indications, no distinct mechanism for As uptake by glauconite is known so far.  
494 Independent from its role in As behaviour, it has been shown that glauconite loses large amounts of Fe  
495 to solution during weathering (Courbe et al. 1981, Patyk-Kara et al. 2008, Hutton and Seelye 1941).  
496 Thus, it is probable that glauconite from the primary reduced facies of the Grafenberg-layers is the  
497 major source for Fe accumulations in the oxidized near-surface part.

498 Siderite mostly represents secondary precipitates in reducing environments (Fisher et al. 1998). In  
499 marine milieu, it may be formed during early diagenesis and then contributes to the sediment cement,  
500 partly replacing calcite, and can be accumulated to concretionary levels (Hounslow 2001). Siderite has  
501 the potential to strongly sorb As(V) at circumneutral pH conditions (Jönsson and Sherman 2008).  
502 However, the affinity towards As(III) is much weaker and it can be assumed that As in the primary  
503 facies of the Grafenberg-layers was mainly present as As(III) during deposition and diagenesis as well  
504 as under present hydrochemical conditions (pH around 7.6, Eh around -50 mV; Mäurer and Wisotzky  
505 2007). Consequently, formation of siderite in such a milieu does not retain significant As quantities  
506 (Tufano and Fendorf 2008) although it cannot be excluded that the carbonate may act as a secondary  
507 sink in adequate redox niches. Supporting the former, analysis of siderite concretions from a  
508 geological environment very similar to the Grafenberg-layers yielded low As contents (Banning et al.  
509 2009).

510 Natural pyrite is well-known for its ability to host As and numerous other minor and trace elements.  
511 An overview is given by Abraitis et al. (2004). Arsenic in pyrite is commonly present at  $\mu\text{g g}^{-1}$  to wt.%  
512 levels with a measured peak value of almost 10 wt.%. In contrast to the Fe minerals introduced before,  
513 arsenic is incorporated into the pyrite structure by substitution of S. In particular, pyrites formed under  
514 relatively low temperatures can have strongly elevated As. They often show habits arguing for rapid  
515 precipitation, e.g. framboids, which have a reactive surface area 4-6 times larger than euhedral (cubic)  
516 pyrite grains (Merinero et al. 2009), explaining high As and other element enrichments. Huerta-Diaz  
517 and Morse (1990) introduced the term “degree of trace metal pyritization” (DTMP) to assess the  
518 importance of incorporation of different trace metals into sedimentary pyrite. They found that the  
519 disulphide is an important sink for As, Hg and Mo which are rapidly and essentially completely taken  
520 up by pyrite. The sink function is significant, but less important, for Co, Cu, Mn and Ni and “generally  
521 unimportant” for Cr, Pb, Zn and Cd, although at least for Pb and Zn, contents close to 1 wt.% have  
522 been detected in pyrite (Abraitis et al. 2004).

523 Considering this discussion on the identified reduced Fe phases and their potential impact on As  
524 behaviour, framboidal pyrite is suspected to represent the main As host in the reduced deep part of the  
525 Grafenberg-layers and thus, the source of As accumulation in the oxidized upper facies. To check this

526 hypothesis, relationships between Fe, S and As were analyzed for these sediments (Fig. 8). In the Fe-S  
527 scatter plot (Fig. 8a), the line of stoichiometric pyrite was implemented for comparison. Most samples  
528 plot along a line parallel to that. The shift from the pyrite line indicates “excess Fe” hosted by further  
529 Fe phases. This is attributable to glauconite and, to a lesser extent, siderite, being present in relatively  
530 homogenous concentrations in the reduced samples. Two distinct outliers were identified, samples  
531 GW\_0201 and GW\_0212. To reiterate, GW\_0201 is the only sample to contain goethite (interpreted to  
532 derive from the redox transition zone), GW\_0212 is the sample showing by far the highest glauconite  
533 content (11.1 %, compared to an average of 2 % in the other samples analyzed by XRD). These results  
534 were accounted for in the As-S scatter plot (Fig. 8b). Samples yielding a pyrite-like development in  
535 figure 8a showed a very close As-S correlation of  $R^2=0.94$ , whereas the total dataset, including the  
536 outliers, only provided  $R^2=0.56$ . This indicates that pyrite is indeed the major As host in large parts of  
537 the reduced Grafenberg-layers. Nevertheless, it also suggests that glauconite, if available in larger  
538 quantities, is able to adsorb at least part of the As to its surface. Furthermore, it is probable that  
539 goethite, derived from oxidation of Fe(II) phases, is an important As sink in the redox transition zone.  
540 Here, also siderite may act as a secondary host mineral as it is present in significant quantities and As  
541 is likely to at least partly occur as As(V).

542 Assuming that all As is bound in pyrite and using whole rock As and sediment pyrite contents as  
543 determined by Rietveld analysis, it is possible to calculate maximum As contents in pyrite. Ignoring  
544 the outliers, an average value of  $0.21 \pm 0.04$  wt.%  $As_{pyr}$  has resulted which plots in the range of  $As_{pyr}$   
545 given by Abraitis et al. (2004) and is very similar to the average  $As_{pyr}$  value (0.23 wt.%) in a limestone  
546 aquifer studied by Price and Pichler (2006).

547

548 Figure 8: Fe-S scatter plot for the reduced part of the Grafenberg-layers (a), As-S scatter plot of the same  
549 samples (b).

550

551 All these considerations indicate a secondary As enrichment in the near-surface Grafenberg-layers, i.e.  
552 an accumulation long after original deposition of the sediments in Oligocene times. The paleo-redox  
553 process under terrestrial conditions in late Miocene/Pliocene (chapter 1.2.2) caused mobilization of Fe

554 (mainly from glauconite) and As (mainly from pyrite) and reaccumulation in the upper part. The fact  
555 that in large part, Fe and As are probably from different sources may have contributed to the lack of  
556 Fe-As correlation in the oxidized sediments. Trace metals showing stronger relationships with Fe, i.e.  
557 Cd, Zn and Cr, belong to the group of heavy metals not preferentially accumulated in pyrite (Huerta-  
558 Diaz and Morse 1992). Instead, at least Zn and Cr are known to be potentially enriched in glauconite  
559 (Dooley 1998) and like Fe, may have derived in largest part from the weathering of this mineral.  
560 Consequently, heterogenous distribution of Fe, As and trace metals results from mobilization through  
561 oxidation, transport and subsequent reaccumulation up to concretionary levels; existing and missing  
562 interrelationships of elements can be attributed to different primary sources.

563

#### 564 4.2 Scale of accumulation

565 In order to assess the degree of As accumulation in the Fe (hydr)oxidic sediments of both study areas  
566 and to estimate its relative importance compared to other trace elements, two approaches were applied  
567 as used for heavy metals in dam reservoir bottom sediments by Loska et al. (1997) and for As in soils  
568 by Loska et al. (2003): Enrichment Factor (EF) and cumulative Contamination Factor (CF).

569 The EF is used to evaluate element contents in the studied environment in relation to a reference  
570 environment (Eq. 1).

$$571 \quad EF = \frac{C_{sam}}{C_{ref}} \bigg/ \frac{B_{sam}}{B_{ref}} \quad (\text{Equation 1})$$

572 where

573  $C_{sam}$  is the concentration of the examined element in the studied environment

574  $C_{ref}$  is the concentration of the examined element in the reference environment

575  $B_{sam}$  is the concentration of the reference element in the studied environment

576  $B_{ref}$  is the concentration of the reference element in the reference environment

577  $EF < 2$  characterize element depletion to minimal enrichment,  $EF=2-5$  moderate enrichment and

578  $EF=5-20$  significant enrichment (Loska et al. 2003). The reference element used for normalization

579 must be of low variability and present in trace amounts. Alternatively, elements occurring in higher  
580 concentrations can be used if they do not show any correlation towards the examined elements.  
581 Fulfilling the latter condition in this study, Mg was used as a reference element for the Jurassic Fe ores  
582 and Al for the oxidized Tertiary sediments (Fig. 7). Reference environments were defined as the  
583 average of non-ore sediments in the Jurassic profile, weighed according to their thicknesses, and the  
584 reduced part of the Grafenberg-layers, respectively.

585 The CF is applied to evaluate the impact of single contaminants on an environment. It is used to  
586 identify major pollutants and to estimate the total degree of contamination, mainly of anthropogenic  
587 nature, compared to pre-industrial times (Loska et al. 1997; Eq. 2).

$$588 \quad CF = \frac{C_{av}}{C_0} \quad (\text{Equation 2})$$

589 where

590  $C_{av}$  is the average content of the examined element in the studied environment

591  $C_0$  is the pre-industrial content of the examined element

592 Like for EF, “pre-industrial” contents in this study are equal to “pre-enrichment” contents, i.e. non-ore  
593 sediment layers in the Jurassic profile and the original reduced facies of the Tertiary sediments were  
594 defined as reference environments. Summing up the CFs of all contaminants allows for estimating the  
595 contribution of single elements to the total contamination of the examined environment. This method  
596 offers a potential impact appraisal as only bulk concentrations and no information on element mobility  
597 or actual availability are included.

598

#### 599 4.2.1 Jurassic Fe ores

600 Results for EF and CF calculations for the Jurassic Fe ores are shown in Figure 9. Enrichment factors  
601 are presented for all Fe ore samples and the six most enriched trace elements, contaminations factors  
602 were calculated for average contents of all Fe ore samples and the relative contribution of each heavy  
603 metal to the overall “contamination pool” was deduced.

604

605 Figure 9: Enrichment Factors of 6 elements for Jurassic Fe ore samples. Pie chart: Single elements' contribution  
606 to total "contamination pool" (UOL: upper ore layer, LOL: lower ore layer; HEL: Haupterzlager, main  
607 Fe ore body).  
608

609

610 Copper and Pb show average EF of 0.76 and 1.39, respectively. Therefore, they are not enriched in the  
611 Fe ores. Cadmium is not included in the calculations because contents in the reference environment  
612 are broadly below or close to the analysis detection limit ( $0.3 \mu\text{g g}^{-1}$ ). Nevertheless, ore samples have  
613 an average Cd content of  $1.5 \mu\text{g g}^{-1}$ , suggesting the element's (in this case not quantifiable)  
614 enrichment. EF average values for Zn (2.11), Ni (2.21), Co (2.30) and Cr (2.41) indicate very  
615 moderate accumulation in ore layers. While Co and Ni are evenly distributed, Cr and Zn are preferably  
616 enriched in HEL. Manganese is accumulated to a higher level (average EF=3.91), where highest  
617 values are reached in the UOL. However, arsenic is the most enriched element, yielding an average EF  
618 of 6.36 and being the only trace element plotting in the "significant enrichment" category of EF. While  
619 the factors are relatively stable within the thinner ore layers (UOL=7.48, LOL=4.97), they are variable  
620 in HEL (EF=2.6-12.7), indicating shifting degrees of favourability for As accumulation during main  
621 ore body deposition. Consequently, the studied ooidic Fe-rich sediments do not only contain  
622 significant amounts of As – they also seem to favour As uptake over heavy metals. Ruling out Mn,  
623 which has been shown to reside in the calcite matrix (chapter 4.1.1), and thus only regarding elements  
624 hosted in Fe ooids, arsenic enrichment potential is ~3 times higher than that of heavy metals. This  
625 finding is supported by CF calculations showing that As accounts for 29 % of the "contamination  
626 pool" and thus is the by far most important "pollutant" (Fig. 9, pie chart).

627

#### 628 4.2.2 Tertiary sediments

629 Results of EF, ordered by Fe enrichment factor (values not shown) and CF calculations are shown in  
630 Figure 10.

631



632 Figure 10 Enrichment Factors of 6 elements for samples from the oxidized part of the Grafenberg-layers. Upper  
633 pie chart: single elements' contribution to total "contamination pool" in one Fe hydroxide concretion,  
634 lower pie chart: single elements' contribution to total "contamination pool" of oxidized sand samples  
635 without concretions. Note changes of scale on the x-axis.

636

637 The pronounced heterogeneity in the oxidized sediments is underlined once more when regarding EF  
638 values, even if concretion GG\_0103 is ruled out. Lead, Cr and Cu, nevertheless, are constantly quite  
639 low (average values around 1, none is exceeding 2) and thus show no enrichment compared to the  
640 reduced deeper sediments. Like for the Jurassic rocks, Cd was not included in the calculations due to  
641 numerous samples in both redox facies showing contents below the detection limit. The other metals  
642 are more variable in accumulation behaviour ranging from depletion to moderate enrichment: Ni (0.4-  
643 6.6), Co (0.5-7.0), Mn (0.4-3.9), As (0.5-3.9), Zn (0.5-8.6). However, a general trend towards higher  
644 overall heavy metal enrichment coming with increasing Fe EF is observable, although not  
645 comprehensible for single elements. This situation results in relatively balanced contributions of single  
646 metals to the total "contamination pool" (Fig. 10, lower pie chart), where As has a proportion of 12 %.  
647 Calculating these proportions for the most Fe-rich concretion, the findings are completely different:  
648 here, arsenic is by far the most important contributor, accounting for 58 % of the total contaminant  
649 pool (Fig. 10, upper pie chart). An EF of 166 for As confirms extremely high accumulation. Although  
650 to a lesser extent, other metals are at least significantly enriched with EFs in the range of 10-50. It is  
651 most probable that highly enriched concretions like that are very abundant in the oxidized facies of the  
652 Grafenberg-layers, also in larger sizes than the exemplar analysed in this study (Fig. 4). Quaas (1917)  
653 describes occurrences of banked "dark iron sandstone containing hard Fe concretions" from several  
654 former quarries backfilled today and thus unfortunately not accessible for sampling anymore.

655 From these findings, it can be concluded that during elemental redistribution after the paleo-redox  
656 event, arsenic was initially not preferentially adsorbed to the ubiquitous Fe hydroxides coating the  
657 quartz grains in the oxidized zone. These coatings only offer a limited number of sorption sites which  
658 were not renewed as further hydroxide attachment did not happen. The sites available were probably  
659 occupied by more abundant, competing phosphate ions as suggested by a close correlation between Fe  
660 and P in the bulk sediments (Fig. 7b). Moreover, it is known that rapidly formed Fe oxyhydroxides at  
661  $\text{pH} > 6.5$  can precipitate without significant As adsorption to the fresh surfaces (Peters 2000).

662 Relatively high pH should have prevailed during weathering due to calcite dissolution from the  
663 original facies, leading to fast and ubiquitous precipitation of Fe coatings without elevated As around  
664 quartz grains. Nevertheless, when it came to formation of Fe concretions in the course of ongoing  
665 oxidation, arsenic was favoured for adsorption over other elements. Continuous replenishment of Fe  
666 made sure that fresh Fe hydroxide precipitates constantly offered new reactive surfaces for arsenate  
667 complexation, while oxyhydroxides slowly aged, i.e. polymerization led to higher degrees of  
668 crystallinity. This is supported by As being dominantly present in hardly extractable fractions in  
669 concretions, whereas higher proportions of NH<sub>4</sub>-oxalate soluble As were detected for the non-  
670 concretion sediments (Fig. 6b). In this late stage of the weathering process, buffer function of calcite  
671 probably became unimportant because of calcite supply running short. This led to decreasing pH  
672 values, allowing for slower Fe precipitation and thereby higher As accumulation (Peters 2000). It can  
673 be assumed that calcite depletion was a quite rapid process, because even in the redox transition zone  
674 tapped by the borehole, calcite was depleted by 95 %, compared to the reduced deeper sediments,  
675 while glauconite and pyrite contents remained on the same level. Calcite dissolution in this zone may  
676 also provide CO<sub>3</sub><sup>2-</sup> for the observed intensified siderite formation (Fig. 3). In consequence, large  
677 amounts of Fe and As would still have been available for precipitation after the period of pH  
678 buffering. This genetic model would explain the heterogeneous As distribution in the sediments and  
679 allocate the formation of rather punctiform high As enrichments to a late stage of the weathering  
680 process.

681

## 682 4.3 Implications for potential As remobilization

### 683 4.3.1 Jurassic sediments

684 Presently, groundwater milieu around the former quarry Kahlenberg is oxidizing. An artificial lake,  
685 located 1 km downstream of the quarry in highly conductive Quaternary gravels ( $K = 1 \cdot 10^{-2} - 1 \cdot 10^{-3}$   
686 m/s) is in proven hydraulic contact with the Jurassic Fe ores. Nevertheless, transport of As or other  
687 contaminants was not detected so far (LGRB 2001), and Fe concentrations are constantly below 0.02  
688 mg L<sup>-1</sup> in wells (information from local water supplier), indicating no output from the ores. This is in

689 good agreement with general hydrochemical conditions in Middle Jurassic aquifers of the region (Tab.  
690 6). Average readily ( $\text{NH}_4\text{H}_2\text{PO}_4^-$ ) soluble As was calculated for UOL, LOL and HEL, applying  
691 thickness-weighted mean values, to be  $4.8 \mu\text{g g}^{-1}$ . Assuming a change to reducing redox conditions,  
692 the average short- to medium-term mobilizable As amount (steps 1-3) would be  $15.9 \mu\text{g g}^{-1}$ . With an  
693 average density of  $3.3 \text{ g cm}^{-3}$  (calculated for an average mineral composition), this would equal  $\sim 16 \text{ g}$   
694  $\text{m}^{-3}$  of easily soluble As and  $\sim 52 \text{ g m}^{-3}$  of potentially soluble As in the ores. Although it was shown  
695 that As is mainly hosted by Fe ooids (chapter 4.1.1), it cannot be excluded that a minor part of reactive  
696 As is present in the matrix, since SEP analysis was conducted for whole rock samples. Nevertheless,  
697 this proportion seems to be negligible as no As was found in downstream groundwater. To access the  
698 pool of potentially mobile As, i.e. to make contact with As-rich Fe ooids, water would have to solve  
699 the calcite matrix first and then would only be successful in leaching As when bringing reducing  
700 conditions along. Both is hardly possible under present physico- and hydrochemical conditions in the  
701 aquifer, which is supported by very low Fe and As background values in groundwater (Tab. 6). The  
702 risk of As remobilization is estimated to be generally insignificant under present conditions because of  
703 an oxidizing and circumneutral groundwater milieu, arsenic being trapped in hardly extractable  
704 mineral fractions and the “protection function” of the As-poor calcite matrix.

705

706 Table 6: Typical groundwater chemistry in the studied aquifers.

707

#### 708 4.3.2 Tertiary sediments

709 Step 1-soluble As in the reduced part of the Grafenberg-layers is  $0.8 \mu\text{g g}^{-1}$  on average, leading to an  
710 amount of  $\sim 1.8 \text{ g m}^{-3}$  sediment. It was shown in chapter 4.1.2 that As in these sediments is largely  
711 hosted by pyrite. Thus, it must be assumed, at least for a worst case szenario, that sediment bulk As is  
712 potentially mobilizable when oxidizing conditions arise. In such an aquifer milieu, pyrite can dissolve  
713 rapidly and thereby release its As to solution (Jones and Pichler 2007). This process may even be  
714 accelerated, relative to pure pyrite, when significant As contents are present in the lattice (Savage et al.  
715 2000). Thus, an As content of  $11.6 \mu\text{g g}^{-1}$  is potentially mobilizable, corresponding to  $\sim 27 \text{ g m}^{-3}$   
716 sediment. Mäurer and Wisotzky (2007) found that present groundwater milieu in the vicinity of the

717 sampled borehole is reducing below a depth of ~35-40 m below ground surface, thus correlating well  
718 with the proposed redox transition zone derived from geochemical results of this study. Below that  
719 depth, water is undersaturated with respect to  $\text{Fe}(\text{OH})_3$  and around  $\text{SI}=0$  for  $\text{FeCO}_3$ , both change to  
720 significant oversaturation around 40 m. This data modelled by Mäurer and Wisotzky (2007) is in good  
721 agreement with the mineralogical findings in this work. Consequently, pyrite is rather stable and thus  
722 should not be an active As source under the given conditions. Nevertheless, in spite of their rather low  
723 hydraulic conductivity of  $4.2 \cdot 10^{-5}$  m/s on average (Mäurer and Wisotzky 2007), the Oligocene  
724 sediments are used for drinking water extraction. In a pumping well near the sampled outcrops, the  
725 groundwater table is lowered by up to 25 m during pumping. It was described in chapter 1.2.2 that the  
726 depth of the paleo-redox boundary is variable in the study area, but mostly around 20-30 m below  
727 ground surface. Therefore, groundwater extraction might change redox conditions to rather oxidizing  
728 in the top of the reduced primary facies, thus enabling Fe(II) phases dissolution and output of Fe and  
729 hosted As into solution. It is unlikely that this happened in case of the mentioned pumping well, with  
730 the raw water showing stable Fe concentrations and As constantly below the detection limit  
731 (information from local water supplier). Nevertheless, the redox boundary should be considered when  
732 constructing and operating pumping wells in the area. A clear positive correlation between Fe and  $\text{SO}_4$   
733 as well as an increase of both parameters in deep wells of one waterworks in the study area since the  
734 start of water extraction from the Grafenberg-layers as described by Mäurer and Wisotzky (2007) hints  
735 towards successive pyrite oxidation and thus, potential As mobilization. Although no critical As  
736 concentrations have been measured so far, continuous groundwater monitoring for As and other  
737 potential contaminants is mandatory. An additional problem arises from the surface input of  
738 agricultural nitrate being transported to deeper aquifers and triggering pyrite oxidation therein. This  
739 phenomenon was described by Cremer et al. (2003) for a fluvial Pliocene aquifer in the vicinity of the  
740 study area. They measured groundwater As concentrations up to  $130 \mu\text{g L}^{-1}$  and identified pyrite as the  
741 As source. It has also been shown from other regions that anthropogenic disturbance of subsurface  
742 redox conditions in an aquifer containing pyrite as a trace mineral and yielding average bulk sediment  
743 As even below the values in this work, can lead to significantly elevated As concentrations in  
744 groundwater (Price and Pichler 2006).

745 Due to the very heterogenous element distribution and limited number of samples in the upper part,  
746 calculations for potential As mobilization must be considered a rough estimate. In the oxidized facies,  
747 unconsolidated sands show an average of  $0.9 \mu\text{g g}^{-1}$  step 1-soluble As, corresponding to  $\sim 2.2 \text{ g As per}$   
748  $\text{m}^3$  sediment. For Fe hydroxide concretions, the  $\text{NH}_4\text{H}_2\text{PO}_4$ -soluble As is  $8.9 \mu\text{g g}^{-1}$  on average,  
749 resulting in  $\sim 28 \text{ g m}^{-3}$ . Assuming a concretion proportion of 1 % of the total sediment, concluded from  
750 own observations in outcrops and earlier geological descriptions (Quaas 1917), an average value for  
751 bulk oxidized sediment may be calculated:  $2.5 \text{ g m}^{-3}$ . Thus,  $\sim 12 \%$  of the total easily mobilizable As in  
752 bulk sediments is contributed by concretions. Conducting these calculations for potentially short- to  
753 medium-term soluble As, sands yield  $5.5 \mu\text{g g}^{-1}$  ( $\sim 12 \text{ g m}^{-3}$ ) and concretions  $20.8 \mu\text{g g}^{-1}$  ( $\sim 67 \text{ g m}^{-3}$ ) on  
754 average. Bulk sediment would have  $12.6 \text{ g m}^{-3}$ . Here, concretions contribute only  $\sim 5 \%$  to the  
755 potentially mobilizable As pool. This can be attributed to the higher degree of hydroxide crystallinity  
756 as indicated in chapter 4.2.2. Calculated As values for concretions are very similar to those established  
757 for the Jurassic Fe ores (chapter 4.3.1). But in contrast to those, the As bound to concretions is much  
758 better available for water-rock-interaction as the sands hosting the Fe accumulations represent an  
759 unconsolidated pore aquifer allowing for larger contact areas. Surface-bound As in the bulk oxidized  
760 part ( $2.5 \text{ g m}^{-3}$ ) is slightly higher than in the reduced facies ( $1.8 \text{ g m}^{-3}$ ). The larger pool of short- to  
761 medium-term mobilizable As in the near-surface sediments, however, will only be accessible for  
762 solution if reducing groundwater conditions occur. Therefore, depth-dependent Eh monitoring in wells  
763 is recommendable for water suppliers.

764 Comparing both redox facies of the Grafenberg-layers in terms of risk assessment for As  
765 remobilization from sediments, the reduced deeper material has a higher potential for causing elevated  
766 As concentrations in groundwater. It is more probable for pyrite-oxidizing conditions to reach the  
767 primary facies as a consequence of groundwater extraction or nitrate input than for the As hosted in  
768 the oxidized facies to be dissolved under reducing conditions (the latter may be imaginable in the  
769 course of rising groundwater table or input of organic matter into the system triggering  
770 microbiologically induced reduction). Moreover, the reduced part hosting As-laden pyrite in a  
771 relatively homogenous distribution would act as an As area source, thus potentially releasing bulk  
772 sediment As to solution. In contrast, the source function in the oxidized facies is rather punctual.

773 Showing partly very high As accumulations, the hosting Fe hydroxide concretions occur rather locally.  
774 Nevertheless, they contribute a measurable proportion to bulk sediment reactive As, yet the absolute  
775 addition is not significant enough to substantially rise this pool. Additional information on the  
776 distribution, amount and geochemistry of these Fe concretions would be needed to better quantify their  
777 impact on As behaviour in the study area.

778 The groundwater background As concentration in the study area is  $1.5 \mu\text{g L}^{-1}$  (LUA NRW and  
779 MUNLV 2000; Tab. 6). If we assume that this is caused by solution of surface-bound As from  
780 Tertiary rocks ( $\sim 2 \text{ g m}^{-3}$ ), we can calculate that, referring to  $1 \text{ m}^3$  sediment (with a known effective  
781 drainage porosity of  $n_f=0.13$ ; Mäurer and Wisotzky 2007), approximately 10000 pore volumes are  
782 needed to produce the background concentration. Further assuming bulk As solubility ( $\sim 27 \text{ g m}^{-3}$ ) in  
783 the reducing sediments, i.e. generation of an oxidizing milieu, this water volume would produce an As  
784 groundwater concentration of  $\sim 21 \mu\text{g L}^{-1}$ , thus exceeding threshold guidelines by more than factor 2.  
785 Again, this calculation must be regarded a rough estimation which, nevertheless, points to the  
786 significant impact of changing redox conditions on As concentration in groundwater.

787

## 788 5 Conclusions

789 Two different As accumulation processes have been identified in Jurassic Fe ores (Aalenian/Bajocian)  
790 at the margin of the Upper Rhine Graben and in Tertiary sediments (Grafenberg-layers, Chattian) in  
791 the Lower Rhine Embayment. The primal As input into the study areas, both of which are  
792 characterized by shallow marine deposition, was accomplished by terrestrial weathering of Variscan  
793 mainlands (first-order sources). Primary, i.e. syndepositional, enrichment is responsible for the  
794 Jurassic Fe ores showing high As which is hosted by mainly goethite ooids (first-order sinks/second-  
795 order sources). While these ooids were slowly formed during condensed sedimentation under mainly  
796 oxidic conditions, thereby offering reactive surfaces for accumulation, arsenic in the Oligocene  
797 sediments was enriched in a reducing milieu and is mainly hosted by framboidal pyrite (first-order  
798 sinks/second-order sources). Secondary As accumulation, i.e. during element redistribution in a late  
799 stage of a paleo-redox event in the late Tertiary, led to partly high As in Fe hydroxide concretions

800 (second-order sinks/third-order sources) occurring in near-surface Tertiary sands. Both accumulation  
801 processes favoured As enrichment over other contaminants, underlining preferential As sorption on Fe  
802 hydroxides. In spite of higher bulk As in oxidic rocks, i.e. Jurassic ooidic ores and Fe oxihydroxide  
803 concretions in the upper Tertiary redox facies, the mainly pyrite-hosted As pool within the reduced  
804 deeper part of the Grafenberg-layers has been shown to be the most probable candidate for potentially  
805 creating elevated As concentrations in groundwater, especially if the present redox milieu is  
806 anthropogenically disturbed through groundwater extraction.

807 This study highlights the importance of geological processes millions of years ago for present day  
808 distribution (sources and sinks) and availability of potential groundwater contaminants, especially As.  
809 Moreover, it underlines the necessity to assess risks arising from single contaminants not on the basis  
810 of bulk contents alone, but also to account for the element fractionation as well as the present  
811 hydrogeochemical situation. The comprehension and distinction of geological As accumulation  
812 processes provides the basis for understanding and forecasting As behaviour in natural systems.

813

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821

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