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Crossing redox boundaries – aquifer redox history and effects on iron mineralogy and arsenic availability

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Abstract

Cretaceous shallow marine sediments from northwestern Germany exhibit a distinct colour and geochemical boundary in a depth of several decametres, witnessing a terrestrial oxidative paleo redox process which resulted in cement loss and oxidation of Fe(II) phases. Sediment samples were obtained from boreholes drilled in near-coastal and further basinward paleo environments, including both reduced and oxidized redox facies, to characterize As and Fe occurrence in unaltered layers and redistributional consequences of the redox event. Geochemical and mineralogical composition and As fractionation were assessed. Arsenic resides in pyrite in the reduced section with a bulk rock maximum concentration of 39 µg g^{-1}, calculated As_{pyrite} is ~0.2 wt.%. Siderite concretions in the fine sands do not function as As sinks, neither does glauconite whose general As/Fe leaching behaviour was characterized. In the zone of redox transition, reduced and oxidized phases coexist and elevated As concentrations (up to 73 µg g^{-1}) with high proportions of reactive As were detected. Arsenic behaviour changes from relatively homogeneous Fe sulphide-control in the unaltered sediments to very heterogeneous Fe hydroxide-control above the paleo redox boundary. The studied characteristics determine recent As availability in the subsurface and must be considered during groundwater extraction from this highly important aquifer.

Keywords: arsenic, paleo redox event, iron minerals, redistribution, glauconite

1 Introduction

In many paleo and recent environments, As reactivity and mobility are controlled by Fe mineral phases. Extensive field and laboratory work has been conducted to characterize the role of different Fe phases in As dynamics under varying environmental conditions. This includes oxidized species like ferrihydrite, goethite and hematite [1, 2, 3] as well as reduced phases like pyrite [4], siderite [5] and glauconite. The latter mineral was discussed as an As source for elevated concentrations in associated soils and water in several study areas, e.g. in the U.S.A. [6, 7], Belgium [8] or Germany [9]. While glauconite potential for As accumulation has been shown under natural [10] and laboratory [11] conditions, the uptake mechanism remains widely unknown. This question will be addressed in a short side note at the end of this study.

Exposing the aforementioned Fe minerals to changing redox conditions may lead to phase transformation and/or mobilization of Fe and possibly co-occurring trace elements like As. These effects can take place on geological time scales but may be anthropogenically triggered by e.g., lowering groundwater tables during exploitation or input of oxidizing agents, and can then lead to significantly increasing groundwater trace element concentrations [12, 13]. Paleo redox events under humid tropical conditions lead to neo-formation and accumulation of oxidized Fe phases and leaching of soluble elements in affected sediments during successive downward advance of the weathering front as described by Felix-Henningsen [14] for Paleozoic shales from central Germany.

This study aims at characterizing geochemical and mineralogical effects of a terrestrial paleo oxidation event during the Tertiary on exposed Cretaceous marine sediments with a focus on As distribution and Fe mineral assemblages. The situations below and above the paleo redox boundary are assessed, compared and set in relation to the interface between both redox facies, i.e. the redox transition zone. Sampling from different positions in the basin allowed for spatial and paleoenvironmental comparison. Consequences for recent As availability in the studied sediments representing an important aquifer for regional water supply are discussed.

2 Study area and As distribution

The study area is located in the western part of the Münsterland Cretaceous Basin (northwestern Germany, Fig. 1), a syncline structure filled with marine Cretaceous sediments on Variscan basement. The studied Santonian (Upper Cretaceous) sediments, locally named Haltern Formation (Fm.), with a thickness of up to 300 m cover an area of ~770 km^2 [15, 16, 17] (Fig. 1).

Figure 1: Location and geology of the Münsterland Cretaceous Basin (modified after [15]), distribution area of the Haltern Fm. and oxidic Fe concretions (PBIOs) therein (modified after [18]) and location of the studied boreholes (white-framed spots).

The Haltern Fm. was deposited under shallow marine conditions (water depths: 40 to 60 m). Its sandy character documents proximity to the provenance area, probably Variscan mainlands to the northwest, e.g. the Winterswijk anticline [19, 20]. This marginal occurrence is in contrast to the otherwise widely carbonatic succession in the basin. Secondary alteration of the primary reduced facies under tropical-humid terrestrial conditions in late Tertiary times, i.e. the paleo redox event, left the near-surface oxidized section as rather unconsolidated, pure quartz sands [15, 21]. Oxidative mobilization of Fe from primarily reduced phases and its accumulation in the oxidized section led to formation of hydroxidic Fe concretions. Dahm-Arens [18] suggested their precipitation from oxidizing groundwater, making the concretions representatives of oscillating paleo groundwater tables. This was supported by Banning [22] conducting geochemical, mineralogical and genetic comparison to recent bog iron ore environments. Based on these results and those of Banning et al. [23], the name “paleo bog iron ores” (PBIOs) was suggested for the concretions. They were subdivided into several types depending on differences in mineralogy, geochemistry and Fe hydroxide ageing level. Selected PBIOs in outcrops and as hand specimen are shown in Fig. 2 and their spatial outcrop distribution in Fig. 1.

Figure 2: Different types of Fe concretions (PBIOs) occurring in otherwise pure quartz sand of the Haltern Fm. with respective Fe phase mineralogy and maximum As concentrations (modified after [22, 23]).

High As concentrations (up to ~1,000 µg g^{-1}) are known in oximorphic Fe-rich (widely goethitic) horizons of lowland gleysols from the western Münsterland [24]. The described PBIOs were identified as the geogenic sources of As in the area [23]. Iron hydroxide PBIOs exhibit distinct enrichment of Fe (up to 29.5 wt.%) and As (up to 140 µg g^{-1}), compared to ambient quartz sands, while siderite concretions (up to 14.1 wt.% Fe) do not function as As hosts (Fig. 2). It was speculated earlier [23] that As in PBIOs, likewise Fe, originally derived from reduced mineral phases of the primary calcitic and glauconitic facies of the Haltern Fm. in the subsurface and was mobilized, transported and accumulated in the course of the Tertiary paleo redox event. To assess this hypothesis, a characterization of the reduced facies and especially the paleo redox boundary is necessary. Nevertheless, no sample material was available for analysis back then since outcrops of the reduced section are not known and the paleo redox boundary was described as 60-70 m below ground surface [21], leading to dependence on boreholes for sampling.

The Haltern Fm. represents an aquifer of major importance for drinking water supply of a large area in western Germany. Hydrochemically, this groundwater is widely characterized as Ca-HCO_3 or Ca-HCO_3-SO_4 type [25]. It is generally oxidizing and circumneutral in pH, although reducing groundwaters with high Fe concentrations occur locally [22]. Heavy temporal redox milieu fluctuations were observed (e.g., Eh dropped from +450 to +50 mV in one well within two years [23]). Groundwater As concentrations exceeding 10 µg L^{-1} are not documented for this aquifer. Nevertheless, in a review of German groundwater As concentrations, values above 5 µg L^{-1} in Cretaceous sediments from North Rhine-Westphalia mainly occurred in the Haltern Fm. [26]. Banning et al. [23] detected a maximum of 8 µg L^{-1} As.

3 Materials and Methods

Sediments were sampled from a 128 m deep research borehole commissioned by the Geological Survey of North Rhine-Westphalia near the municipality of Nordvelen, and from two ~83 m deep boreholes in the vicinity of Flaesheim (Fig. 1). The drillcores contain the described paleo redox boundary. It was thus possible to characterize the primary reduced facies of the Santonian sediments, study As occurrence and behaviour, and derive mobilization and reaccumulation mechanisms.

From the Nordvelen borehole in the northwestern distribution area of the Haltern Fm., 23 samples were included in this study covering a depth range from 5.5 to 127.6 m below ground surface (Fig. 3). Greyish reduced and yellowish oxidized sands were considered. Eye-catching concretionary sections within the reduced facies, obviously rich in Fe(II) mineral phases, were also sampled. Their freshly cut surfaces altered within minutes upon contact with air, resulting in a colour change from greyish-greenish to orange which indicates oxidation to Fe(III). The material was sealed in gastight PE bags and stored in the dark until analysis (~2 weeks at ~10°C).

A total of 15 samples were obtained from the two Flaesheim boreholes in the southeastern distribution area of the Haltern Fm. Because sampling aimed at finding the paleo redox boundary, it was arranged around a distinct sediment colour change in the first borehole (referred to as Flaesheim 1 in the following). Thereby, a depth interval from 53 to 69 m below ground surface was covered. Samples from the second borehole (Flaesheim 2) were taken from the same depth interval. Obtained unconsolidated material was sealed and stored like for the Nordvelen borehole. Nevertheless, long-term storage of the samples (archived by the regional sand pit operating company in boxes containing mixed samples each covering a sediment thickness of one metre) was not under complete air exclusion. Therefore, partly oxidation of primarily reduced material cannot be excluded.

Bulk rock geochemistry was assessed for all sediment samples using INAA or ICP-OES following digestion with $HClO_4$-HNO_3-HCl-HF. These analyses were conducted by Activation Laboratories, Ontario, Canada.

Six samples from the Nordvelen borehole were selected for XRD measurement (Bruker AXS D8 Advance) after pulverizing in a corundum mill. Rietveld analysis for mineral phase quantification was conducted with the software BGMN 4.2.3.

A sequential extraction procedure (SEP) was carried out for eight samples. The procedure included four operationally defined As target fractions selected to characterize remobilization potential and mineralogical As fractionation, especially between oxidized and reduced phases (Table 1). Arsenic determination in extraction solutions was performed using graphite furnace AAS (PerkinElmer AAnalyst 800) with a detection limit of 0.1 µg L^{-1}. All reagents used were p.a. grade (Merck).

Table 1: Applied sequential extraction procedure.

In an attempt to characterize As and Fe fractionation in the mineral, a commercially available glauconite powder sold as natural green pigment for painting (Rublev Colours "Glauconite", mineral origin: Baltic states) was obtained. It was studied in terms of geochemistry, mineralogy and sequential extractability as described above for the sediment samples. However, in addition to As, Fe concentrations in SEP solutions were determined by spectrophotometry (Lange Cadas 100).

4 Results and Discussion

4.1 Proximal Santonian sediments

Iron and selected trace element concentrations for the Nordvelen borehole, distinguished by sample groups, are given in Table 2.

Table 2: Statistics on Fe and trace element concentrations in sediments from the borehole Nordvelen (DL: detection limit). Cf. Fig. 3 for respective depth intervals.

Figure 3 illustrates a simplified profile of the Nordvelen borehole and vertical development of Fe, As and S concentrations.

Iron(II) concretions of several dm thickness (cf. Fig. 4; median Fe concentration: 12.4 wt.%) occurring within the reduced sands of the profile turned out to be composed of siderite [$FeCO_3$] with an average proportion of 27.2 wt.% as determined by Rietveld analysis. Like Jurassic marine siderite concretions studied by Hounslow [29], these are likely to have developed in early stages of diagenesis, from initially disperse carbonate cement and subsequent overgrowth with successive burial. These concretions may represent the precursors of the Fe hydroxide-encrusted siderites from the near-surface oxidized section of the Haltern Fm. (Fig. 2).

Figure 3: Simplified lithological and geochemical (As, S, Fe) profile of the Nordvelen borehole (cf. Fig. 1). Depth intervals shown in Figs. 4 and 6 are indicated on the right side.

While no siderite was detected in the other reduced samples, the presence of glauconite [$(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$] and pyrite [$FeS_2$] is a common feature in all analyzed samples with average contents of 1.5 and 0.6 wt.%, respectively. Similar non-carbonate mineralogy of siderite concretions and surrounding rocks, including the common presence of pyrite, is also documented by Hounslow [29]. Concerning As uptake potential, each of the three identified reduced Fe phases is a candidate. Besides glauconite and pyrite, the Fe hydroxide lepidocrocite [γ-FeOOH] was detected in an orange sample from the zone of redox transition at 23.5 m below ground surface (cf. Figs. 3, 6). The presence of lepidocrocite is associated with temporally changing redox conditions in the subsurface, where the mineral occurs as weathering product of pyrite [30]. Lepidocrocite is known as an effective As adsorbent, especially in slightly acid to circumneutral conditions [31]. Generally, quartz is the dominant mineral in all samples, accounting for 95-98 wt.% in reduced sands and 60-74 wt.% in siderite concretions. Additional ubiquitous minor components are muscovite and microcline, together occurring at levels of 0.8-4.2 wt.%.

In the reduced greyish sands, an As concentration of 15±12 $\mu g\ g^{-1}$ with a maximum of 39 $\mu g\ g^{-1}$ was detected (Fig. 3). Compared to these sands, siderite concretions (13±4 $\mu g\ g^{-1}$) do not show any tendency towards As accumulation while mean values of Fe and Mn are enriched by a factor of 17 and 50, respectively. Apart from that, no significant enrichment of other trace elements was observed with the exception of U (by a factor of 5, Table 2). While high Mn concentrations in siderite concretions are attributable to occurrence of $MnCO_3$ in these inclusions [29], U(VI) can be immobilized at the siderite surface by incorporation in Fe precipitates with subsequent reduction to U(IV) [32]. Mean concentrations of S are well comparable between these sample groups (0.36±0.29 wt.% and 0.32±0.18 wt.% in reduced sands and siderite concretions, respectively).

Figure 4: Core photograph from 50-53 m below ground surface in the Nordvelen borehole, containing two siderite concretions (rapidly oxidized), with respective concentrations of Fe, S and As therein.

Comparison of two siderite concretions between 50 and 53 m below ground surface (Fig. 4) illustrates that higher As concentrations prevail in the lower Fe concretion together with higher S, indicating sulphide-controlled rather than carbonate-controlled As behaviour. To check this assumption for the whole reduced section, correlation analyses of As vs. S and Fe were conducted for greyish fine sands and siderite concretions (Fig. 5).

Figure 5: Scatter plots of S vs. As (left side) and Fe vs. As (right side) for reduced sands and siderite concretions from the Nordvelen borehole.

Both the reduced fine sands and the siderite concretions therein exhibit a close positive correlation between As and S (Fig. 5) suggesting that indeed, pyrite can be considered the major As host in both sample groups. The trend between As and Fe is positive but less distinct for the greyish sands (R^2=0.52), explainable by the presence of varying glauconite contents. Siderite concretions, on the other hand, show a negative correlation between As and Fe (R^2=0.55) which clearly indicates that $FeCO_3$ is not an As sink in these sections. Being by far the dominant Fe host, siderite obscures a Fe_{pyrite}-As interrelation. Assuming bulk As hosting in pyrite, average As_{pyrite} calculated from geochemical and mineralogical results is 0.20 wt.% for reduced sands and 0.18 wt.% for siderite concretions and thus, rather similar in these sample groups.

High As concentrations (61-73 µg g^{-1}) prevail around the aforementioned redox transition zone while other elements are not, or significantly less, enriched as compared to the reduced zone. The transition zone is therefore analyzed in more detail (Fig. 6). Oxidized yellowish sands in the profile are depleted in Fe and all trace elements (As: 5±3 µg g^{-1}) in comparison to the reduced section and especially the redox transition zone (Table 1, Fig. 3). Sulphur concentration is generally below the detection limit, i.e. <0.01 wt.%. These observations argue for component dissolution and mobilization processes during the paleo redox event.

The homogeneous oxidized sandy horizon occurring at around 100 m depth below ground surface (Fig. 3) is hardly explainable by the paleo redox model developed here as it is overlain by thick reduced layers. It rather represents subaerial (probably beach facies) deposits as indicated by missing bioturbation (while reduced sands in the profile exhibit intensive bioturbation). Such rather high-energy deposits are not known from more distal parts of the Santonian sediments. Thus, primarily oxidized layers exist in proximity to the provenance area in the northwest. These indicate paleo sea level variations and further support the paleogeographical configuration described in chapter 2.

Figure 6: Geochemical profile (As, S, Fe) around the redox transition zone (dark dotted rectangle) in the Nordvelen borehole (cf. Fig. 3). Inset: core photograph of the redox transition zone from greyish sands (darker colours) to yellowish sands (lighter colours), with white dotted rectangles indicating the position of analyzed samples.

The visually sharp redox boundary between greyish and yellowish fine sands is also expressed in the geochemical profile (Fig. 6). Concentrations of As, S and Fe develop parallel in the reduced sediments, As and S reach peak values ~30 cm below the color-based redox boundary. While S sharply decreases at the transition point, As remains on a similarly high level and Fe exhibits a concentration peak (1.64 wt.%, the top value of the profile apart from siderite concretions). It can be concluded that As occurrence is pyrite-controlled in the reduced layers. Pyrite oxidation in the redox transition zone led to Fe_{tot} accumulation and lepidocrocite formation (as detected by XRD), whereby the majority of As is probably retained by this Fe hydroxide. Its coexistence with pyrite and glauconite indicates that sediment oxidation is incomplete. Sulphur concentration drops to 0.01 wt.% at ~50 cm above the boundary while As is still high. Oxidation of Fe(II) phases should be completed here and bulk Fe present as hydroxides. In the oxidized section, As develops parallel to Fe (Fig. 6) while S is

<0.01 wt.%. Obviously, a change of As-controlling host phases from Fe sulphides to Fe hydroxides occurs at the redox boundary.

The transition zone is likely to have successively proceeded to greater depth during terrestrial weathering in Tertiary times. This process should have produced numerous As-rich Fe hydroxide concretions from Fe(II) phase mobilization and subsequent accumulation. It can be assumed that the lepidocrocite-bearing transition zone represents a precursor of what later develops into a more stable goethite (α-FeOOH) concretion. This mechanism of "autochthonous" Fe hydroxide formation must be considered in addition to the precipitation of "allochthonous" Fe hydroxides from groundwater (PBIOs). With respect to the generally lower concentrations of Fe and As in the oxidized compared to the reduced zone, and thus the obvious dominance of mobilization over direct local reaccumulation, the latter process is probably of higher significance.

4.2 Distal Santonian sediments

A summary of Fe and trace element concentrations for the Flaesheim boreholes, differentiated by redox milieu, is given in Table 3.

Table 3: Statistics on Fe and selected trace element concentrations in the studied sediments from the two Flaesheim boreholes (DL: detection limit). Cf. Fig. 7 for respective depth intervals.

A relatively homogeneous Fe and trace element distribution is observable in the reduced layers. However, As shows a significant range (6.3-14.3 µg g^{-1}). The values are comparable to those from the reduced zone of the Nordvelen borehole (Table 2), albeit generally slightly lower. Average trace element and Fe concentrations in the oxidized sands are very similar to the reduced material but exhibit higher variability. Only As is significantly depleted (by a factor of 2) which is in agreement with the findings from Nordvelen. Therefore, a generally rather homogeneous Fe and trace element distribution can be assumed in non-concretionary sections of the Santonian sediments. Higher concentrations and variabilities in Nordvelen are explainable by a more proximal position with regard to the paleo coastline in the northwest, leading to fluctuating terrestrial input and changing trace element incorporation into the sediments. We conclude that the more distal area around Flaesheim rather received a more stable "background" amount of trace elements not immobilized in the shallower facies.

Figure 7 illustrates geochemical profiles of the Flaesheim boreholes with depth developments of As, S, Fe and Ca concentrations.

Figure 7: Geochemical profiles (As, S, Fe, Ca) and estimated positions of the redox boundary in the boreholes Flaesheim 1 (a) and Flaesheim 2 (b). "HCl test" indicates reaction of the samples towards treatment with 10 % HCl, with + strong reaction, +/- weak reaction, - no reaction.

Sediment colour changes significantly within the sampled profile shown in Fig. 7a. Greenish to greyish colours dominate below a depth of ~57 m. The sample taken from 57 m below ground surface contains orange fragments, obviously Fe hydroxides, indicating proximity to the redox boundary. Further upwards, strongly orange coloured sands are observed around 55 m, followed by light yellowish sands containing single Fe hydroxide fragments. Calcium concentration in the sediment decreases sharply between 61 and 57 m. Reaction intensity on 10 % HCl treatment decreases accordingly. The calcitic cement of the deeper reduced layers was obviously dissolved during the paleo redox process suggesting that not only oxidation but also material loss occurs. This observation explains the unconsolidated status of the pure near-surface oxidized Santonian quartz sands. Sulphur and As concentrations develop parallel in the reduced section with a distinct common peak at ~61 m below ground surface. A sharp S decrease towards the redox boundary accompanies calcite loss and argues for sulphide oxidation. Sulphur values fall to <0.01 wt.% within a few meters (Fig. 7a) while As and Fe show a common smaller positive peak shortly above the redox boundary. This indicates the potential for autochthonous accumulation of As after mobilization during the paleo redox process. In conclusion, As behaviour appears to be Fe sulphide-controlled in the reduced section. In the redox transition zone, a decoupling is observable, and Fe hydroxides take over As control in the oxidized section. These results are in accordance to what was described for the northwestern distribution area in the previous chapter, albeit at a lower concentration scale.

Commonalities and differences are documented in the profile of the second Flaesheim borehole (Flaesheim 2, Fig. 7b). Taken from the same depth interval as in Flaesheim 1, geochemical proxies in Flaesheim 2 exhibit partly different behaviour. Calcium concentration is universally low with a maximum in the bottommost sample which exclusively shows a reaction with HCl (Fig. 7b). The paleo redox boundary appears to be in a considerably deeper position compared to Flaesheim 1. An As/Fe peak in the oxidized section occurs at ~58 m with S <0.01 wt.% at that point. Interpretations on As control mechanisms and behaviour are akin to Flaesheim 1. However, it is remarkable that depth of the paleo redox boundary appears to vary by ~10 m within a distance of only ~500 m between the two boreholes at similar drilling site heights (67 and 69 m a.s.l.). This observation argues for a rather heterogeneous depth influence of the terrestrial weathering process even at short range, and must be considered during groundwater extraction.

Since no XRD measurements were conducted for the samples from the Flaesheim boreholes, As_{pyrite} for the reduced section was calculated under the assumption that both bulk S and bulk As are present as pyrite. The result is an average of 0.21 wt.% As_{pyrite} which is in good agreement with the values determined for the northwestern reduced sands and siderite concretions (0.20 and 0.18 wt.%, respectively) and well comparable to other aquifer studies (e.g. 0.23 wt.% As_{pyrite} determined by [13]). It is concluded that in spite of lower Fe and As amounts reaching the more distal parts through terrigenous input, the incorporation potential for As in pyrite is rather constant within the Santonian shallow marine system.

4.3 Arsenic fractionation and remobilization potential

Results of As fractionation as determined by SEP are presented in Fig. 8.

Figure 8: SEP results for samples from the boreholes Nordvelen (top) and Flaesheim 1 (bottom) with absolute $NH_4H_2PO_4$-soluble (exchangeable) As concentrations, ordered by redox facies. Nordvelen borehole:

samples at 23.5 and 23.8 m are from the redox transition zone (cf. Fig. 6), those from 28.4, 88.5 m and 127.6 m represent reduced sands and that from 61.8 m a siderite concretion.

Exchangeable As shows highest proportions in reduced sands (up to 38 % As_{tot}). However, significant absolute values of up to 17.9 µg g^{-1} are dissolvable in the redox transition zone indicating high reactivity and remobilization potential during water-rock-interaction in this sector. In contrast, the siderite concretion as well as the Flaesheim samples (both redox facies) are negligible in this respect. The fraction of As bound to amorphous Fe (hydr)oxides is considerably larger than that prevailing in crystalline phases within all reduced samples. This may partly be explained by rather recent oxidation of reduced Fe phases, probably via air contact during sampling and storage. Higher proportions of step 3-soluble As are found at the paleo redox boundary in the Nordvelen borehole and the oxidized sample from Flaesheim 1. In these samples, Fe hydroxides were identified by XRD or visually, and As hosting is thus interpreted to be a primary signal. Sulphide-bound As is likely to be generally underestimated in the reduced samples due to artificially induced oxidation as described above. Nevertheless, trends are clearly visible. Between 4 and 34 % As_{tot} are dissolved in this step in the reduced layers while <1.5 % As_{tot} are detected in the oxidized samples. In the redox transition zone, this proportion decreases by a factor of 10 within 30 cm depth between the sample from directly below the paleo redox boundary and the lepidocrocite-bearing layer marking it (cf. Fig. 6). Meanwhile, step 3-soluble As increases by around the same factor. A very similar behaviour is observable when comparing reduced and oxidized sample from the Flaesheim borehole (Fig. 8). These results clearly support the aforementioned decoupling of As from sulphide control and the uptake by Fe hydroxides in the course of the redox event.

In comparison to the paleo bog Fe ores (PBIOs, cf. Fig. 2) in the near-surface oxidized section of the Santonian sediments, a higher degree of exchangeable As is evident in the redox transition zone, i.e. in the presumed precursor material of PBIOs. On average, only 2.8 % As_{tot} was $NH_4H_2PO_4$-dissolvable from the consolidated, mainly goethitic Fe crusts. This proportion is elevated by a factor of 10 around the paleo redox boundary studied here. In consequence, successive oxidation of concretionary Fe/As accumulations leads to ageing of Fe hydroxides and significantly more stable As bonding forms [e.g., 33] and thus, decreasing remobilization potential while bulk As concentrations in precursor material (mean: 68 µg g^{-1}) and PBIOs (mean: 44 µg g^{-1}) are in the same order of magnitude.

4.4 Excursus: Arsenic uptake mechanisms in natural glauconite

Besides surface sorption as one possibility, As input in the crystal lattice of glauconite may be arguable in view of the glauconite chemical heterogeneity and the As tendency to isomorphically substitute a wide range of ions [34, 35].

The commercially available glauconite powder used as green pigment in painting yielded As and Fe concentrations of 16 µg g^{-1} and 13.3 wt.%, respectively. Arsenic in the powder is in the range of values given by Dooley [10] reporting 7.1-31 µg g^{-1} As in New Jersey greensands. Quantitative XRD analysis determined about 86 wt.% glauconite in the sample with minor amounts of celadonite, quartz, jarosite and calcite (a second commercial green pigment turned out to mainly consist of gypsum and barite and was not considered for further analysis). Hence, the pigment can be characterized as relatively pure glauconite which is thus suitable for studying the mineral´s As and Fe leaching behaviour. SEP results are illustrated in figure 9.

Figure 9: SEP results for the glauconite powder.

During the sequential extraction, As was entirely dissolved from the sample, i.e. there is no residual fraction which would be attributable to especially silicate-bound As. About 10 % As_{tot} can be classified as exchangeable (step 1), the rest is distributed almost equally to reducible (steps 2 and 3) and oxidizable (step 4) fractions. Iron, on the other hand, mainly resides in the residual fraction (73 % Fe_{tot}), probably as structural component of the glauconite crystal lattice. These observations lead to the following considerations: As is obviously not able to become a stoichiometric part of the glauconite structure under natural conditions. Its partly high concentrations in glauconitic samples are rather attributable to the mineral´s high capacity for As surface sorption. It may be assumed that the metalloid is mainly hosted by oxidation rims of Fe-hydroxides around the glauconite pellets. Haque et al. [36] report highest proportions of As in glauconitic sediments in the reducible fraction. A high proportion of oxidizable As (43.8 % As_{tot}, Fig. 9) might be explainable by hosting in finely dispersed pyrite co-occurring with glauconite as inclusions or crack fillings [10]. Though not identified by XRD, a sulphur concentration of 700 µg g^{-1} in the sample studied here indicates minor amounts of sulphides, also supported by the presence of a small oxidizable Fe fraction (Fig. 9).

In consequence, elevated As in glauconite is not a primary signal inherited from the time of mineral formation. It is more likely that glauconite surface alteration to hydroxide provides sorption sites for As accumulation from external solution in addition to stoichiometric substitution in glauconite-associated pyrite. The chosen approach can only provide indirect evidence on As enrichment mechanisms in glauconitic sediments. Derived conclusions are therefore rather hypothetical and must be confirmed by further analyses (e.g. electron microprobe or LA-ICP-MS measurements in hydroxidic glauconite rims and pyrite inclusions).

5 Conclusions

Upper Cretaceous shallow marine sediments (Haltern Fm.) from the western Münsterland were affected by deep terrestrial weathering in Tertiary times, leading to loss of carbonatic cement and oxidation of Fe(II) mineral phases. It was shown in this study that pyrite represents the major As carrier in the unaltered layers while a shift towards As control by Fe hydroxides is observable above the redox boundary. Coexistence of oxidized and reduced Fe phases characterizes the transition zone.

The reduced Santonian sediments represent the primary As source in the area. Heterogeneous redistribution in the course of the paleo redox process led to abundant concretionary accumulation in mainly goethitic As-rich Fe concretions widespread in the near-surface oxidized facies. Elevated As concentrations and significant proportions of exchangeable As indicate high reactivity in the redox transition zone whose depth below ground surface varies considerably in the sediment distribution area. Attention should therefore be paid in the operation of wells within this prominent groundwater system. The artificial induction of oxidizing conditions due to lowered groundwater tables might lead to mobilization of As from reduced layers and redox transition zone, potentially resulting in elevated groundwater concentrations. Knowledge of the paleo redox boundary position and monitoring of As concentrations as well as physico-chemical conditions are thus essential to optimize groundwater extraction.

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