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

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Abstract

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

Keywords

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

1 Introduction

1.1 Background and objectives

During the past two decades, the intensity of arsenic (As) research has increased substantially. Reasons for that are the recognition of As toxicity and its initially underestimated impact on human health on a global scale, focussing on large problem areas, especially in Southeast Asia (e.g. Ravenscroft et al. 2005, Zahid et al. 2009). Consequently, drinking water threshold values were broadly lowered in the 1990ies, mostly down to $10 \mu\text{g L}^{-1}$. This confronted water suppliers with the problem of an increased need to process raw water in order to match drinking water requirements. In recent years, it was also found that in the large majority of cases, naturally occurring As is responsible for elevated groundwater concentrations. Thereby, mobilization from As-enriched minerals is the dominating process (e.g. Lowers et al. 2007, Armienta et al. 2001). Showing characteristics of both chalcophile and siderophile behaviour, arsenic tends to be preferably hosted by sulphide minerals like pyrite or (hydr)oxidic Fe phases like goethite, both of which can contain As up to several wt.% (Smedley and Kinniburgh 2002). In spite of its low average abundance in the upper earth's crust ($1.5\text{--}2 \mu\text{g g}^{-1}$; Matschullat 1999), arsenic can accumulate in rocks to concentrations several orders of magnitude higher than this value. The fate of As in the environment is controlled by the prevailing physico-chemical conditions and the presence of other ions. Redox potential, pH and ionic 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).

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

While As accumulation in Southeast Asia is subject to extensive research and ongoing lively 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, Rude and Königskötter 2009, Banning et al. 2009), although elevated As concentrations have been detected in many parts of the country, an overview is given by Heinrichs and Udluft (1996).

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

1.2 Study areas

Two investigation areas in Germany were selected for rock sampling in the Upper Rhine Graben and in 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).

1.2.1 Upper Rhine Graben (URG)

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

1.2.2 Lower Rhine Embayment (LRE)

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

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

2 Material and methods

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.

The profile starts at the bottom with clays (*opalinus* clay) and calcareous sandstones (lowest Aalenian), both of which were not accessible for sampling. Subsequently, the main ore body (“Haupterzlager” – HEL) follows with a thickness of ~11 m. The ore consists of Fe phase ooids in mainly calcitic cement. It is very fossiliferous, especially containing echinoderm remains. Sedimentological studies showed that Fe ooid formation occurred in a shallow marine environment with long-term relatively stable flow velocities in a facies transition zone between rather carbonate-dominated and more sandy sediments. The latter can be found some kilometres north of the Kahlenberg outcrop, arguing for higher flow velocities, lower water depths and proximity to the coastline (Aldinger 1957; Urban 1966). Clastic and Fe input into the system are estimated to derive

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

From the range of the Grafenberg-layers in the LRE, a total number of 36 sediment samples were taken, 16 of which stem from the reduced lower part and were sampled from cores of up to 182 m 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.

The reduced lower facies of the Grafenberg-layers comprises a quite homogenous marine fine sand of greyish to greenish colours with a total thickness of up to ~300 m in the study area (Nickel 2003). They are little consolidated and contain calcite, glauconite and abundant mollusc shells. Sediment habit hardly changes on a length of ~140 m in the sampled core (with an important exception in the uppermost section of the strata which is discussed later on), documenting relatively stable shallow marine depositional conditions during the Chattian. Clastic input into the basin derived from the weathering of Variscan mainlands to the east of the LRE.

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 during sampling.

2.2 Methods

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

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

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

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

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

Table 1: Sequential Extraction Procedure.

3 Results

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

3.1 Bulk rock geochemistry and mineralogy

3.1.1 Jurassic sediments

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

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.

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

wt.% (LOL) and 21.3 ± 6.9 wt.% (HEL), respectively. Arsenic in all ore samples is present at $123 \pm 48.5 \mu\text{g g}^{-1}$ (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 sediments at $18.0 \pm 7.8 \mu\text{g g}^{-1}$. 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.

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

The mineralogical composition of the ooidic Fe ores, calculated from X-ray diffractograms using Rietveld analysis is summarized in Table 3. Iron phase fractionation is additionally indicated in Figure 2. Goethite ($\alpha\text{-FeOOH}$) is the most important Fe host mineral in the ore layers, accounting for 67 ± 9 % of the present Fe phases, whereby the proportion is slightly higher in the ore layers, compared to the main ore body. Other Fe phases, hematite ($\alpha\text{-Fe}_2\text{O}_3$; 23.8 ± 16 %) and the Fe silicate 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 ± 10 %), show much higher variabilities. Hematite is more abundant in the main ore body, while chamosite reaches significant amounts in the ore layers only (Fig. 2). Besides Fe host minerals, bulk ore samples contain calcite (CaCO_3) as the main matrix mineral, detrital quartz (SiO_2) and minor amounts of muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$) and microcline (KAlSi_3O_8). Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is partly detectable, pyrite (FeS_2) is present in trace amounts in the two thinner ore layers only.

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

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

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

3.1.2 Tertiary sediments

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

Table 4: Whole rock geochemical results of selected elements from the Tertiary sediments (DL: detection limit; Ox_G: oxidized Grafenberg-layers; QC_G: Quarternary cover sediment; Red_G: reduced Grafenberg-layers; Red_H: Reduced Grafenberg-layers from the borehole in Hamminkeln). Samples marked with grey background were analyzed with XRD, see also Table 5.

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

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

Bulk sediment mineralogical results can be found in Table 5. Moreover, Figure 3 contains Fe phase fractionation in borehole samples. XRD analysis identified several reduced Fe minerals, wherein glauconite $((K,Na)(Fe,Al,Mg)_2[(OH)_2(Si,Al)_4O_{10}])$ is dominant (60 % of all Fe phases on average), followed by pyrite (FeS_2) and siderite ($FeCO_3$). Greenish glauconite and framboidal pyrite grains were observable in the sediments under the microscope. One layer at the bottom of the borehole contains a high glauconite proportion of 11.1 % of the bulk sample. Goethite ($FeOOH$) was identified in the uppermost Tertiary sample (GW_0201) only, coexisting with siderite, glauconite and pyrite and thus indicating a zone of redox transition. The calcite content here (0.09 %) is depleted, compared to the deeper sediments (1.82 ± 0.79 %); on the other hand, Fe and As are enriched by factor 3 and 2, respectively. The discordantly following Quarternary cover sediments yield significantly lower contents of Fe and As (Fig. 3). Besides quartz as the dominant mineral phase, calcite and the mentioned Fe phases (Tab. 5), the samples contain minor amounts of muscovite, clay minerals and feldspar.

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

In contrary to the deep sediments, the upper oxidized facies of the Grafenberg-layers shows a very heterogenous distribution of Fe, As and other trace elements, so mean values are not given in Table 4. Iron content averages 3.93 ± 2.2 wt.% in the unconsolidated sands, but can be as high as 23.4 wt.% in concretions. All samples contain goethite whose proportion ranges from 1.04 to 34.51 %. Lepidocrocite (γ - $FeOOH$) as a second Fe hydroxide was identified in two samples. XRD analysis of one sample in the grain fraction $<0.63 \mu m$ (GG_0102f; obtained through wet sieving) indicated that Fe hydroxides are preferably occurring in the fine-grained sediment proportion. Calcite is not detectable in any sample (Tab. 5).

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 Fe concretion, thus underlining the pronounced heterogeneity of element distribution in the oxidized 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

seems to contain less Fe than the average cortex), thus probably representing an ooid fragment of a previous generation. A profile of point measurements, shown for another Fe ooid in Figure 5b (backscattered light), supports these findings. Iron is enriched in the “lighter” parts (areas of higher electron density) of the cortex and in the nucleus, exceeding 50 wt.%, while the “darker” layers contain around 40 wt.% Fe. On the contrary, Al and Si are more abundant in the darker parts. Unlike 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 $\mu\text{g g}^{-1}$ in the cortex layers, it drops to below 500 $\mu\text{g g}^{-1}$ in the nucleus.

3.3 SEP results

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

3.3.1 Jurassic sediments

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. $\text{NH}_4\text{H}_2\text{PO}_4$ -soluble and thus quite readily available through pH changes or P addition, Wenzel et al. 2001) in Fe ore layers, corresponding to more variable absolute amounts of 1.9-10.3 $\mu\text{g g}^{-1}$. Mudstone (RT) and sandstone (WS) from the Jurassic sediment profile both show comparable relative proportions of 3.7 %, but absolute As amounts of only 0.8-1.5 $\mu\text{g g}^{-1}$ soluble in step 1. Arsenic bound to Mn (hydr)oxides, targeted with $\text{NH}_2\text{OH-HCl}$ (step 2), is of minor importance ($0.69 \pm 0.4\%$ in ore layers). NH_4 -oxalate-soluble As (step 3) is most important in RT mudstone (27 %), fresh Fe hydroxide striation was observable in the sampled sediments. The As proportion dissolved in this step is higher in UOL and LOL (~13 %) than in HEL (~7 %, decreasing towards the lower part). Arsenic fractions of lower extractability (step 4 and step 6) are dominant in all ore layers. Within HEL, residual As increases with depth. Step 5-soluble As is negligible except for

RT (8.5 %). Assuming a change in redox conditions from presently oxidizing to rather reducing conditions, the potentially short- to medium-term mobilizable As amount corresponds to steps 1-3 soluble As (Banning et al. 2009). This proportion is higher for the thinner ore layers (~18 %) than for 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.

3.3.2 Tertiary sediments

Sequential extraction results for samples from the range of the Grafenberg-layers are illustrated in Figure 6b. The reduced lower part of the Grafenberg-layers comprises a relatively homogenous As 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 ± 5.6 % in step 5. In the redox transition zone, H_2O_2 -soluble As decreases to 16 %. Potential mobilizability is similar in all samples (38.57 ± 2.3 % As_{tot}), but higher absolute amounts are found in the transition zone (Fig. 6b).

Arsenic extractability in the oxidized facies is more heterogenous. Fractions of steps 4 and 6 are dominant in all samples, but proportions of higher extractability (steps 1-3) vary heavily in 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 $62.6 \mu g g^{-1}$ with a peak value for Fe concretion GG_0103 (Fig. 6b).

4 Discussion

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

4.1 Geochemical characterization and timing of As accumulation

4.1.1 Jurassic sediments

The studied Fe ores from the former quarry Kahlenberg represent a significant As sink with a maximum content of 223 $\mu\text{g g}^{-1}$ at 32.2 wt.% Fe in HEL. The overall average of the ore samples (123 $\mu\text{g g}^{-1}$) is elevated by ~factor 7, compared to the non-ore sediments of the profile. Lithologically and facially similar Jurassic ooidic Fe ores from Luxemburg and France (so called Minette Fe ores) are known to be potential As hosts: Siehl and Thein (1978) detected maximum As contents of 435 $\mu\text{g g}^{-1}$ 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 more detail in chapter 4.2.1.

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

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

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

1968). Most probably, it was adsorbed as PO_4^{3-} from sea water during the precipitation of positively charged $\text{Fe}(\text{OH})_3$ particles.

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

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

formation (Burkhalter 1995). Under these conditions, Fe together with As and trace metals, was transported in solution or colloidal form from the weathering mainland towards shallow marine environments. There, it was able to accumulate, before conditions changed once more and the calcitic matrix settled. During the slow process of Fe ooid formation, reactive surfaces were available for a long time for AsO_4^{3-} adsorption on hydroxides as described above for the geochemically very similar PO_4^{3-} . Additionally, these surfaces were renewed through rhythmic formation of ooid cortices and periodical reworking of the sediments. This way, syndepositional As enrichment potential in Fe ooids is obvious. After the main accumulation (HEL), a sedimentary milieu favouring Fe and As enrichment returned twice as documented by LOL and UOL.

4.1.2 Tertiary sediment

The oxidized upper part of the Grafenberg-layers, compared to the reduced lower part, is enriched in As by ~factor 2, considering average values. However, due to the extremely heterogenous element distribution, the scale of enrichment has to be analysed in more detail (chapter 4.2.2). Like for the Jurassic samples described in chapter 4.1.1, statistical analysis for the oxidized near-surface facies of the Grafenberg-layers was conducted using SPSS software. The Pearson element correlation matrix is shown in figure 7b. Due to its partly extremely high concentrations, especially for Fe and As, concretion GG_0103 was not included in the calculations. Like in the Fe ooids, a striking positive correlation ($R^2=0.93$) between Fe and P is observable – again, P is bound to Fe hydroxides (goethite and, less abundant, lepidocrocite), ubiquitarily available in the oxidized sediments. Iron correlations 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 clear positive relation towards Fe, regression is much weaker for Ce ($R^2=0.39$), Mn ($R^2=0.37$), Co ($R^2=0.37$), 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 second group, Mn, Co, Ni and Ce provide positive interrelations ($R^2=0.63-0.97$) arguing for a common occurrence, while Cu, Al and As do not yield any significant correlation with the other metals. These results underline the extreme heterogenous element distribution. Nevertheless, the lack of As-Al correlation and SEP results indicate that no clay minerals or other silicates but rather Fe hydroxides act as As sinks, albeit with large variations in adsorbed As amounts. The by far highest As content has

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

The source of near-surface Fe (and As) is believed to be the reduced Fe phases from the deeper sediments, i.e. the primary depositional facies, nowadays only accessible in boreholes. Several “candidate” minerals were identified by XRD: glauconite, pyrite and siderite, additionally goethite was detected in the uppermost Tertiary sample GW_0201, indicating a redox transition zone (chapter 3.1.2). The potential role of the reduced Fe phases for As behaviour in the Tertiary sediments will be discussed in the course of a short literature overview in the following.

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

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

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

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

hypothesis, relationships between Fe, S and As were analyzed for these sediments (Fig. 8). In the Fe-S scatter plot (Fig. 8a), the line of stoichiometric pyrite was implemented for comparison. Most samples plot along a line parallel to that. The shift from the pyrite line indicates “excess Fe” hosted by further Fe phases. This is attributable to glauconite and, to a lesser extent, siderite, being present in relatively homogenous concentrations in the reduced samples. Two distinct outliers were identified, samples GW_0201 and GW_0212. To reiterate, GW_0201 is the only sample to contain goethite (interpreted to derive from the redox transition zone), GW_0212 is the sample showing by far the highest glauconite content (11.1 %, compared to an average of 2 % in the other samples analyzed by XRD). These results were accounted for in the As-S scatter plot (Fig. 8b). Samples yielding a pyrite-like development in figure 8a showed a very close As-S correlation of $R^2=0.94$, whereas the total dataset, including the outliers, only provided $R^2=0.56$. This indicates that pyrite is indeed the major As host in large parts of the reduced Grafenberg-layers. Nevertheless, it also suggests that glauconite, if available in larger quantities, is able to adsorb at least part of the As to its surface. Furthermore, it is probable that goethite, derived from oxidation of Fe(II) phases, is an important As sink in the redox transition zone. Here, also siderite may act as a secondary host mineral as it is present in significant quantities and As 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 Abratis 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).

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

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

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

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 reference environment (Eq. 1).

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

where

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

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

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

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

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

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

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

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

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

where

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

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.

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).

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

4.2.2 Tertiary sediments

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

The pronounced heterogeneity in the oxidized sediments is underlined once more when regarding EF values, even if concretion GG_0103 is ruled out. Lead, Cr and Cu, nevertheless, are constantly quite low (average values around 1, none is exceeding 2) and thus show no enrichment compared to the reduced deeper sediments. Like for the Jurassic rocks, Cd was not included in the calculations due to numerous samples in both redox facies showing contents below the detection limit. The other metals are more variable in accumulation behaviour ranging from depletion to moderate enrichment: Ni (0.4-6.6), 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 overall heavy metal enrichment coming with increasing Fe EF is observable, although not comprehensible for single elements. This situation results in relatively balanced contributions of single metals to the total "contamination pool" (Fig. 10, lower pie chart), where As has a proportion of 12 %. Calculating these proportions for the most Fe-rich concretion, the findings are completely different: here, arsenic is by far the most important contributor, accounting for 58 % of the total contaminant pool (Fig. 10, upper pie chart). An EF of 166 for As confirms extremely high accumulation. Although to a lesser extent, other metals are at least significantly enriched with EFs in the range of 10-50. It is most probable that highly enriched concretions like that are very abundant in the oxidized facies of the Grafenberg-layers, also in larger sizes than the exemplar analysed in this study (Fig. 4). Quaas (1917) describes occurrences of banked "dark iron sandstone containing hard Fe concretions" from several former quarries backfilled today and thus unfortunately not accessible for sampling anymore.

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

Relatively high pH should have prevailed during weathering due to calcite dissolution from the original facies, leading to fast and ubiquitary precipitation of Fe coatings without elevated As around quartz grains. Nevertheless, when it came to formation of Fe concretions in the course of ongoing oxidation, arsenic was favoured for adsorption over other elements. Continuous replenishment of Fe made sure that fresh Fe hydroxide precipitates constantly offered new reactive surfaces for arsenate complexation, while oxyhydroxides slowly aged, i.e. polymerization led to higher degrees of crystallinity. This is supported by As being dominantly present in hardly extractable fractions in concretions, whereas higher proportions of NH_4 -oxalate soluble As were detected for the non-concretion sediments (Fig. 6b). In this late stage of the weathering process, buffer function of calcite probably became unimportant because of calcite supply running short. This led to decreasing pH values, allowing for slower Fe precipitation and thereby higher As accumulation (Peters 2000). It can be assumed that calcite depletion was a quite rapid process, because even in the redox transition zone tapped by the borehole, calcite was depleted by 95 %, compared to the reduced deeper sediments, while glauconite and pyrite contents remained on the same level. Calcite dissolution in this zone may also provide CO_3^{2-} for the observed intensified siderite formation (Fig. 3). In consequence, large amounts of Fe and As would still have been available for precipitation after the period of pH buffering. This genetic model would explain the heterogenous As distribution in the sediments and allocate the formation of rather punctiform high As enrichments to a late stage of the weathering process.

4.3 Implications for potential As remobilization

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 ($K = 1 \cdot 10^{-2} - 1 \cdot 10^{-3}$ 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

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

Table 6: Typical groundwater chemistry in the studied aquifers.

4.3.2 Tertiary sediments

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 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 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 $11.6 \mu\text{g g}^{-1}$ is potentially mobilizable, corresponding to $\sim 27 \text{ g m}^{-3}$ sediment. Mäurer and Wisotzky (2007) found that present groundwater milieu in the vicinity of the

sampled borehole is reducing below a depth of ~35-40 m below ground surface, thus correlating well with the proposed redox transition zone derived from geochemical results of this study. Below that depth, water is undersaturated with respect to $\text{Fe}(\text{OH})_3$ and around $\text{SI}=0$ for FeCO_3 , both change to significant oversaturation around 40 m. This data modelled by Mäurer and Wisotzky (2007) is in good agreement with the mineralogical findings in this work. Consequently, pyrite is rather stable and thus should not be an active As source under the given conditions. Nevertheless, in spite of their rather low hydraulic conductivity of $4.2 \cdot 10^{-5}$ m/s on average (Mäurer and Wisotzky 2007), the Oligocene sediments are used for drinking water extraction. In a pumping well near the sampled outcrops, the groundwater table is lowered by up to 25 m during pumping. It was described in chapter 1.2.2 that the depth of the paleo-redox boundary is variable in the study area, but mostly around 20-30 m below ground surface. Therefore, groundwater extraction might change redox conditions to rather oxidizing in the top of the reduced primary facies, thus enabling Fe(II) phases dissolution and output of Fe and hosted As into solution. It is unlikely that this happened in case of the mentioned pumping well, with the raw water showing stable Fe concentrations and As constantly below the detection limit (information from local water supplier). Nevertheless, the redox boundary should be considered when constructing and operating pumping wells in the area. A clear positive correlation between Fe and SO_4 as well as an increase of both parameters in deep wells of one waterworks in the study area since the start of water extraction from the Grafenberg-layers as described by Mäurer and Wisotzky (2007) hints towards successive pyrite oxidation and thus, potential As mobilization. Although no critical As concentrations have been measured so far, continuous groundwater monitoring for As and other potential contaminants is mandatory. An additional problem arises from the surface input of agricultural nitrate being transported to deeper aquifers and triggering pyrite oxidation therein. This 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 $130 \mu\text{g L}^{-1}$ and identified pyrite as the As source. It has also been shown from other regions that anthropogenic disturbance of subsurface redox conditions in an aquifer containing pyrite as a trace mineral and yielding average bulk sediment As even below the values in this work, can lead to significantly elevated As concentrations in groundwater (Price and Pichler 2006).

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

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 than 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 $1.5 \mu\text{g L}^{-1}$ (LUA NRW and MUNLV 2000; Tab. 6). If we assume that this is caused by solution of surface-bound As from Tertiary rocks ($\sim 2 \text{ g m}^{-3}$), we can calculate that, referring to 1 m^3 sediment (with a known effective 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 $\sim 21 \mu\text{g L}^{-1}$, thus exceeding threshold guidelines by more than factor 2. Again, this calculation must be regarded a rough estimation which, nevertheless, points to the significant impact of changing redox conditions on As concentration in groundwater.

5 Conclusions

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

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