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Authors	Banning, Andre;Rüde, Thomas R.
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University College Cork, Ireland Coláiste na hOllscoile Corcaigh

1	Enrichment processes of arsenic in oxidic sedimentary rocks - from geochemical and genetic
2	characterization to potential mobility
3	
4	Banning, Andre (corresponding author)
5	Institute of Hydrogeology, RWTH Aachen University, Lochnerstraße 4-20, 52064 Aachen, Germany
6	banning@hydro.rwth-aachen.de,
7	Tel.: +49-241-80-99775
8	Fax: +49-241-80-92280
9	
10	Rüde, Thomas R.
11	Institute of Hydrogeology, RWTH Aachen University, Lochnerstraße 4-20, 52064 Aachen, Germany
12	ruede@hydro.rwth-aachen.de
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 $\mu g \ g^{\text{-1}}$ 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 μ 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

calculating Enrichment Factors, indicating that arsenic accumulation was favoured over other potential contaminants. In spite of higher bulk arsenic contents in the oxidic rocks, the mainly pyrite-hosted As pool within the reduced deeper part of the Tertiary sediments is shown to have a higher potential for 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 µg 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 (1.5-2

49 µg 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

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

of geogenic As accumulations in Germany which have been studied sporadically and on a rather local

to regional scale (e.g. Bayer 1997, Heinrichs and Udluft 1999, Rüde 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

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

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

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 Süchteln (Fig. 1).

117

118 2 Material and methods

119 2.1 Material

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

for comparison). All borehole samples were sealed in gastight bags and stored at 4° C. The remaining
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

154 uppermost section of the strata which is discussed later on), documenting relatively stable shallow

habit hardly changes on a length of ~140 m in the sampled core (with an important exception in the

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.

153

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

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*10¹² n cm⁻² s⁻¹; Ge detector: resolution

168 better than 1.7 keV for the 1332 keV, ⁶⁰Co photopeak) or total digestion (HClO₄-HNO₃-HCl-HF at

169 240°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; 20=2-92°). 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

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 µm). 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 μ m 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	
210 211 212 213	Table 2: Whole rock geochemical results of selected elements from the Jurassic samples (DL: detection limit; HK: Hangende Kalke, limestone; RT: Rimsinger Ton, mudstone; UOL: upper ore layer, LOL: lower ore layer; WS: Wedelsandstein, sandstone; GM: Gryhitenmergel, marlstone; HEL: Haupterzlager, main Fe 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 ± 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

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

222

- Figure 2: Lithological profile, Fe and As contents development and Fe phase fractionation of the sampled
 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 (α -FeOOH) is the most important Fe host mineral in the ore layers, accounting for 229 67 ± 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 (α -Fe₂O₃; 23.8 ± 16 %) and the Fe silicate 231 mineral chamosite (($Fe^{2+},Mg,Fe^{3+})_5Al(Si_3Al)O_{10}(OH,O)_8$; 8.8 ± 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 ($CaCO_3$) as the 234 main matrix mineral, detrital quartz (SiO₂) and minor amounts of muscovite (KAl₂(Si₃Al)O₁₀(OH,F)₂) 235 and microcline (KAlSi₃ O_8). Dolomite (CaMg(CO₃)₂) is partly detectable, pyrite (FeS₂) is present in 236 trace amounts in the two thinner ore layers only.

237

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

240

In all Fe ore thin sections, oval to nearly round ooid grains of brownish to reddish colour in a mainly greyish calcitic matrix were observed. In some parts, the latter is of yellowish-orange colour, indicating matrix areas with elevated Fe. Sub-rounded detrital quartz grains and bioclasts are further components. Among the fossils found in the samples, echinoderms, especially crinoids, are most 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 μ g g⁻¹, respectively. Sulphur content is 0.22 \pm 0.09 wt.% on average, it correlates well with As for a large part of the profile (Fig. 3). 271 272 273 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 $((K,Na)(Fe,Al,Mg)_2[(OH)_2 (Si,Al)_4O_{10}])$ is dominant (60 % of all Fe phases on average),
279	followed by pyrite (FeS ₂) and siderite (FeCO ₃). 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 \pm 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.

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 $20.3 \pm 11.8 \ \mu g \ g^{-1}$ in sands, but yield a peak value of 1860 $\ \mu g \ g^{-1}$ 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).

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

305 306 307 Figure 4: Example of heterogenous Fe and As distribution in the oxidized part of the Grafenberg-layers. The inset (upper left corner) shows Fe concretions found in the darker (orange) layer on the left side.

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

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 μ g g⁻¹.

322

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

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

³²⁶

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, A1 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 scale. While, independent from Fe, arsenic content is around 1000 μ g g⁻¹ in the cortex layers, it drops 339 340 to below 500 μ 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 \pm 1.9 % As_{tot} is surface-bound (i.e. NH₄H₂PO₄-soluble and thus quite readily available through pH 350 351 changes or P addition, Wenzel et al. 2001) in Fe ore layers, corresponding to more variable absolute 352 amounts of 1.9-10.3 µg 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 μ g g⁻¹ 354 soluble in step 1. Arsenic bound to Mn (hydr)oxides, targeted with NH₂OH-HCl (step 2), is of minor 355 importance $(0.69 \pm 0.4 \%$ in ore layers). NH₄-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).

- Figure 6: Sequential extraction results of samples from the Jurassic profile (a) (RT: Rimsinger Ton, mudstone;
 UOL: upper ore layer, LOL: lower ore layer; WS: Wedelsandstein, sandstone; HEL: Haupterzlager,
 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 ± 0.4 %, 31.89 ± 2.1 % in step 3, 28.76 ± 5.2 % in step
- 4 and 27.47 \pm 5.6 % in step 5. In the redox transition zone, H₂O₂-soluble As decreases to 16 %.
- Potential mobilizability is similar in all samples ($38.57 \pm 2.3 \% \text{ As}_{tot}$), but higher absolute amounts are
- 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
- potentially mobile As varies between 1.3 and 62.6 μ 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 µg g⁻¹ at 32.2 wt.% Fe in HEL. The overall average of the ore samples (123 389 $\mu g g^{-1}$) 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 µg g⁻¹ 392 at 50 wt.% Fe in one profile (with As and Fe correlating well), thus showing conditions comparable to the ooid ores studied in this work. The scale of As (and other elements) enrichment is discussed in 393 394 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

Figure 7: Pearson element correlation matrices for samples from the HEL (a) and the oxidized facies of the 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 PO_4^{3-} from sea water during the precipitation of positively 416 charged Fe(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 Fe²⁺ remained in the form of chamosite (the presence of chamosite is interpreted as a proxy for mildly 428 429 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).

In contrary to Mn, Pb, Zn, Co, Cd, Cr and Ni correlate positively with Fe and As, and with each other, and negatively with Ca and Mn, clearly indicating that these heavy metals are hosted by Fe ooids, and hardly appear in the matrix. The correlation of Fe and As is weaker at the grain scale as deviated by single ooid measurements (Fig. 5b). This suggests that conditions for As accumulation varied before (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 AsO₄³⁻ adsorption on hydroxides as described above for the geochemically very similar 448 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 (R²=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 µg 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).

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

547

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

550

All these considerations indicate a secondary As enrichment in the near-surface Grafenberg-layers, i.e. an accumulation long after original deposition of the sediments in Oligocene times. The paleo-redox 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

interrelationships of elements can be attributed to different primary sources.

563

562

564 4.2 Scale of accumulation

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

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

571
$$EF = \frac{C_{sam}}{C_{ref}} / \frac{B_{sam}}{B_{ref}}$$
(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
$$CF = \frac{C_{av}}{C_0}$$
 (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

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

598

599 4.2.1 Jurassic Fe ores

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

- Figure 9: Enrichment Factors of 6 elements for Jurassic Fe ore samples. Pie chart: Single elements' contribution to total "contamination pool" (UOL: upper ore layer, LOL: lower ore layer; HEL: Haupterzlager, main Fe ore body).
- 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 μ g g⁻¹). Nevertheless, ore samples have 613 an average Cd content of 1.5 μ 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

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

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

635 636

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 ubiquitary 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 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 ubiquitary 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 NH₄-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_3^{2-} 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 heterogenous 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

Presently, groundwater milieu around the former quarry Kahlenberg is oxidizing. An artificial lake, located 1 km downstream of the quarry in highly conductive Quaternary gravels ($K = 1*10^2 - 1*10^3$ m/s) is in proven hydraulic contact with the Jurassic Fe ores. Nevertheless, transport of As or other contaminants was not detected so far (LGRB 2001), and Fe concentrations are constantly below 0.02 mg L⁻¹ 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 $(NH_4H_2PO_4-)$ soluble As was calculated for UOL, LOL and HEL, applying 691 thickness-weighted mean values, to be 4.8 µg 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 μ g g⁻¹. With an 693 average density of 3.3 g cm⁻³ (calculated for an average mineral composition), this would equal ~16 g 694 m^{-3} of easily soluble As and ~52 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

Table 6: Typical groundwater chemistry in the studied aquifers.

707

708 4.3.2 Tertiary sediments

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

sediment. Mäurer and Wisotzky (2007) found that present groundwater milieu in the vicinity of the

717 sampled borehole is reducing below a depth of \sim 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 $Fe(OH)_3$ and around SI=0 for FeCO₃, 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 hydraulic conductivity of 4.2*10⁻⁵ m/s on average (Mäurer and Wisotzky 2007), the Oligocene 723 724 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 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 study area. They measured groundwater As concentrations up to 130 μ g L⁻¹ and identified pyrite as the 740 741 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 μ g g⁻¹ step 1-soluble As, corresponding to ~2.2 g As per 748 m³ sediment. For Fe hydroxide concretions, the $NH_4H_2PO_4$ -soluble As is 8.9 µg g⁻¹ on average, 749 resulting in ~28 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 g m⁻³. Thus, ~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 μ g g⁻¹ (~12 g m⁻³) and concretions 20.8 μ g g⁻¹ (~67 g m⁻³) on 754 average. Bulk sediment would have 12.6 g m⁻³. Here, concretions contribute only ~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 g m⁻³) is slightly higher than in the reduced facies (1.8 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

remobilization from sediments, the reduced deeper material has a higher potential for causing elevated As concentrations in groundwater. It is more probable for pyrite-oxidizing conditions to reach the primary facies as a consequence of groundwater extraction or nitrate input then for the As hosted in the oxidized facies to be dissolved under reducing conditions (the latter may be imaginable in the course of rising groundwater table or input of organic matter into the system triggering microbiologically induced reduction). Moreover, the reduced part hosting As-laden pyrite in a

relatively homogenous distribution would act as an As area source, thus potentially releasing bulk

sediment As to solution. In contrast, the source function in the oxidized facies is rather punctual.

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

- The groundwater background As concentration in the study area is 1.5 µg 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 (~2 g m⁻³), we can calculate that, referring to 1 m³ sediment (with a known effective
- 781 drainage porosity of n_f=0.13; Mäurer and Wisotzky 2007), approximately 10000 pore volumes are
- needed to produce the background concentration. Further assuming bulk As solubility ($\sim 27 \text{ g m}^{-3}$) in
- the reducing sediments, i.e. generation of an oxidizing milieu, this water volume would produce an As
- groundwater concentration of ~21 μ 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

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

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

813

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821

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