

Natural arsenic and uranium accumulation and remobilization in different geological environments

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General introduction

Arsenic and uranium – a short geochemical overview

Showing characteristics of both chalcophile and siderophile behaviour, arsenic (As) 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, Taylor 1964: $1.8\ \mu\text{g g}^{-1}$ in the continental crust), As can accumulate in rocks to concentrations several orders of magnitude higher than these values. The metalloid's fate in the environment is controlled by the prevailing physico-chemical conditions and the presence of other ions. Redox milieu, 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 (e.g. Stollenwerk 2002, Smedley and Kinniburgh 2002, Pedersen et al. 2006).

Taylor (1964) cites the average uranium (U) abundance in the continental crust as $2.7\ \mu\text{g g}^{-1}$. Thereby, generally higher concentrations are detected in felsic rocks (granite average: $4.8\ \mu\text{g g}^{-1}$ U) compared to mafic lithologies (basalt average: $0.6\ \mu\text{g g}^{-1}$ U) (Taylor 1964), indicating the element's rather incompatible character in magmatic differentiation. The mobility of U in the environment is, akin to that of As, governed by the Eh-pH milieu and the presence of adsorbers like Fe (hydr)oxides, clay minerals or organic matter (e.g. Doi et al. 1975, Giblin et al. 1981, Merkel and Sperling 1998, Missana et al. 2003, Bots and Behrends 2008). Nevertheless, contrary to As, U is significantly more mobile in its oxidized form U(VI) which is reasoned by its affinity to form stable uranylhydroxo or –carbonato complexes (e.g. Katsoyiannis et al. 2007).

Since the hydrogeochemical occurrence and behaviour of both trace elements is highly dependent on the geological and hydrochemical conditions in a study area, additional information and discussion of relevant literature regarding the fate of As and U in the environment, preferential carrier phases and remobilization processes are site-specifically given in the five substudies (parts 1 to 5) of this work.

In spite of their differing redox and transport properties, As and U frequently occur together in (ground)water of affected areas (e.g. Brown et al. 2007, Kipp et al. 2009, Nicolli et al. 2010). This apparent contradiction, together with the increasing interest in U as a potentially harmful element in groundwater and drinking water (see next chapter), led to its choice as a second element besides As to be studied in the present work.

Arsenic and uranium as contaminants – health aspects and affected areas

The recognition of As toxicity and its initially underestimated impact on human health on a global scale substantially increased the intensity of As research during the past two decades, focussing on large problem areas, especially in Southeast Asia (e.g. Berg et al. 2001, 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).

Besides the large tropical, mainly deltaic regions with As-exposed populations (e.g. Bangladesh, West Bengal, Vietnam, Taiwan), (semi)arid As problem areas have been identified worldwide. Prominent examples can be found in Chile (e.g. Oyarzun et al. 2004) and the western U.S.A. (e.g. Welch and Lico 1998). Identified As problem areas in Mexico include the Zimapán Valley (Armienta et al. 2001) and the Rioverde Basin (Planer-Friedrich et al. 2001), even endemic As poisoning was described in the Lagunera region (Del Razo et al. 1990). An overview of elevated As occurrences in Mexico is given by Armienta and Segovia (2008). Tertiary volcanic rocks are under suspicion as one potential carrier of elevated As concentrations, and thus a potential geogenic source. However, more detailed characterization of the source or mobilization processes remain largely unknown (Gutiérrez and Alarcón Herrera 2010).

While the toxicity of As is well documented and drinking water limitations are established and reconsidered for several decades (actually $10 \mu\text{g L}^{-1}$, WHO 2006), U was neglected in this respect for a long time. It was shown that the risk of U exposure primarily derives from its toxicity as a nephrotoxic heavy metal (i.e., leading to kidney diseases), rather than from its radioactive character (Zamora et al. 1998, Orloff et al. 2004, Kurttio et al. 2006). For adults in Germany, a total radiation exposure of 2.1 mSv a^{-1} was determined, whereby exposure via drinking water only contributes 0.009 mSv a^{-1} (BfS 2009), i.e. $\sim 0.4 \%$ of the annual radiation dosage. There is no general agreement on fixed limitations for U concentrations in drinking water up to date, although drinking water is considered the most important source of U uptake. WHO announced a “provisional guideline value” of $15 \mu\text{g L}^{-1}$, US-EPA a MCL (“maximum contamination level”) of $30 \mu\text{g L}^{-1}$, German legislation recently decided on a fixed limitation of $10 \mu\text{g L}^{-1}$, valid from 11/2011. Germany will be the first member state of the European Union with a fixed drinking water limitation for U then.

Compared to As, the number of identified geogenic groundwater U problem areas worldwide is low until now. Nevertheless, it has been recognized that high-U aquifers represent a phenomenon of global

extent. Felsic magmatic aquifers in Scandinavia are partly affected by elevated concentrations (Frengstad et al. 2000 and citations therein). Sherman et al. (2007) found 29 % of the studied water samples from a sandstone aquifer in Michigan in excess of the EPA-MCL (see above). These authors also give a short overview of case studies from other affected states and countries (Sherman et al. 2007 and citations therein). In the course of a national monitoring of domestic well water in the U.S.A., Focazio et al. (2006) detected 4 % of all samples exceeding $30 \mu\text{g L}^{-1}$ U.

Known cases of elevated As and U contents in Germany (sediments and groundwater)

While the mechanism of As accumulation in delta sediments of 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, although elevated As concentrations in groundwater have been detected in many parts of the country, an overview is given by Heinrichs and Udluft (1996). Figure 1 illustrates a survey of conducted studies on elevated As occurrences in sedimentary rocks and groundwater, whereby no claim to completeness is made. It does neither include high As observed in thermal waters which is known from e.g., Baden-Baden (Rüde 1996), Aachen (Herch 1997) and Wiesbaden (Rosenberg et al. 1999), nor anthropogenically induced As problems (e.g., from former mining, past agricultural techniques or ammunition). The studies shown in Fig. 1 will be shortly summarized in the following.

Banning et al. (2009) detected partly high As contents up to $140 \mu\text{g g}^{-1}$ in secondary Fe concretions in oxidized Upper Cretaceous (Santonian) sediments from the Münsterland Cretaceous Basin (area [1] in Fig. 1) and identified them as the source for significant concentrations occurring in soils of the region described by Peronne (2003). Part 3 of the present work deals with the primary source and the dynamics of As in this area. Concentrations of As in groundwater from southern Lower Saxony [2] above the drinking water standard was attributed to output from Lower Triassic (“Buntsandstein”) clastic sediments (up to $693 \mu\text{g g}^{-1}$ As) by Goldberg et al. (1995). Mertens (2000) found an average of $108 \mu\text{g g}^{-1}$ As in Upper Cretaceous (Cenomanian) glauconitic sands in the Ruhr Area [3] whereby output from the rocks to groundwater was not observed. In a Pliocene aquifer from the Lower Rhine Embayment [4], Cremer et al. (2003) detected up to $130 \mu\text{g L}^{-1}$ As in groundwater, attributable to mobilization via pyrite oxidation, triggered by anthropogenic NO_3^- input. In oxidized Oligocene sediments from the same basin [4], Jansen (2006) observed up to $150 \mu\text{g g}^{-1}$ As in Fe hydroxide bearing strata. Detailed characterization and development of As occurring in these sediments is subject to part 4 of the present work.

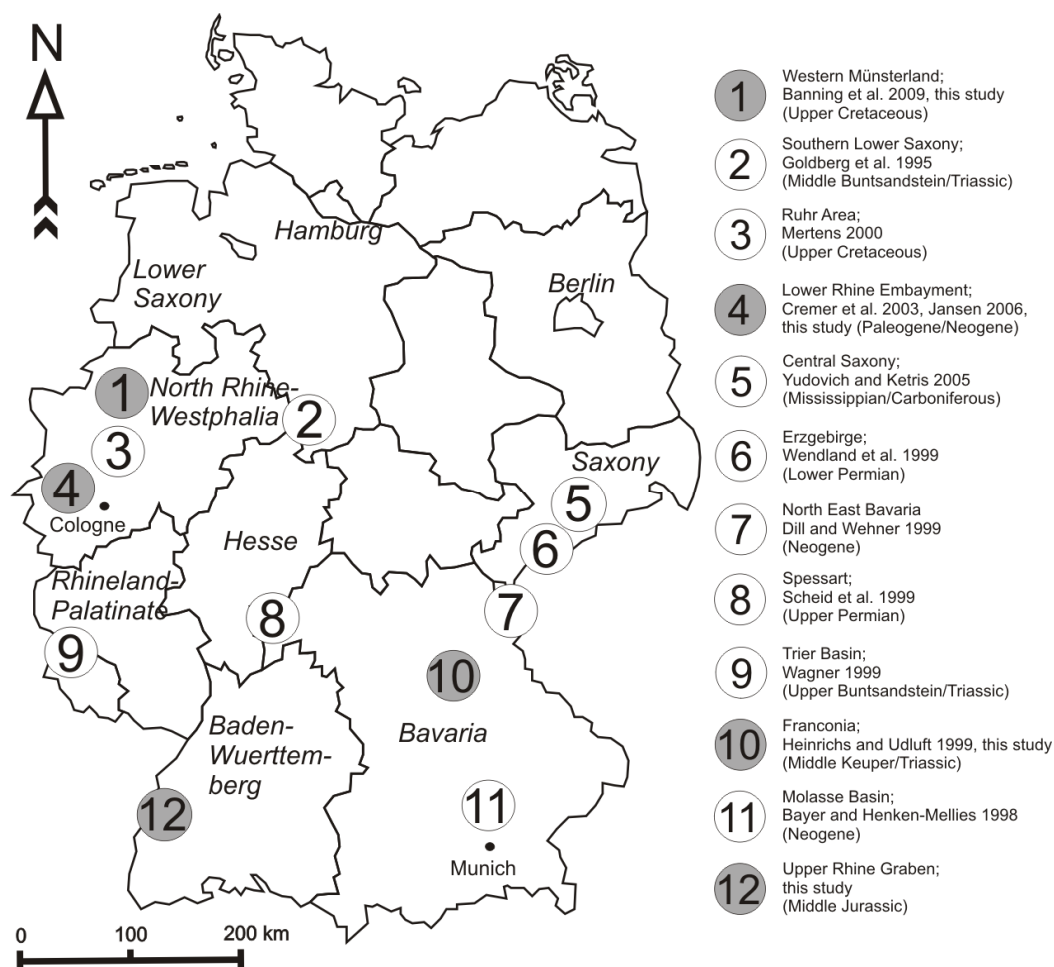


Fig. 1: Distribution of case studies on As in sedimentary rocks and groundwater in Germany. Greyish circles indicate German study areas of the present work (numbering ascending from north to south).

Arsenic contents are partly elevated in coal, an overview is given by Yudovich and Ketris (2005). Therein, the authors mention contents of up to $400 \mu\text{g g}^{-1}$ As in Mississippian (Lower Carboniferous) bituminous coals from Saxony [5]. Interestingly, they found that Eastern German black coal is significantly more enriched than the Western German Upper Carboniferous coal with average As contents of $6.8 \mu\text{g g}^{-1}$. For comparison: the Clarke value for bituminous coal is $9.0 \pm 0.8 \mu\text{g g}^{-1}$. The As host in coal is dominantly pyrite but also organic As can be of importance (Yudovich and Ketris 2005). Wendland et al. (1999) determined a mean As concentration of $55 \mu\text{g g}^{-1}$ in Lower Permian (“Rotliegend”) basin sediments in Saxony [6] and correlated elevated values to groundwater As anomalies. In Miocene lignite from northeastern Bavaria [7], Dill and Wehner (1999) detected $89 \mu\text{g g}^{-1}$ As on average (Clarke value for lignite: $7.4 \pm 1.4 \mu\text{g g}^{-1}$, Yudovich and Ketris 2005). In single wells in the Spessart (northwestern Bavaria, [8]), a correlation between elevated groundwater As and the distribution of Upper Permian (“Zechstein”) sediments was observed by Scheid et al. (1999). Lower Triassic (“Buntsandstein”) sandstones containing plant fossils in the Trier Basin [9] were shown to partly have

high As concentrations of up to $880 \mu\text{g g}^{-1}$ (Wagner 1999). Heinrichs and Udluft (1999) found that the distribution of extensively elevated As concentrations in Middle Franconian (northern Bavaria) [10] groundwater (up to $150 \mu\text{g L}^{-1}$) is dependent on depositional aquifer facies: only terrestrial sediments of the Upper Triassic (“Keuper”) seem to produce groundwater As in excess of the drinking water standard. Part 1 of the present work is dedicated to a detailed hydrogeochemical analysis of the most affected aquifer in this area, taking both As and co-occurring U into account. In southern Bavaria, Middle Miocene terrestrial sands („Obere Süßwassermolasse“) [11] contain Fe hydroxide concretions with up to $1900 \mu\text{g g}^{-1}$ As that can locally lead to elevated groundwater concentrations when reducing conditions occur (Bayer and Henken-Mellies 1998). Enrichment processes of As in Middle Jurassic (“Dogger”) sedimentary Fe ores in the Upper Rhine Graben/Baden-Wuerttemberg [12] will be described in part 2 of the present work.

Studies on sedimentary aquifer U and associated concentrations in groundwater derived from water-rock-interaction in Germany are scarce. In contrary, the environmental impact of former extensive U mining, especially in Eastern Germany, has been characterized in detail (e.g. Wolkersdorfer 1996, Winkelmann et al. 2001, Baborowski and Bozau 2006). More recently, the inventory of geogenic background U in groundwater has come under scrutiny when the new drinking water limitation began to loom on the horizon. Birke et al. (2010) found a median of $0.17 \mu\text{g L}^{-1}$ U in 908 German bottled water samples (maximum: $16 \mu\text{g L}^{-1}$). They statistically found that Triassic sandstone and crystalline basement aquifers (mainly Black Forest) represent the main hosts for elevated groundwater U. A survey in the southern Lower Rhine Embayment and adjacent areas (North Rhine-Westphalia) documented a mean groundwater concentration of $1.43 \mu\text{g L}^{-1}$ U with values above $10 \mu\text{g L}^{-1}$ in 0.01 % of the samples, whereby highest values (up to $21 \mu\text{g L}^{-1}$) were found in Triassic aquifers (Kurth 2010). Hessian environmental authorities detected contents above $10 \mu\text{g L}^{-1}$ U in 2.7 % of 965 analyzed wells with a maximum concentration of $86 \mu\text{g L}^{-1}$, elevated contents were ascribed to geogenic input from Triassic rocks or Holocene peat deposits (HLUG 2008). Uraniferous Upper Triassic sediments are known from Middle Franconia (Abele et al. 1962). These will be assessed in detail in part 1 of the present work wherein also information on the groundwater U situation in Bavaria is given.

Objectives and structure of this work

The basis to understand and forecast geogenic As and U cycling and the impact of water-rock-interaction leading to groundwater contamination is the comprehension of the mechanisms responsible for trace element accumulation. These often took place millions of years ago, but still have a major

influence on the recent occurrence and thus, hydrogeochemical behaviour, of As, U and other potential groundwater contaminants.

This work aims at unravelling geogenic trace element accumulation processes in aquifers with different geological and stratigraphical background, and their timings in geological history. Selected aquifers were hydrogeochemically, mineralogically and genetically characterized. They are actually or potentially affected by naturally elevated groundwater concentrations of As and, partly, of U. Identification of geogenic trace element sources and derivation of respective structures of their sources and sinks in the different study areas were assessed. Explanations for the common occurrence of As and U in different systems, contradictory at first glance, represent another challenge of this work. This is, vice versa, also valid for the observation of high-As/low-U environments. Remobilization mechanisms and potentials of both trace elements from solid source material to solution, i.e. to groundwater, differ considerably in the studied areas, they were determined and compared.

The present work includes five study areas of different geological age and environment. After this common introduction, the applied approaches and results will be treated consecutively in stratigraphical order as parts 1 to 5. Thereby, parts 1 to 4 address different sedimentary environments in Germany covering the Meso- and Cenozoic (Triassic – Jurassic – Cretaceous – Paleogene). To include and compare aquifers in volcanic areas, part 5 treats a volcano-sedimentary basin in central Mexico (Paleogene-Neogene).

The design of the single substudies as well as this work as a whole was oriented on the following core theses which will be reassessed in part 6:

1. Terrestrial uraniferous phosphates (“active arkoses”) represent As and U sinks and contribute to elevated concentrations in groundwater (Part 1).
2. Shallow marine environments fostering ooidic Fe ore formation provide conditions for syngenetic As accumulation (Part 2).
3. Postdepositional paleo redox events cause extremely heterogeneous As and other trace element distribution in shallow marine sediments, leading to partly massively enriched secondary concretions (Parts 3 and 4).
4. Large-scale redox events alter comparable lithologies and redistribute trace elements hosted therein in the same way, independent of sediment age (Parts 3 and 4).
5. Both U and As are incompatible elements in magmatic differentiation and therefore enriched in felsic lithologies (Part 5).

6. The observation of common geogenic As and U occurrence despite oppositional redox and transport behaviour in groundwater of a given area is indicative for a common source (Parts 1 and 5).
7. Secondary hydrogeochemical processes in affected aquifers are responsible for As and U separation upon input into groundwater (Parts 1 and 5).
8. In an actuogeological approach, characterization of recent trace element dynamics in a given geological-climatic environment can help understand As and U accumulation and remobilization processes in comparable paleo milieus (Parts 1 and 5).
9. High-As/U primary sources are a prerequisite for elevated concentrations in sediments/groundwater of a given area (Parts 1 to 5).
10. Trace element accumulation processes and reservoirs can be of different orders such that spatio-temporal structure models of sources and sinks can be developed for a given area (Parts 1 to 6).
11. The structure of As and U sources and sinks in the different geo-environments characterized in this work can help unravel trace element dynamics in similar milieus worldwide (Parts 1 to 6).
12. Geological evolution, expressed by geochemical proxies, can explain trace element distribution on different temporal and spatial scales, and help forecast potential problem areas (Parts 1 to 6).
13. There is an ultimate large-scale control mechanism of U and As distribution in sedimentary environments which may still be traceable in basins where internal processes account for redistribution and the present-day situation (Part 6).

The five substudies are roughly structured as follows: after a list of publications derived in the course of this research from each substudy, and a compilation of key questions to be addressed therein, chapters introducing the respective problems and objectives as well as the studied area, characterized materials and applied methods follow. Obtained results are presented and discussed (whereby discussion of the relevant literature is included in the suitable places), and conclusions are drawn, separately for each study. However, all cited references are assembled at the very end of this work. Parts 1 and 5 deal with both As and U dynamics. Parts 2 to 4 focus on As, whereby information on U in these areas is given in part 6 representing a common discussion. The latter will summarize and compare main findings from the single studies, reassess the core theses formulated above and develop a model explaining the geogenic As and U situation in Germany as a whole.

Part 1 – Triassic: Sources and hydrogeochemical mechanisms behind the geogenic uranium and arsenic problems in Franconian groundwater

Some preliminary results from this study area were presented in modified form in the following conference contributions:

- Banning, A., Rüde, T.R., 2011. Triassic francolite – a player in Franconia's groundwater arsenic and uranium problems? Arsen 2011 – Verhalten von Arsen in geologischen, hydrologischen und biologischen Systemen, September 12-13, 2011, Leipzig/Germany.
- Rubinos, D.A., Banning, A., Rüde, T.R., 2011. Mobilisation of arsenic and uranium from sedimentary rocks of the Keuper aquifer (Franconia, southern Germany). Arsen 2011 – Verhalten von Arsen in geologischen, hydrologischen und biologischen Systemen, September 12-13, 2011, Leipzig/Germany.
- Rubinos, D.A., Banning, A., Rüde, T.R., 2011. Interacting effect of pH and Bicarbonate on the Mobilization of Arsenic and Uranium in Sedimentary Rocks from the Keuper Aquifer (Franconia, Southern Germany). 11th International Conference on the Biogeochemistry of Trace Metals (ICOBTE 2011), July 3-7, 2011, Florence/Italy.
- Banning, A., Rüde, T.R., Cardona, A., Aguillón-Robles, A., Padilla-Sanchez, L., 2010. Uranium and arsenic in some aquifers from Mexico and Germany – a common geogenic development? 13th Water-Rock-Interaction conference (WRI-13), August 16-20, 2010, Guanajuato/Mexico.

Key questions

How are U and As distributed in Middle Franconian groundwater and aquifer materials?

Does the common occurrence of both trace elements hint towards a common geogenic source?

Which role do uraniferous carbonate fluorapatite intercalations in the affected aquifer play?

Did the paleogeographical constellation and depositional facies allow for U/As input into the system?

Can U/As solid fractionation and susceptibility to remobilization explain the present-day situation?

1.1 Introduction

Drinking water suppliers in Middle Franconia (northern Bavaria) are confronted with several groundwater quality related challenges, two of which – elevated As and U concentrations – gave reasons for this study. In terms of groundwater As affected area and concentration levels, Middle Franconia is the most significant region in Germany known so far (Heinrichs and Udluft 1996). The Keuper Sandstone, the most important regional aquifer system in northern Bavaria, is especially concerned. From 424 wells studied by Heinrichs and Udluft (1999), nearly 37 % comprised As concentrations exceeding the WHO and German limitation of 10 µg L⁻¹, maximum values are as high as 150 µg L⁻¹. More recently,

also elevated U has been detected in groundwater of the region which is of current interest in view of the approaching limitation of $10 \mu\text{g L}^{-1}$ in German drinking water regulation. Bavarian environmental authorities (LGL and LfU 2007; Friedmann and Lindenthal 2009) identified Middle Franconia as the most important groundwater U area in Bavaria with 16 % of the wells extracting from the Keuper sandstone aquifer in excess of the new limitation.

Both trace elements are geogenic in nature, their occurrence in groundwater is assumed to derive from water-rock interaction within the aquifer, whereby distinct source materials remain unknown. In the case of As, a distributive dependency from sedimentary facies is suggested by Heinrichs and Udluft (1999, cf. chapter 1.2.2), As may locally also derive from deep groundwater ascendancy in fault zones or leaching of As-enriched aquifer overburden. In the case of U, an analysis of potential sources and release mechanisms is completely missing until now.

The comprehension of the region's U and As sources and sinks structure would aid in the understanding of – and the reaction to – the observed trace element accumulations in groundwater. The common occurrence of both elevated As and U in the same region and aquifer can be indicative for a common source material. Therefore, Burgsandstein aquifer material was sampled and characterized in this study. This hydrogeologically important unit of the Keuper Sandstone system shows highest average As concentrations in groundwater ($17 \mu\text{g L}^{-1}$, Heinrichs 1994) and is famous for U-rich intercalations in the rocks, so-called “active arkoses” (Abele et al. 1962, chapter 1.2.1).

1.2 Studied area and materials

1.2.1 Geology and “active arkoses”

The study area is located in Middle Franconia (northern Bavaria) in the region around Nürnberg (about 150 km north of Munich, Figs. 1.1 and 1.3). Geologically, it is part of the epicontinental South German Keuper Basin which is bordered by the Vindelician-Bohemian Massif – a part of the Central European Variscides consisting of crystalline magmatic and metamorphic rocks (Dill 2010) – in the south and east. The sedimentary Keuper basin filling derived from erosion of this Variscan massif under arid conditions and may be subdivided into a terrestrial (alluvial fan with playa lakes) and a basinal (shallow marine) facies (Fig. 1.2) with transitional character (sabhka) in between (Abele et al. 1962, Aigner and Bachmann 1992, Heinrichs 1996, Heinrichs and Udluft 1999).

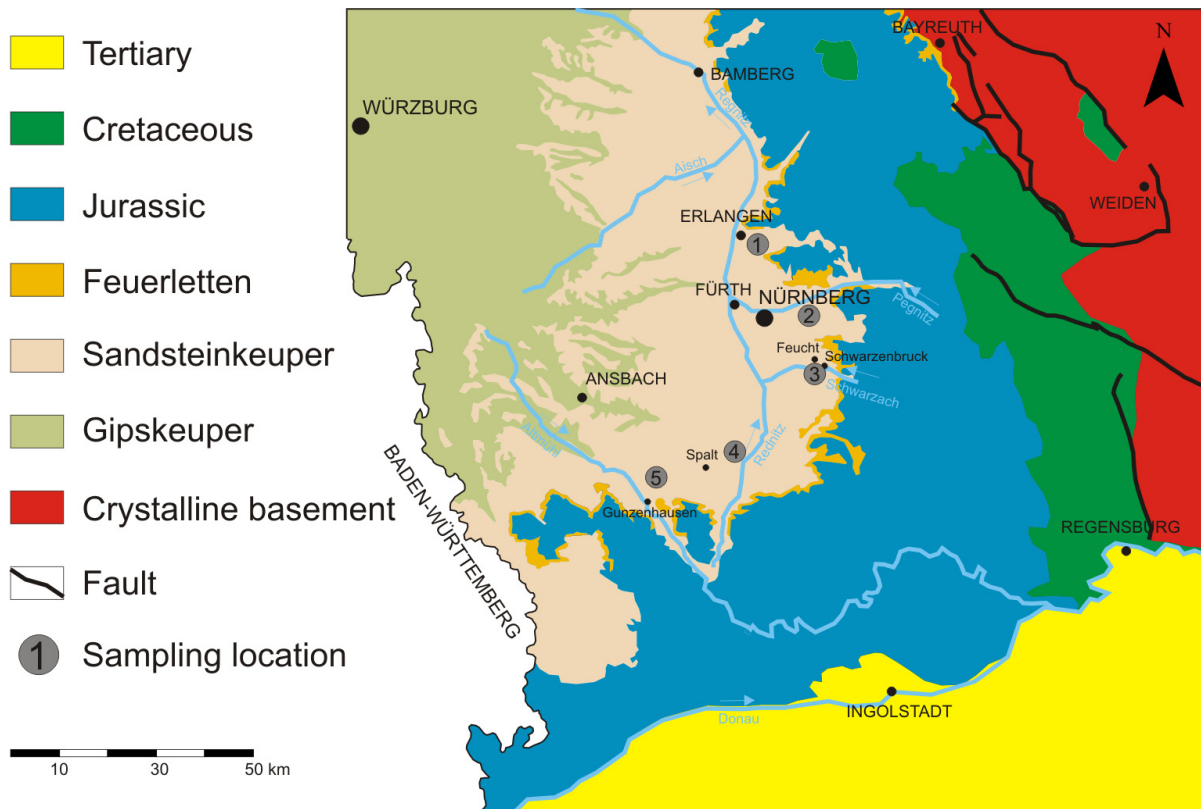


Fig. 1.1: Location of the study area and its present day geological situation (redrawn after GLA Bayern 1996), cf. Fig. 1.2 for stratigraphical allocation of the mentioned units.

The sediments sampled for this study are of Upper Triassic (Norian) age and belong to the terrestrial facies of the Middle and Upper Burgsandstein (Fig. 1.2), a medium to coarse grained, feldspathic sandstone with fine-grained interbeddings. It represents the thickest unit within the Sandstein-Keuper (Dill 1988b) and one of the major sources for water extraction in Franconia (Heinrichs 1994). Figure 1.2 illustrates the stratigraphical position of the studied units and general hydrogeological characteristics of the Middle Keuper sediments in the study area.

The Bursandstein contains abundant U-rich intercalations in its middle and upper parts (Fig. 1.2). The following information on occurrence and genesis of this phenomenon is after Abele et al. (1962), Welte (1962), Dill (1988a, 1988b, 2010) and Heinrichs (1996). Uranium anomalies in Franconian sandstones were first discovered in the 1950s in the course of U exploration programmes. Nevertheless, due to their rather patchy distribution in the hosting sandstone, they were of little economic interest and therefore never mined although whole rock U concentrations reach several hundreds of $\mu\text{g g}^{-1}$.

		Unit names and thicknesses (m)			
Unit		Terrestrial facies	Basin facies		
Upper Keuper		Rhät		Hydro-geology	
Middle Keuper	Sandstein-Keuper	20-60 m	Feuerletten 	40-80 m	
		~30 m	Upper Burgsandstein 	25-40 m	Aq
		~40 m	Middle Burgsandstein 	30-50 m	
		40-60 m	Lower Burgsandstein 	25-75 m	Aq
		~10 m	Coburger Sandstein 	3-15 m	
		~20 m	Blasensandstein 	30-45 m	
	Gips-Keuper	Lehrbergsandstein 25-50 m	Lehrbergsschichten 25-40 m	Local Aq	
		Schilfsandstein 0-50 m		Local Aq	
Estheriensandstein 10-40 m		Estheriensschichten 20-50 m			
	Benker Sandstein 75-100 m	Myophorienschichten 40-100 m	Aq		
Lower Keuper		Lettenkohle			

Aq

Aquifer



Low permeability layers

Fig. 1.2: Keuper stratigraphy of the study area with sampled units highlighted by hachures, approximate unit thicknesses and basic hydrogeology (modified after Heinrichs and Udluft 1999).

Two main types of uraniferous sediments were distinguished according to their paleogeographical position in the basin (Fig. 1.3): 1) calcretes in the northern, basinward part (playa margin) which are U-bearing ($\text{Ø } 13 \mu\text{g g}^{-1}$, Dill 1988b) calcitic sediments, U accumulation happened during evaporation of former playa lakes, and 2) phoscretes deposited in a more proximal part of the sedimentary fan. The latter are also referred to as “active arkoses”. Carbonate-fluorapatite (francolite, an apatite with partly substitution of CO_3^{2-} for PO_4^{3-} , cf. chapters 1.4.2.2 and 1.4.2.4) occurring as fine grained cement between the silicate grains was suggested as U carrier phase.

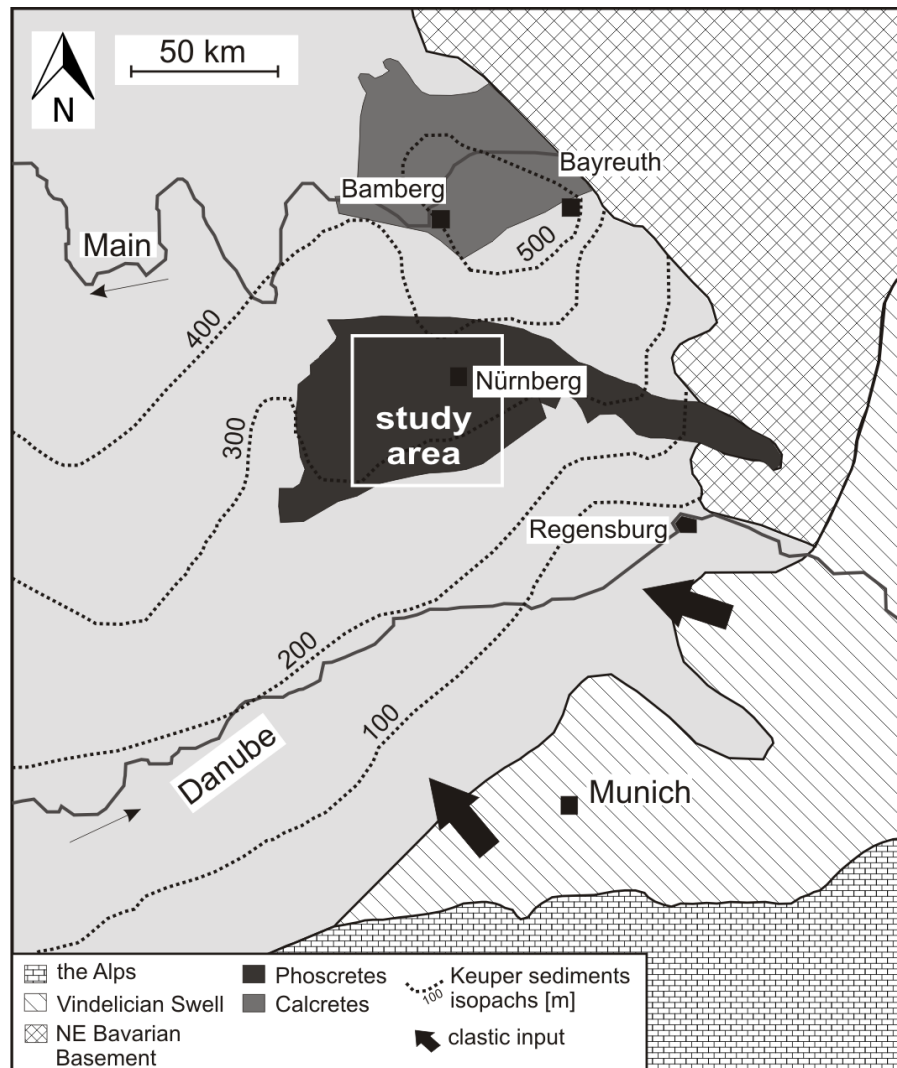


Fig. 1.3: Paleogeographical situation during the Middle Keuper with sediment input directions, sediment thicknesses and distribution of the main U-bearing depositional facies (modified after Dill 1988a and Dill 2010).

“Active arkoses” are interpreted as syndiagenetic formations deriving from apatite precipitation from basinward flowing, U- and PO_4^{3-} -enriched groundwater with simultaneous immobilization of U (cf. chapter 1.4.2.3). This groundwater was reducing and slightly acid, thus probably also bringing dissolved Fe and As along. Precipitation of fine-grained apatite and Fe phases occurred during a substantial rise of pH when the solution encountered abundant evaporative playa lake carbonates (calcretes; caliches). The apatites replaced the latter which is evident from high contents of structural CO_2 (cf. chapter 1.4.2.2) and very small carbonate grains ($<1 \mu\text{m}$) found in apatite cores. “Active arkose” distribution therefore resembles the paleo-distribution of Triassic playa lakes in the study area. This genetic model is clearly supported by McArthur (1985) who compared different types of francolite occurrences worldwide and found numerous examples for what he classifies as replacement francolite

(e.g. in Morocco, South Africa, New Zealand). These sites represent marine carbonate fluorapatite deposits. Nevertheless, also terrestrial occurrences with a development very similar to the studied area are known from e.g. the U.S.A. (Swirydczuk et al. 1981) and Sri Lanka (Dahanayake and Subasinghe 1989).

After apatite precipitation in the terrestrial facies of the Triassic basin, the relic solution was depleted in P, Fe, As and U, which is why the calcretes in the north “survived” as carbonates and at the same time, yield lower (but still significant) U concentrations derived from evaporative enrichment (see above). This accumulation mechanism and its impact on present day trace element distribution were studied in an actuogeological approach in Mexico in the course of this work (see part 5 of this thesis).

The described paleo-groundwater, as well as the sediments in this part of the basin, primarily derived from crystalline rocks of the Vindelician Swell in the southeast (Fig. 1.3), a nowadays eroded part of the Vindelician-Bohemian Massif, representing the primary source of elevated trace elements in the study area. The sediments deposited during the middle part of the Upper Triassic are also referred to as “Vindelician Keuper”.

“Active arkoses” are found in outcrops as mainly red to violet lenses, shards or cloudy patches with partly significant dimensions (Fig. 1.4).

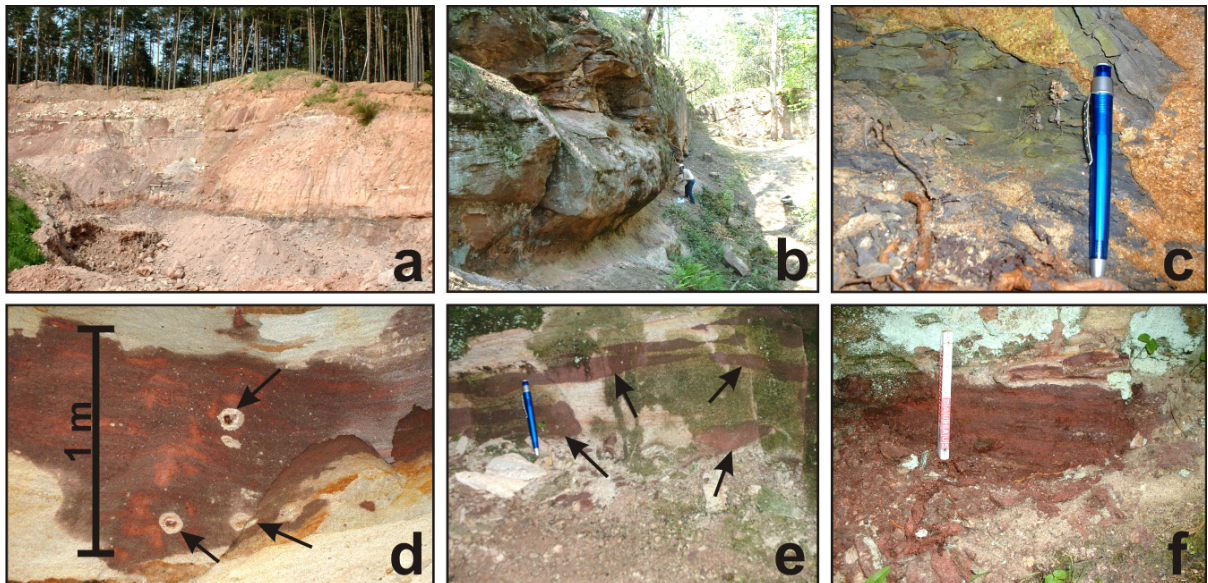


Fig. 1.4: Images of sampled Bursandstein sedimentite types: typical appearance of partly lively coloured sandstones in active (a, location 5, cf. Fig. 1.1) and abandoned (b, location 1) quarries, clay band intercalated in sandstone (c, location 2), “active arkoses” with cloudy appearance in a very fresh outcrop (d, location 3) with arrows indicating bulb-like concretionary zones with light-coloured halos (cf. chapter 1.4.2.3); with lenticular appearance (e, location 3) with arrows highlighting the “active” lenses; and “active”, rather soft zone in a weathered outcrop (f, location 4).

Higher average U and As concentrations in “active arkoses” ($\bar{O}$ 30 $\mu\text{g g}^{-1}$ U, 17 $\mu\text{g g}^{-1}$ As, Dill 1988b), compared to calcretes ($\bar{O}$ 13 $\mu\text{g g}^{-1}$ U, 12 $\mu\text{g g}^{-1}$ As, Dill 1988b) and proximity of the phoscrete facies to elevated contents of both trace element in groundwater (Figs. 1.5 and 1.6) make these sediments a preferential candidate for contribution to the As and U signature in groundwater of the region and thus, for further analysis in this study. Accordingly, sedimentites from the Bургsandstein were sampled from five locations (nine outcrops) along the terrestrial facies of the Keuper Basin (Fig. 1.1). A total of 47 samples were obtained, including 12 “active arkoses”, 30 samples from the aquifer sandstone and 5 samples of intercalated clay bands occurring therein.

1.2.2 Groundwater As and U situation

The distribution of U concentrations in Bavarian drinking water is presented in Fig. 1.5 (see chapter 1.3.1 for information on data base and map construction methods).

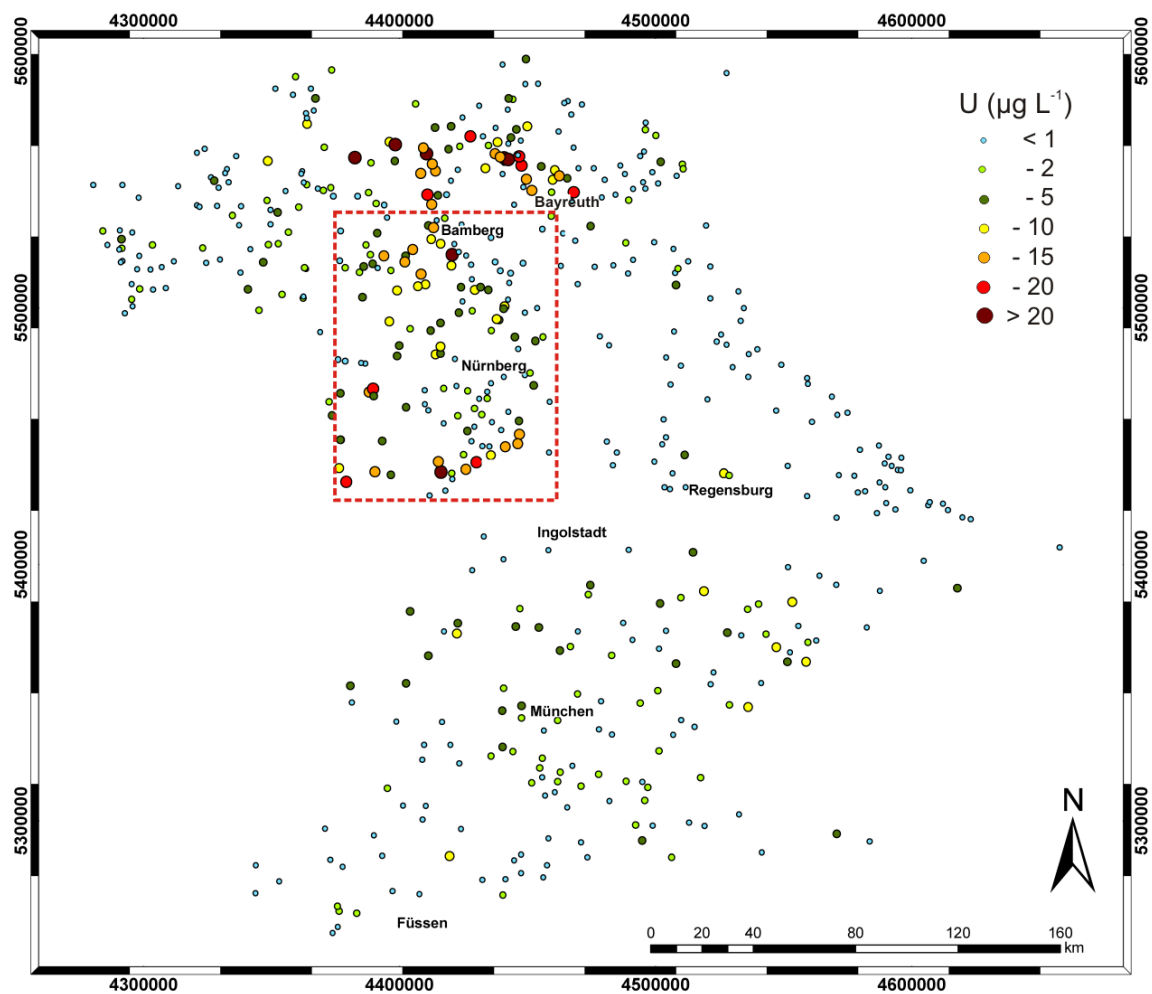


Fig. 1.5: Uranium concentrations in Bavarian tap water and area shown in Fig. 1.6 (dotted red box).

The obtained U distribution is in good agreement with the map constructed by Bavarian authorities (LGL and LfU 2007) on the basis of a different dataset, especially the U “hot spots” in Franconia are characterized very similarly. Elevated concentrations in southern and eastern Bavaria occur only locally, although in contrary to Fig. 1.5, the map of LGL and LfU (2007) contains several values above $10 \mu\text{g L}^{-1}$ in these regions mainly interpreted to derive from organic substance in swampy river valleys. High U contents in excess of the new limitation value are mainly observed along the margin of the South German Keuper Basin (cf. Fig. 1.1) around Nürnberg and Bamberg. The coincidence of this spatial groundwater-U pattern with the facies distribution of U-rich phoscretes (“active arkoses”) and calcretes (Fig. 1.3) is eye-catching. Figure 1.6 illustrates the groundwater As and U occurrence in a narrower area.

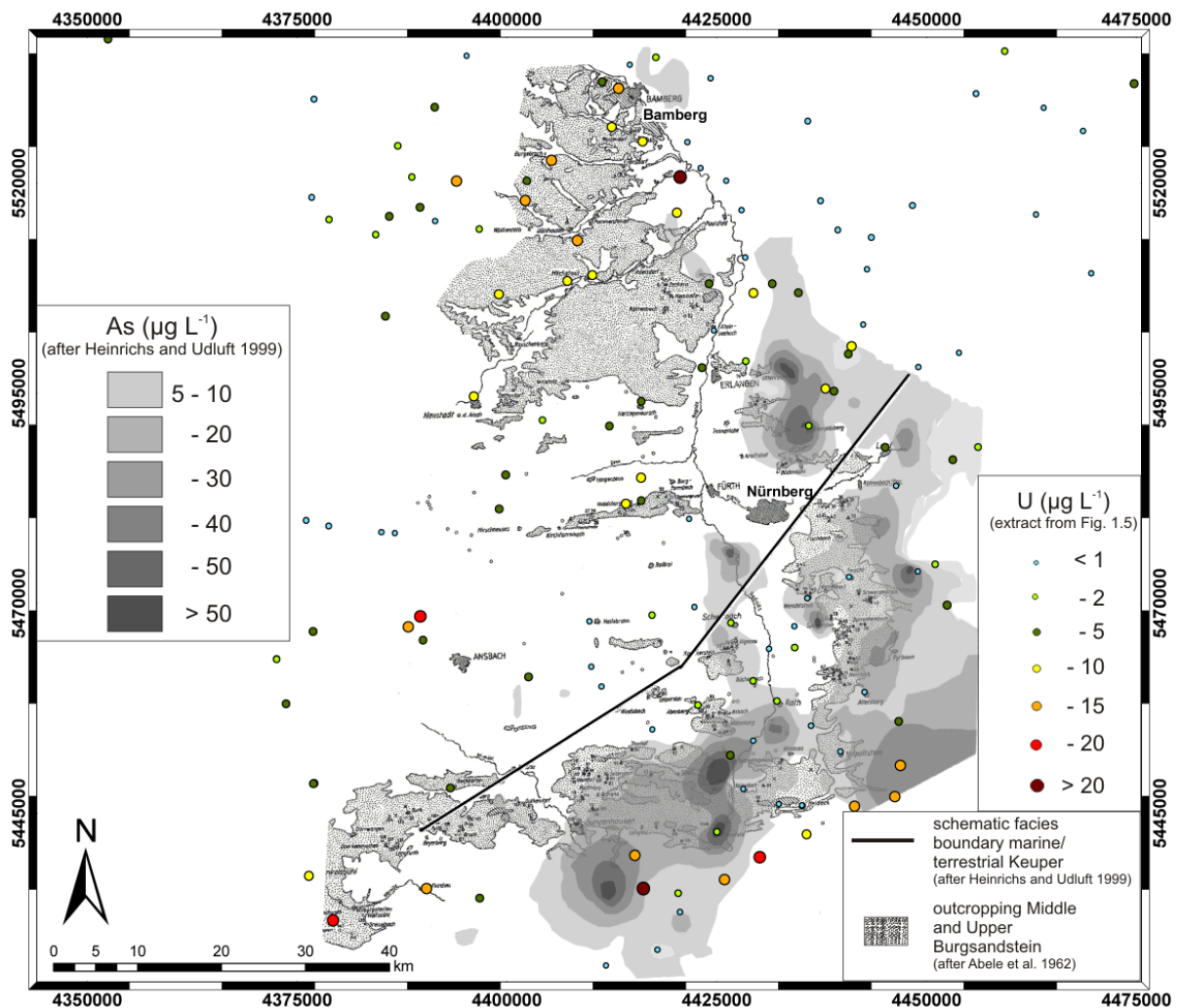


Fig. 1.6: As and U distribution in groundwater and tap water, respectively, of the study area and its northern vicinity, schematic depositional facies boundary between terrestrial (SE) and brackish-marine (NW) Keuper sandstone and distribution of outcropping, calcrete- and phoscrete-bearing Bursandstein (modified after Abele et al. 1962 and Heinrichs and Udluft 1999).

The distribution of groundwater As is heavily dependent on depositional facies with elevated values occurring in the terrestrial and transitional facies only (Heinrichs and Udluft 1999). If plotted together with the distribution of Middle and Upper Bursandstein (Fig. 1.6) – the units containing “active arkoses” and calcretes – a striking similarity in the spatial shapes of aquifer occurrence and distribution of elevated As content in groundwater is observable in the southern and eastern parts. Furthermore, also U concentrations above $10 \mu\text{g L}^{-1}$ appear to follow these sedimentites (Figs. 1.5 and 1.6), supporting a common source material with As. Basinwards, Heinrichs and Udluft (1999) did not detect elevated As values beyond Nürnberg. In contrast, high U concentrations appear in the northern distribution area of the Bursandstein which contains U-bearing dolomitic calcretes (chapter 1.2.1). This present-day trace element pattern in groundwater supports the genetic model of the different U-rich sediment facies described above – most of the dissolved Fe (and probably As) was lost from groundwater as precipitates in the phoscrete facies, P immobilized as apatite (together with the largest part of U). The dolomitic facies only received relic U which accumulated in the calcretes and, concluding from their spatial patterns and that of U in groundwater (Figs. 1.3, 1.5, 1.6), appears to be a candidate source for elevated concentrations in the latter.

1.3 Methods

1.3.1 Hydrochemical data

For the construction of the U distribution map in Bavarian drinking water (Fig. 1.5), freely available data was obtained from an internet source (foodwatch 2008). This data was published by the German non-profit organisation “foodwatch” which collected U analysis from numerous Bavarian health authorities. The dataset includes 703 single values obtained between 2000 and 2006. Drinking water U concentrations may partly have changed significantly since then, mainly because of remediation measures taken by water suppliers as a reaction to this publication and the political discussion on U limitations. Nevertheless, the map offers a general impression of the U occurrence in Bavarian groundwater, the by far most important drinking water source. This approach – drawing conclusions from tap water quality to groundwater composition – is only possible because of the special structure of drinking water supply in Bavaria: the highly decentralized system consists of around 2,350 municipal water suppliers (STMUG 2011) enabling a spatially accurate and high-resolution visualization of U distribution. Thereby, however, information on geology and tapped aquifers cannot be derived from the given database.

The U data was georeferenced using Google Earth (only sampling location names are given in the original data table) and imported into Esri ArcGIS 9.3 applying the KML tool. An interpolation of spatial groundwater U distribution (as conducted for As in the study area by Heinrichs and Udluft

1999, cf. Fig. 1.6) was tried using Ordinary Kriging and Inverse Distance Weighting (IDW) with the GIS software. Nevertheless, due to a high nugget effect preventing further evaluation (Kriging) and massive discrepancies between measured and predicted values observable from cross validation (IDW), both caused by the large heterogeneity of the data even at small distances, illustration as point data was preferred.

For the study area, hydrochemical data from the Burgsandstein aquifer (99 wells totally) was kindly provided by the Bayerisches Landesamt für Umwelt (Bavarian Environment Agency, LfU). From this database, 20 analysis offer concentrations for both As and U. No Eh values are available in the dataset, therefore a calculation sheet for identifying redox processes and categories in groundwater on the basis of available redox-sensitive parameters (dissolved O₂, NO₃⁻, SO₄²⁻, Fe²⁺, Mn²⁺, sulfides) developed by the U.S. Geological Survey (Jurgens et al. 2009) was applied.

1.3.2 Rock samples

All (47) rock samples were analyzed by 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, ⁶⁰Co photopeak) and total digestion (HClO₄-HNO₃-HCl-HF at 240°C) followed by ICP-OES analysis (Varian 735ES) for bulk rock geochemistry (49 elements, execution: Activation Laboratories Ltd., Ontario/Canada).

Ten samples (seven “active arkoses”, two sandstones and one clay band) were selected for X-ray diffractometry (XRD) analysis to characterize their mineralogical composition. These were ground to powder grain size in a corundum mill before measurements applying a Huber Co- α diffractometer (operational adjustments: 40 kV, 40 mA; 2 θ range: 2-110°, step size: 0.02° 2 θ à 10 s counting time; measurements conducted at the Institute of Clay and Interface Mineralogy, RWTH Aachen University). Quantitative phase analysis was accomplished performing peak profile modelling (Rietveld analysis) with the software BGMN 4.2.3.

Thin sections were produced from three “active arkose” samples and studied microscopically before selecting two of them for analysis with laser-ablation (NewWave UP193Fx, ArF-Excimer-Laser) ICP-MS (PerkinElmer Elan DRCe) (LA-ICP-MS, calibration standard: NIST 612, spot diameter: 150 μm) to characterize major and trace element abundance and distribution on a microscale. Analyzed elements included Si, Al, Ca, P, Fe, Mn, Zn, Cr, Ni, Pb, U, Th, As, V, La, Eu and Yb (measurements conducted at the Institute of Mineralogy and Mineral Deposits, RWTH Aachen University).

To compare the mineralogical fractionation and remobilization potential of U and As in the studied rocks, eight samples (five “active arkoses”, two sandstones, one clay band) were subjected to a se-

quential extraction procedure (SEP). The BCR (Bureau Communautaire de Référence, today called EU Standards, Measurement and Testing Programme) approach after Ure et al. (1993) was used as a basis. It was modified according to Sahuquillo et al. (1999) who found that method reproducibility is improved when increasing the solution concentration in step 2 (Tab. 1.1) from 0.1 to 0.5 mol L⁻¹ and centrifugation speed during solid/liquid separation after each step from 1500 to 3000 rpm. Moreover, an extraction step targeting the trace element fraction bound to apatite after Nezat et al. (2007) was added to the procedure. They found that 1 M HNO₃ congruently dissolves apatite at 20° C but that the solution becomes saturated with respect to this mineral at ~90 mmol apatite L⁻¹. Converting this finding to 10 mL solution (needed if working with 1 g solid sample and the solid-solution ratio 1:10 used by Nezat et al. 2007), ~0.44 g of apatite are dissolvable. As according to the geochemical and mineralogical results in this study (chapters 1.4.2.1 and 1.4.2.2), up to 0.5 g apatite g⁻¹ solid sample are expectable, the solid-solution ratio for this step was increased to 1:20.

Aliquots of the samples (1 g) were ground in an agate mortar and placed in 50 mL centrifugation tubes. Extraction solutions were added in each step and the respective procedure was carried out (Tab. 1.1). After centrifugation (15 min at 3000 rpm) and filtration (0.45 µm cellulose acetate filters) of the supernatant solution, a washing step with 20 mL of deionized water (15 min shaking, 15 min centrifugation, supernatant discarded) was implemented to avoid mobilized trace element transfer to the next fraction. Subsequently, the remaining sediment was subjected to the following procedure. The extracted solutions were analyzed for U and As by ICP-MS (execution: Institute of Mineralogy and Mineral Deposits, RWTH Aachen University) and for Fe by spectrophotometry (Dr. Lange Cadas 100; measurements conducted at the Institute of Hydrogeology, RWTH Aachen University). The applied SEP is presented in Tab. 1.1.

Tab. 1.1: Applied sequential extraction procedure (“BCR+apatite”).

Fraction no.	Targeted fraction	Extractant	Procedure
1	Easily mobilizable	CH ₃ COOH (0.11 M)	16 h shaking, 20°C
2	Reducible	NH ₂ OH-HCl (0.5 M)	16 h shaking, 20°C
3	Oxidizable	H ₂ O ₂ (30 %)	2 h in a water bath (85°C)
4	Bound to apatite	HNO ₃ (1 M)	16 h shaking, 20°C
5	Residual	element (total) – element (sum steps 1-4)	

1.4 Results and Discussion

1.4.1 Groundwater

General groundwater type in the Burgsandstein aquifer is Ca-Mg-HCO₃ (Heinrichs 1996). The pH milieu is circumneutral with a mean pH of 7.1, eC mean value is 515 $\mu\text{S cm}^{-1}$. Dissolved O₂ concentration ($\bar{\text{O}}$: 5.3 mg L⁻¹) and O₂ saturation levels ($\bar{\text{O}}$: 49 %) are highly variable in groundwater, indicating the presence of both oxidizing and reducing conditions in the aquifer. Statistics on some trace elements occurrences derived from the hydrochemical dataset are presented in Tab. 1.2.

Tab. 1.2: Selected trace element data in Burgsandstein groundwater (n=20). All analyses were conducted with ICP-MS except for Fe (ICP-OES). Mean values were calculated including values below the detection limit (<DL) for which half the DL was taken as input value. No mean value is given for elements where >1/3 of the dataset is <DL.

	As $\mu\text{g L}^{-1}$	U $\mu\text{g L}^{-1}$	Fe $\mu\text{g L}^{-1}$	Mn $\mu\text{g L}^{-1}$	Pb $\mu\text{g L}^{-1}$	Cr $\mu\text{g L}^{-1}$	V $\mu\text{g L}^{-1}$
DL	0.013	0.0005	2.69	0.004	0.005	0.048	0.007
min	0.20	0.04	<DL	<DL	<DL	<DL	<DL
max	36.4	42.1	372	425	0.52	1.51	4.06
mean	6.8	6.6	-	-	-	0.4	1.2

Figure 1.7 shows groundwater As and U data and illustrates redox conditions in the aquifer. In the studied dataset, 10 % of the samples exceed the U drinking water limitation and 25 % that of As. Positive relations between the trace elements are implied in the low concentration ranges only (indicated by dotted black lines in Fig. 1.7), higher concentrations of both elements are independent from each other. The latter observation is explainable by differing redox-dependent mobility characteristics – As is more mobile as As(III) under reducing conditions while U mobility is greatly enhanced as U(VI) in oxidizing environments (e.g. Katsoyiannis et al. 2007). Consequently, elevated As contents of up to 36.4 $\mu\text{g L}^{-1}$ are found in anoxic, Fe(III)/SO₄-reducing groundwater zones in the studied aquifer (Fig. 1.7) with relatively high concentrations of dissolved Fe and Mn, and NO₃⁻ below the detection limit. With increasing oxidic character of the environment, As decreases together with Fe and Mn while detectable amounts of NO₃⁻ arise. Elevated U concentrations of up to 42.1 $\mu\text{g L}^{-1}$ occur in more oxidized water only, characterized by low As, Fe and Mn contents below the detection limit and relatively high NO₃⁻ (Fig. 1.7). In consequence, the finding that As and U are present in high concentrations in the Burgsandstein aquifer (cf. chapters 1.1 and 1.2) is supported by the studied data.

Nevertheless, only one of the trace elements occurs in elevated quantity in each sample, whereas their signature in the lower concentration ranges argues for a potential common source creating “background” levels which are subsequently modified in either As or U direction by heterogeneity of the aquifer redox milieu.

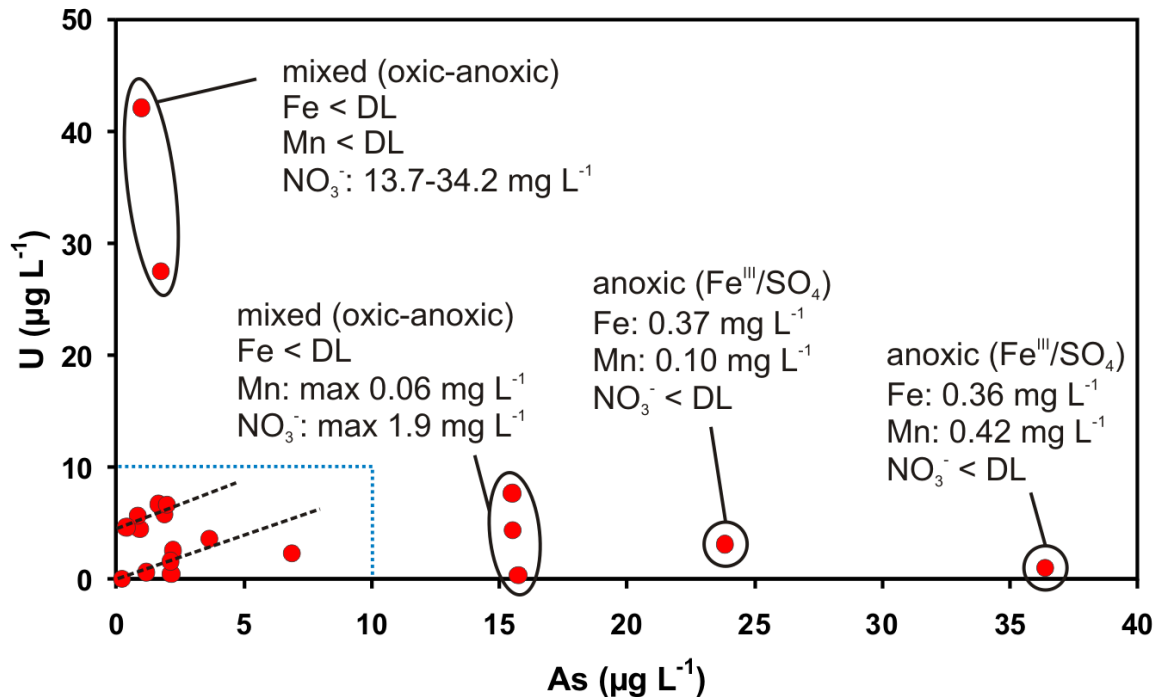


Fig. 1.7: Scatter plot of As vs. U for Bursandstein aquifer groundwater data, together with redox milieus after Jurgens et al. (2009) and concentrations for some redox-sensitive parameters. Blue dotted lines indicate German drinking water limitations for As and U.

1.4.2 Triassic rocks

1.4.2.1 Bulk rock geochemistry

An overview of bulk rock trace element concentrations in the studied solid samples is given in Tab. 1.3. With a median concentration of 1.3 $\mu\text{g g}^{-1}$, U in the sampled aquifer sandstone exhibits typical values for arkose sandstones (average of 1.5 $\mu\text{g g}^{-1}$, Wedepohl 1978) whereas 12 $\mu\text{g g}^{-1}$ As represent a significant enrichment compared to the global estimated average in sandstones of 1 $\mu\text{g g}^{-1}$ (Wedepohl 1978). Quite a large range of concentrations is documented for some elements with distinct outliers especially for As (one sample with 170 $\mu\text{g g}^{-1}$), Mn (up to 0.5 wt.%), Ni and V. Clay bands intercalating the sandstone show elevated median concentrations for As (17 $\mu\text{g g}^{-1}$) and U (6.4 $\mu\text{g g}^{-1}$) and also enrichments for most other trace elements (exception: Pb), compared to sandstone samples.

Tab. 1.3: Statistics on trace element concentrations for the rock samples from the Burgsandstein, distinguished by sample classes. Mean values were calculated including values below the detection limit (<DL) for which half the DL was taken as input value. No mean value is given for elements where >1/3 of the data-set is <DL.

	As μg g ⁻¹	U μg g ⁻¹	Th μg g ⁻¹	Pb μg g ⁻¹	Mn μg g ⁻¹	Zn μg g ⁻¹	Cr μg g ⁻¹	Ni μg g ⁻¹	V μg g ⁻¹
DL	0.5	0.5	0.2	3	1	1	2	1	2
Sandstones (n=30)									
min	1.8	<DL	2.2	11	15	6	5	3	7
max	170	4.5	31	32	4990	51	89	108	371
mean	17	1.5	9.2	23	377	19	32	14	34
median	12	1.3	7.4	23	43	17	28	9	22
Clay bands (n=5)									
min	8.7	2.7	16	12	51	38	66	20	36
max	36	6.7	31	29	112	72	235	35	78
mean	21	5.6	24	20	88	56	145	27	60
median	17	6.4	24	20	93	57	162	28	63
„Active arkoses“ (n=12)									
min	3.3	18	2.5	15	27	2	19	3	21
max	26	260	18	196	409	75	151	162	550
mean	12	103	7.6	68	129	15	70	27	128
median	11	65	6.0	58	76	7	65	8	106

Enrichment factors (EF) for most analyzed major and trace elements were calculated for comparison of “active arkoses” to aquifer sandstones with

$$EF = \frac{C_{sam}}{C_{avs}}$$

where C_{sam} is the whole rock concentration in the “active arkose” sample and C_{avs} the average concentration in all sandstone samples). Results are presented as element-specific box plots in Fig. 1.8.

As mentioned previously, “active arkoses” accumulated high U concentrations which is also obvious from the data obtained in this study (median EF: 43.6, maximum concentration 260 μg g⁻¹), also Ca and P show high enrichment with median EF of 31.6 and 98.2, respectively, suggesting significant apatite presence. Furthermore, “active arkoses” represent sinks for Fe (EF: 5.9, median concentration 5.7 wt.%), REE, Y, V, Pb and Cr while other heavy metals (Mn, Zn, Ni, Co) are generally in equal range or even depleted, compared to the sandstone, although with some enriched outliers.

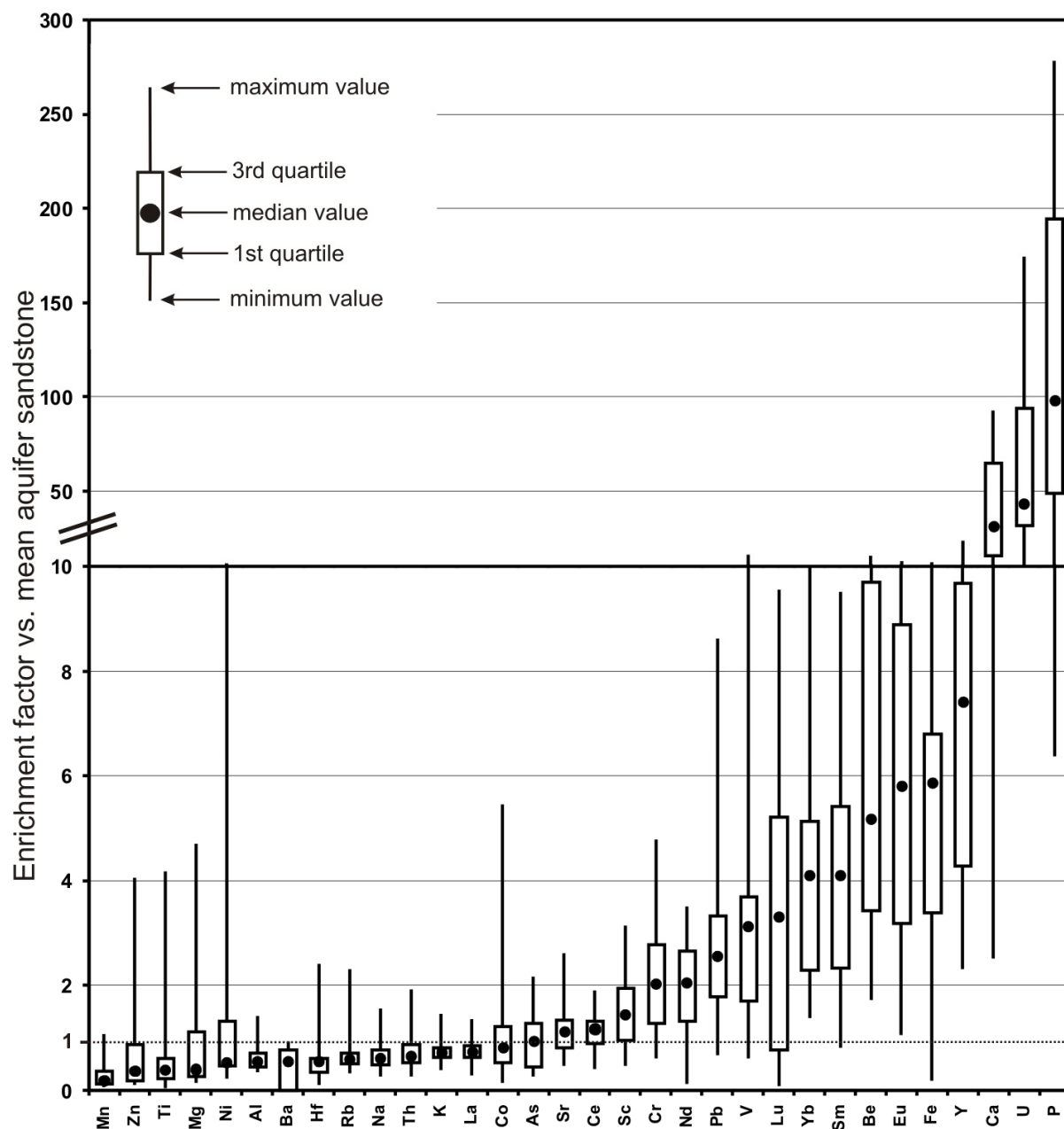


Fig. 1.8: Element enrichment/depletion of “active arkoses”, compared to aquifer sandstones, ordered by increasing median of enrichment factors (see inset in the upper left corner for box plot explanation).

Arsenic occurs in the same range as in sandstones (EF: 1.0), neither massive enrichment nor depletion is observable from whole rock data.

Figure 1.9 illustrates an As-U scatter plot for whole rock data of all Burgsandstein rock samples to analyze trace element distribution and potential interrelation in the different sample types.

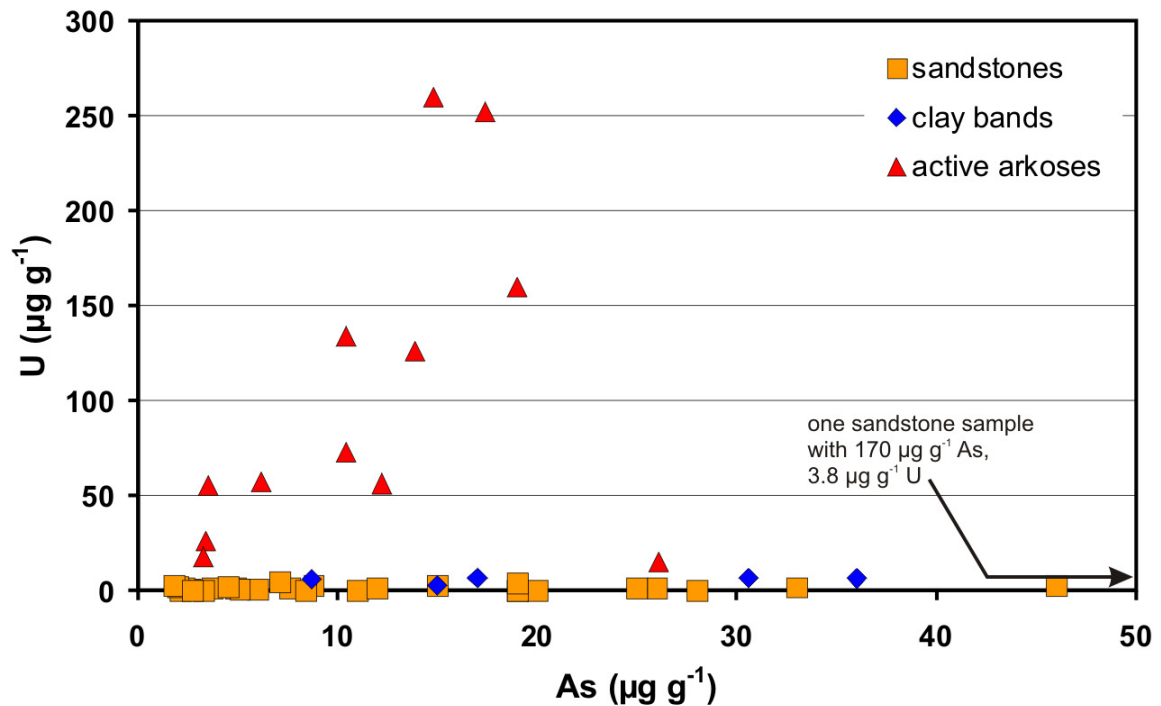


Fig. 1.9: As-U scatter plot for Bursandstein samples (bulk rock data).

Sandstone and clay samples scatter along the x-axis in comparable concentration ranges while no single U value above $7 \mu\text{g g}^{-1}$ is reached in these sample classes. No trend is observable between the two trace elements. On the other hand, “active arkose” samples, plotting in the same As range as sandstones and clay bands but containing significantly higher U (no single value below $15 \mu\text{g g}^{-1}$), indicate a positive correlation between As and U (Fig. 1.9). Nevertheless, in view of highly different enrichment factors of both elements (Fig. 1.8) with massive U accumulation but As concentrations in the range of the ambient sandstones, this trend might be interpretable as pseudo-correlation rather than as process-sensitive interrelation. The apparent contradiction gave rise to more detailed analysis of trace element hosting phases as will be described in the following. Bulk rock data, however, generally appear to support the hypothesis of “active arkoses” representing a common host for both trace elements while sandstones and clays are likely to rather have different modes for accommodating As and U. “Double correlation” scatter plots (i.e. correlation coefficient for As with other parameters vs. correlation coefficient for U with the same parameters) were developed as diagnostic tools for evaluating the dimension of similarity in geochemical occurrence and behaviour of As and U towards other major and trace elements in a given environment (Fig. 1.10).

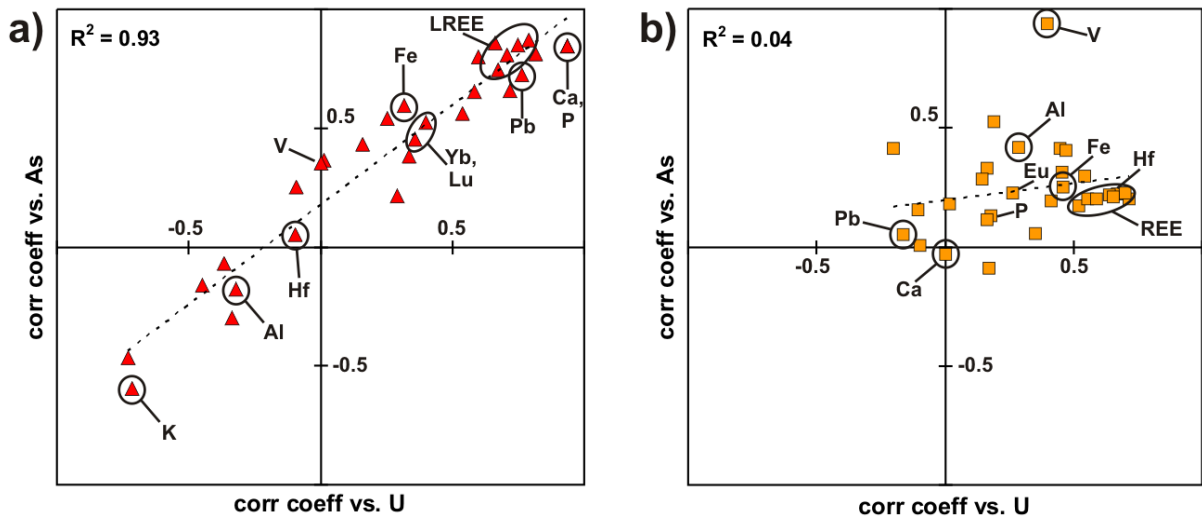


Fig. 1.10: „Double correlation“ plots for (a) “active arkoses” and (b) sandstone samples (bulk rock data).

In the “active arkose” samples (Fig. 1.10a), U and As exhibit similar geochemical trends, not only towards each other (Fig. 1.9) but also towards most other chemical parameters as indicated by R^2 ($R(\text{As}/\text{parameter})$ vs. $R(\text{U}/\text{parameter})$) = 0.93. Common positive correlation with Ca and P (slightly stronger for U than for As) indicate common accommodation (but not As enrichment, cf. Fig. 1.8) in Ca-P phases, most likely apatite (cf. chapter 1.4.2.2). Elevated concentrations of REE and Pb mentioned before (Fig. 1.8), both of which are known to be able to reside in apatite (Rakovan and Reeder 1996, White and ZhiLi 2003), seem to occur together with As and U. Furthermore, a positive behaviour towards Fe is obvious which is significantly more evident for As than for U, thus Fe phases might be involved especially in As hosting. The rather indifferent behaviour of both trace elements towards Hf indicates little influence of zircon which is generally capable of especially U accommodation by substitution for Zr (Wedepohl 1978 cites up to $6000 \mu\text{g g}^{-1}$ U) and dominates the heavy mineral associations in the Burgsandstein (Abele et al. 1962). Potassium-Al phases like feldspars and clay minerals also seem to be of minor importance for As-U distribution in “active arkoses” as indicated by rather negative correlations towards these elements.

Evaluating the sandstone samples from the Burgsandstein aquifer with the “double correlation” approach (Fig. 1.10b), a different situation is observable. Hardly any geochemical similarity between As and U is derivable from the plot in view of $R^2=0.04$. Calcium and P do not show distinct trends towards both trace elements indicating that apatite is not likely to be a significant host in the sediments whereas positive correlations of U with REE and Hf suggest U accommodation in detrital zircon. A close positive correlation between As and V, oxyanion-forming elements known to compete for surface sorption sites (e.g. Henke 2009), rather argues for As being present on hosting phases like clay minerals and Fe (hydr)oxides.

The results of this extended bulk rock data correlation analysis for “active arkoses” argue for a common input of As and U into the sedimentary system. They also offer first indications for differences in preferential host mechanisms between the two elements. Nevertheless, characterization of solid phase composition as discussed in the following chapter, high-resolution determination of U and As concentrations (cf. chapter 1.4.2.3) and their mineralogical fractionation (cf. chapter 1.4.2.4) in these sediments are required to finally uncover the present-day trace element distribution and the processes responsible for it.

1.4.2.2 Mineralogical composition

To characterize the mineralogical composition of the sampled sedimentites and to identify potential trace element carrier phases, quantitative XRD analyses were carried out. Results are given in Tab. 1.4.

Tab. 1.4: Results of quantitative XRD analyses. “Feldspars” represent the sum of orthoclase and microcline, “Clay minerals” include detected kaolinite, illite and chlorite. n.d. – not detected. See Fig. 1.12 for “AA_1” sample allocation.

	Quartz wt.%	Feldspars wt.%	Clay minerals wt.%	F-Apatite wt.%	Hematite wt.%	Ti oxide wt.%
Sandstones						
Sand_1	87.2	6.4	6.3	n.d.	n.d.	n.d.
Sand_2	89.0	7.3	3.6	n.d.	n.d.	n.d.
Clay band						
Clay_1	21.2	15.6	58.5	n.d.	2.9	0.4
„Active arkoses“						
AA_1_inner core	58.7	16.8	18.4	0.9	5.2	n.d.
AA_1_outer core	23.9	6.2	9.3	49.8	10.8	n.d.
AA_1_purple rim	74.0	9.8	6.0	9.5	0.5	n.d.
AA_2	69.1	8.5	0.8	19.5	2.1	n.d.
AA_3	67.6	12.7	3.6	11.5	4.6	n.d.
AA_4	81.3	6.3	1.2	9.9	1.4	n.d.
AA_5	81.2	10.1	2.3	1.9	4.5	n.d.

The Burgsandstein sandstone samples are composed of dominantly quartz and varying amounts of feldspars and clay minerals, other constituents were not detected. The latter is also true for hematite, goethite and other Fe(hydr)oxides which, nevertheless, should be present within at least part of the sandstones in minor amounts as silicate grain coatings, concluding from sedimentite colouration. The

analyzed clay band, on the other hand, consists of mainly clay minerals. The occurrence of hematite, together with the absence of pyrite and sulfide-S concentrations largely <0.01 wt.% in this sample group, argue for complete oxidation of the clays intercalated in the sandstones. “Active arkoses” contain varying degrees of quartz (~24-81 wt.%), feldspars (~6-17 wt.%) and clay minerals (~1-18 wt.%). Fluorapatite is always present, partly as dominant component with up to ~50 wt.%. The relatively high Fe concentrations (cf. chapter 1.4.2.2) are hosted as hematite and probably in Fe-bearing clay minerals like chlorite and illite.

For better characterization of the apatite phase occurring in the “active arkoses”, bulk Ca and P concentrations in these samples were analyzed for interrelation and compared to stoichiometric Ca:P ratios of “classical” apatite and francolite, differing from each other due to partial coupled substitution of $\text{CO}_3^{2-} + \text{F}^-$ for PO_4^{3-} in the crystal structure (Fig. 1.11; McArthur 1985, Binder and Troll 1989, Ragnier et al. 1994).

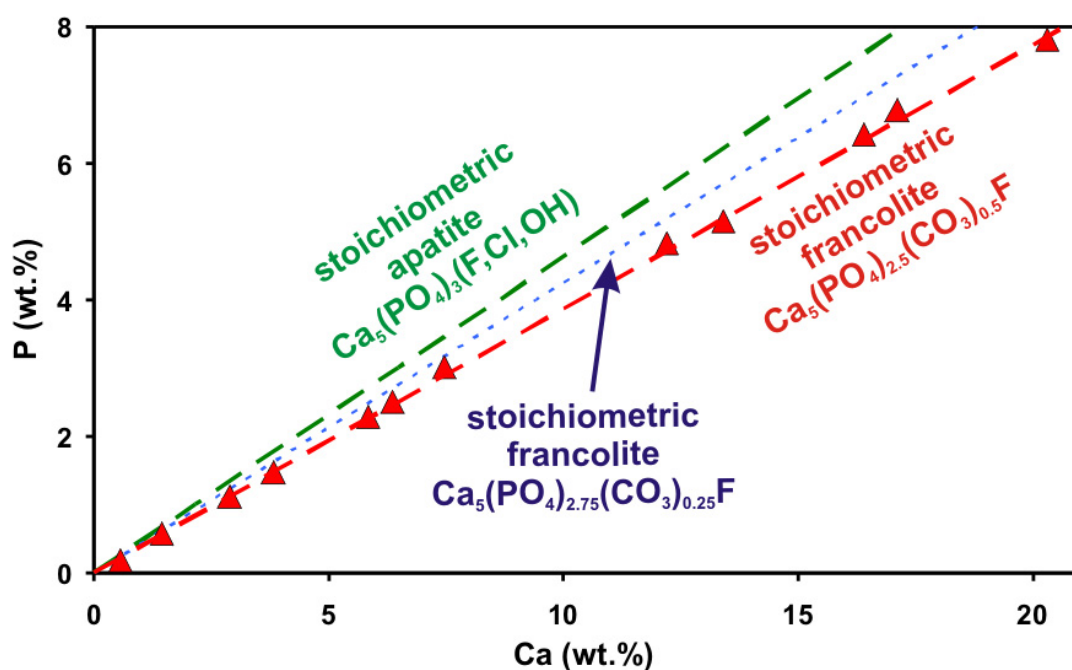


Fig. 1.11: Ca-P scatter plot for “active arkose” samples and stoichiometric Ca-P lines for “classical” apatite (green line) and two carbonate fluorapatites (francolites) with different contents of structural CO_2 – 2.25 wt.% (blue dotted line) and 4.5 wt.% (red line).

Calcium and P show a very close positive correlation ($R^2 > 0.99$) in “active arkose” samples with a distinct offset from stoichiometric “classical” apatite. Instead, the trendline resembles exactly the red stoichiometric francolite line, indicating that Ca and P are most likely present as $\text{Ca}_5(\text{PO}_4)_{2.5}(\text{CO}_3)_{0.5}\text{F}$ in the studied material. The empirical formula for this francolite (red line) was given for a mineral

composition with 3.9 wt.% F and 4.5 wt.% CO₂ (after Barthelmy 2011, for comparison: the maximum carbonate substitution until disruption of the francolite structure corresponds to 6.3 wt.% CO₂, McArthur 1985). Given the excellent plot of the studied samples along this stoichiometric line, similar concentrations can be assumed for the studied samples. Compared to the chemical analysis for “active arkoses” conducted by Abele et al. (1962), the F value fits well into the range given by these authors. Nevertheless, they only found 0.7-2.5 wt.% CO₂ in their samples but acknowledge that the concentrations they determined are too low to account for the detected P deficiency. For better comparison, a stoichiometric Ca-P line for a francolite containing 2.25 wt.% CO₂, which plots in the upper range of CO₂ values given by Abele et al. (1962), was implemented in Fig. 1.11 (blue line). There is still a large offset from the samples analyzed here. Thus, the higher value indirectly obtained in this study is probably more realistic.

An evaluation of apatite crystal structure parameters was obtained from XRD analysis. Important unit cell parameters in the tetrahedral apatite include the a (=b) axis and the c axis. Results are shown in Tab. 1.5 in comparison to some standard values obtained by Hughes et al. (1989) for F-, Cl- and OH-apatite end members and a carbonate fluorapatite characterized by Gulbrandsen et al. (1966).

Tab. 1.5: Apatite unit cell parameters in this study, compared to end members of the Ca₅(PO₄)₃(F,OH,Cl) structure analyzed by Hughes et al. (1989) and a carbonate fluorapatite (Carb-F) characterized by Gulbrandsen et al. (1966).

	F	OH	Cl	Carb-F	this study
a (Å)	9.3973	9.4166	9.5979	9.368±0.002	9.364±0.003
Offset of apatites in this study (Å)	-0.033	-0.053	-0.234	-0.004	
c (Å)	6.8782	6.8745	6.7762	6.890±0.002	6.895±0.005
Offset of apatites in this study (Å)	+0.017	+0.021	+0.119	+0.005	

Values for the a-axis in the studied apatites are smaller than in all reference materials after Hughes et al. (1989), but most similar to fluorapatite. Also c values resemble best the fluorapatite end member although there is a positive offset from all standard materials. Nevertheless, with regard to cell dimensions, the analyzed apatites are almost identical with the carbonate fluorapatite analyzed by Gulbrandsen et al. (1966). Indeed, the substitution of planar CO₃²⁻ for tetrahedral PO₄³⁻, accompanied by the occupation of the vacant oxygen site by a fluoride ion, may cause significant changes in the apatite crystal structure, expressed by changes in unit cell parameters. The substitution is accompanied by shortening of the a-axis and elongation of the c-axis, compared to end members (Smith and Lehr

1966), which exactly is the observation derivable from Tab. 1.5. Consequently, the apatites analyzed in this study can be characterized as carbonate fluorapatite (francolite) containing significant amounts of structural CO₂.

In summary, concerning the hosting of As and U, three main candidate phases – clay minerals, hematite and francolite – have been identified. Their potential for uptake of these trace elements will be discussed by means of a short literature overview in the following.

Clay minerals are known to adsorb As, present as oxyanion in most natural waters, to their positively charged flake edges (Smedley and Kinniburgh 2002). Nevertheless, they exhibit a significantly lower affinity towards As than e.g. Fe oxides (Manning and Goldberg 1997) and are thus expected to only play a considerable role in As retention when present in quantity or in absence of higher affinity phases. Supporting this, Ladeira and Ciminelli (2004) found negligible As adsorption to clay minerals in the presence of Fe oxides. The overall net charge of clay minerals was found to be always negative at pH>3 (Giblin et al. 1981), making aluminosilicates a rather unattractive sorption target for anionic species like H₂AsO₄⁻/HAsO₄²⁻, but also uncharged or anionic U carbonate complexes dominating in most groundwaters (Langmuir 1978, Katsoyiannis et al. 2006).

Oxides and hydroxides of Fe represent the most important As adsorbents in sandy aquifers (Smedley and Kinniburgh 2002 and references therein). Giménez et al. (2010) show that hematite retains both As(III) and As(V), although less effectively than goethite and lepidocrocite (Bowell 1994) whereas Mamindy-Pajany et al. (2009) observed equal As sorption capacity of goethite and hematite; Etschmann et al. (2010) determined 0.32 wt.% As in natural hematite. Iron (hydr)oxides are also capable of U immobilization, either by surface complexation of e.g. UO₂(CO₃)₂²⁻ (Katsoyiannis et al. 2006) or by coprecipitation as schoepite [(UO₂)₈O₂(OH)₁₂*12 H₂O] on oxide surfaces (Bruno et al. 1995). Shuibo et al. (2009) describe good efficiency of U sorption by hematite, Wernicke and Lippolt (1993) detected hematite-U concentrations of up to 600 µg g⁻¹.

Apatite is known to incorporate a large range of trace elements (Baikie et al. 2008). In spite of being considered a rather insignificant contributor to As concentrations in sediments due to their comparably low abundance (Smedley and Kinniburgh 2002), apatites can host high As contents. Råde (2005) detected a range of 3.71-192 µg g⁻¹ As in magmatic and metamorphic apatites and up to 960 µg g⁻¹ in a pegmatitic specimen from Durango/Mexico. Belousova et al. (2002) determined apatite composition in different geological environments and found highest As concentrations in samples from the Kiruna iron ore complex/Sweden (median 768 µg g⁻¹ with a maximum of 1174 µg g⁻¹). Even more striking, Perseil et al. (2000) measured up to 6.5 wt.% As in fluorapatite from an Italian manganese ore deposit while Etschmann et al. (2010) report up to 9.3 wt.% As in fluorapatite from a Fe-Mn deposit in Switzerland. Obviously, high apatite-As is favoured in metal oxidic environments. The main uptake

mechanism behind these high concentrations is the substitution of pentavalent As for P in the tetrahedral site of the apatite structure (Grisafe and Hummel 1970). Lee et al. (2009) achieved complete substitution within the solid solution series between hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) and the As equivalent johnbaumite ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$). Nevertheless, Etschmann et al. (2010) applied XANES imaging of high As fluorapatite and found a significant proportion of As being present as As(III), indicating that both redox species may substitute into the apatite structure.

Also U is well known for its ability to substitute in the crystal structure of apatite, albeit on the Ca site, which is explainable by the similarity of U(IV) and Ca(II) ionic radii (Starinsky et al. 1982). Nevertheless, Rakovan et al. (2002) produced synthetic fluorapatite containing 2.3 wt.% structural U(VI) on the Ca site, thus demonstrating that, akin to As, both U redox species can be accommodated in apatite. Furthermore, Fuller et al. (2002) describe the mineral's ability for surface uptake of large amounts of U(VI), either adsorbed as inner-sphere complexes, or coprecipitated as U-phosphate solid phases, e.g. chernikovite $[(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6 \text{H}_2\text{O}]$. Wedepohl (1978) gives a range of 31-430 $\mu\text{g g}^{-1}$ U in apatite, Clarke and Altschuler (1958) report a range of 50-300 $\mu\text{g g}^{-1}$ U in sedimentary apatite. Sha and Chappell (1999) measured a maximum of 151 $\mu\text{g g}^{-1}$ U in apatites from Australian I-type granites while Rde (unpubl. data) determined 376 $\mu\text{g g}^{-1}$ in a pegmatitic specimen from Wales. Abele et al. (1962) calculated carbonate fluorapatite-U contents from bulk rock data of "active arkose" samples from Franconia and report a range of 200-4700 $\mu\text{g g}^{-1}$. Indeed, U concentrations in natural apatites can reach several wt.% (Rakovan et al. 2002).

1.4.2.3 Trace element distribution in "active arkoses"

Laser ablation ICP-MS measurements were conducted for "active arkose" samples to characterize the distribution of As and U on a microscale and to verify or falsify the statements derived from bulk rock analysis. Figure 1.12a shows a bulb-like "active arkose" with distinct zonation, sampled from a very fresh outcrop (Fig. 1.4d) which was chosen for microscopical characterization (Fig. 1.12b) and chemical profiling using bulk rock geochemical data for the different zones (profile A-A', Fig. 1.12c) and, with higher resolution, applying LA-ICP-MS (profile B-B', Fig. 1.12d).

The red inner core of the sample (Fig. 1.12a, mineralogical composition see Tab. 1.4, sample AA_1_inner core) contains little fluorapatite (0.9 wt.%), the red colouring is from hematite in the matrix. In terms of bulk rock data, the inner core has highest As (26.1 $\mu\text{g g}^{-1}$) and lowest U concentration (15.1 $\mu\text{g g}^{-1}$) of all "active arkose" samples and is the only one with As/U>1.

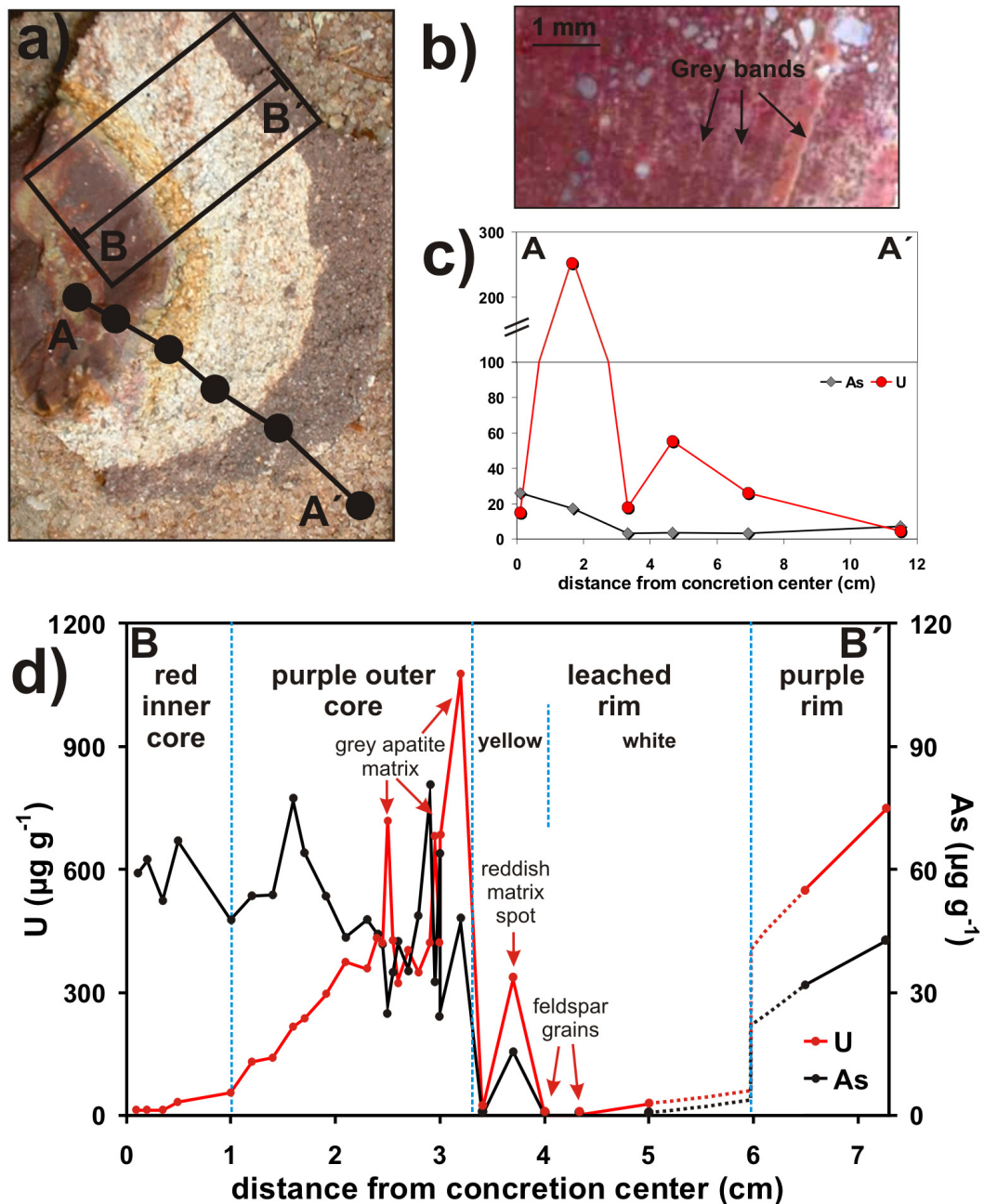


Fig. 1.12: Geochemical profiling of a freshly exposed „active arkose“ sample, (a) photograph with approximate location of the produced thin section (rectangle), the sampling points for bulk rock geochemical analysis of the different zones (profile A-A') and position of the LA-ICP-MS point profile (B-B'), (b) extract of a thin section photograph from the purple outer core, (c) bulk rock geochemical profile for As and U, note change of scale on the y-axis, (d) geochemical point profile for As and U with zonation borderlines, note different scales on the y-axis for U (left) and As (right). Dotted lines: assumed concentration curve.

Conversely, the thicker dense purple outer core (Fig. 1.12a, mineralogical composition see Tab. 1.4, sample AA_1_outer core) comprises 50 wt.% fluorapatite (representing the dominant matrix mineral, followed by hematite and clay minerals), $252 \mu\text{g g}^{-1}$ U (highest concentration in the profile) and $17.4 \mu\text{g g}^{-1}$ As. The optical homogeneity of this zone is less obvious when conducting microscopical

characterization (Fig. 1.12b). Especially in the outer parts, grey areas interrupt the purplish colours, mainly in band shape, indicating an internal zoning of the outer core. These areas contain very high concentrations of Ca and P and much lower Fe contents than the purple zones and are thus interpreted as relatively pure fluorapatite matrix (cf. Fig. 1.13). The thin yellow and thicker white rims around the purple core yield significantly less U and As (Fig. 1.12c), also Fe, Ca and P decrease considerably (cf. Fig. 1.13). The sediment is silicate grain-dominated (compared to the matrix-dominated core zones) and less consolidated here, with strongly elevated porosity, evident from microscopical analysis. Some reddish to purplish matrix spots are observable under the microscope, probably representing relics of a formerly more abundant matrix similar to the sample core. Due to these observations, the yellow-whitish zone is referred to as the leached rim. The last zone of the analyzed “active arkose” is a purple rim (Fig. 1.12a, mineralogical composition see Tab. 1.4, sample AA_1_purple rim) with ~10 wt.% fluorapatite, relatively low Fe and bulk sample As and U concentrations similar to the leached rim (Fig. 1.12c). The light-coloured, coarse sandstone around this zoned „active arkose“ yields typical As and U concentrations for the aquifer sandstones (Fig. 1.12 a, c).

Regarding the point profile created from LA-ICP-MS measurements (Fig. 1.12d), distinct As and U developments are observable. Analysis spots concentrate on matrix material of the different zones which is assumed to host the trace element carriers rather than the silicate grains. To underline this assumption, few measurements have been conducted on silicate grains and yielded $\emptyset U = 0.3 \mu\text{g g}^{-1}$ and $As < DL$.

As expected from bulk rock data, the red inner core yields $As (\emptyset 58 \mu\text{g g}^{-1}) > U (\emptyset 25 \mu\text{g g}^{-1})$ concentrations. While As content is relatively stable in this zone, U increases from $12.8 \mu\text{g g}^{-1}$ in the center to $56.5 \mu\text{g g}^{-1}$ near the border to the purple outer core. This concentration increase continues in the outer core to arrive on a plateau in the purple-reddish matrix of $\sim 400 \mu\text{g g}^{-1}$. Several significantly higher concentration peaks $> 650 \mu\text{g g}^{-1}$ are observed, all of which were measured in the relatively pure, grey apatite matrix, with a maximum of $1071 \mu\text{g g}^{-1} U (\emptyset 784 \mu\text{g g}^{-1})$. Conversely, As contents trend to gradually lower values (Fig. 1.12d). Overall U averages $425 \mu\text{g g}^{-1}$ ($132\text{--}1071 \mu\text{g g}^{-1}$) in this zone while $\emptyset As$ is $48 \mu\text{g g}^{-1}$ ($25\text{--}77 \mu\text{g g}^{-1}$) with peak concentrations in the purple-reddish matrix; the pure apatite areas yield $33 \mu\text{g g}^{-1} As$ on average. Significantly lower contents of both U ($11.5\text{--}28.1 \mu\text{g g}^{-1}$) and As ($< DL$) were detected in the leached rim. Nevertheless, single reddish matrix spots obviously host higher concentrations (Fig. 1.12d), supporting the idea that these represent relics of a once more abundant material. Arsenic ($\emptyset 38 \mu\text{g g}^{-1}$) and U ($\emptyset 653 \mu\text{g g}^{-1}$) concentrations re-increase considerably in the purple rim matrix which has not been observed in bulk rock data (Fig. 1.12c). Obviously, the scarcity of the matrix in this grain-dominated zone does not allow for higher whole rock concentrations.

From the development of profile concentration lines, differences in As and U accommodation become evident which are assessed in more detail evaluating trace element trends towards other major and trace elements determined with LA-ICP-MS (Fig. 1.13).

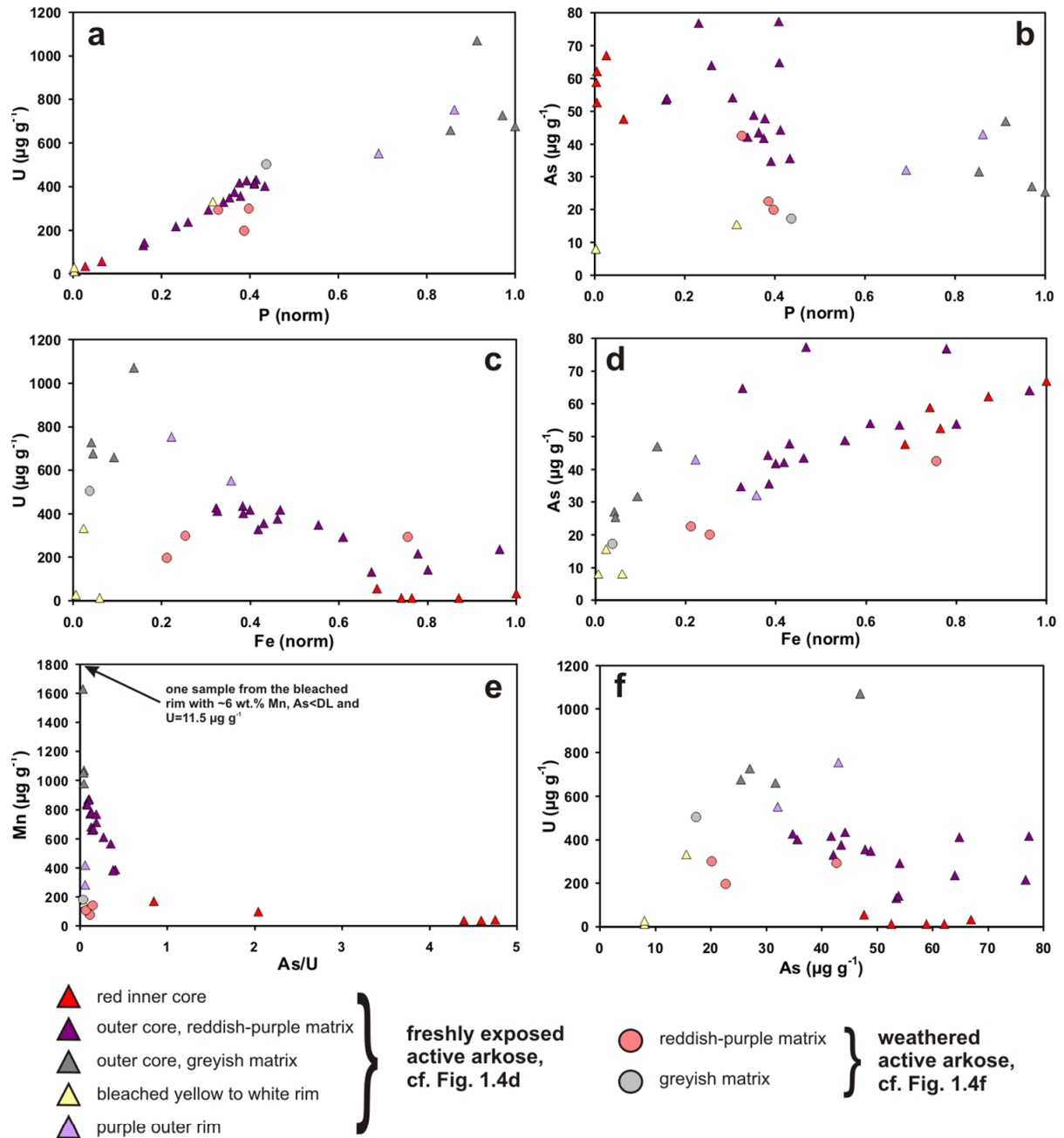


Fig. 1.13: Selected scatter plots from LA-ICP-MS data, differentiated by sample groups of the zoned “active arkose” (triangles, cf. Fig. 1.12) and single spot measurements of a more weathered “active arkose” (circles). Determined major element concentrations (here: P, Fe) were normalized to the highest detected value of the respective element because the applied NIST 612 standard is designed for trace element measurements, making absolute major element determinations error-prone. (a) P vs. U, (b) P vs. As, (c) Fe vs. U, (d) Fe vs. As, (e) As/U ratio vs. Mn, (f) As vs. U.

Generally, the purple matrix of the outer core, consisting of a dense apatite-hematite-clay mineral mixture, plots between the end members hematite-dominated red inner core and apatite-dominated greyish matrix in all diagrams in Fig. 1.13. Uranium exhibits a distinct positive trend towards P (Fig. 1.13a), supporting that apatite is the dominant U carrier phase in “active arkoses”. As mentioned above, highest U and P concentrations were found in greyish relatively pure apatite matrix areas while the red inner core and the leached rim yield low contents (exception: the enriched relic matrix spot within the leached rim, cf. 1.12d). Arsenic vs. P does not show a positive correlation (Fig. 1.13b) which is contradictory to the findings from bulk rock data of all “active arkoses” (Fig. 1.10a) and supports different hosting mechanisms for As and U. High As concentrations prevail in the red inner core and in parts of the purple outer core (reddish purple matrix) while lower (but still significant, see above) contents are found in the pure apatite matrix. Likewise U, considerably lower As values are reached in the leached rim. The trace element behaviour towards Fe shows even more explicit diametrical tendencies. While U-Fe exhibits a clearly negative trend (taking out the leached rim spots with very low Fe contents, Fig. 1.13c), As-Fe shows an overall positive correlation (Fig. 1.13d). As a consequence, As vs. U yield a rather negative interrelation, though with broad scattering (Fig. 1.13f). Accordingly, the distinct geochemical similarity of both elements derived from Fig. 1.10a cannot be fully supported here. Arsenic and U both prevail in the “active arkose” matrix and thus mimic a positive trend towards each other when evaluating bulk rock data (the aforementioned pseudo-correlation, cf. chapter 1.4.2.1, Fig. 1.9). Nevertheless, this analogy in spatial occurrence turns out not to be interpretable in terms of preferential common host phases when analyzing in higher resolution (LA-ICP-MS) – U quantitatively resides in carbonate fluorapatite while As is most likely hosted by hematite and, to a lower degree, francolite. Evaluating the accommodation of As between these two phases from the obtained data and taking into account that measurements in relatively pure apatite matrix still brought considerable As concentrations while also small Fe contents were detected, an average As distribution ratio in hematite and francolite of ~3:2 is estimated for the reddish-purple matrix. Approaching the “end members” red inner core and pure apatite, close to 100 % As_{hematite} and $As_{\text{francolite}}$, respectively, are expectable. These findings, together with the genesis of the zoned “active arkose” (see last paragraph of this chapter), strongly support a common paleo input of As and U into the sediments but differences in main host phases.

Aluminium in the matrix materials is likely to occur as Fe-rich clay minerals (illite, chlorite) indicated by positive correlations with Fe and Si (not shown) together with XRD results (Tab. 1.4). From comparative behaviour of other trace elements towards Fe, Al, Ca, Si and P, it may be concluded that Ni is preferentially hosted by clay minerals while Zn and V reside on hematite, together with As (which shows no distinct trends towards Al and Si making sorption to clay minerals unlikely). Lead, Mn and REE are evidently hosted by francolite, together with U (negative trend towards Al and Si – no clay

mineral association) as suggested by significant positive correlations ($R^2 > 0.8$) with Ca and P. One preliminary idea with regard to potential As hosting mechanisms in “active arkoses” – mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) formation (Baikie et al. 2008) or precipitation of $\text{Pb}_5(\text{AsO}_4)_3\text{OH}$ (Vaca-Escobar and Villalobos 2010) – is thus not supported by the obtained data, also underlined by comparison of the As-Pb scatter plot to the stoichiometric mimetite line which brought no fit at all. Distinct positive U-Pb correlation ($R^2 = 0.85$) rather suggests a radiogenic Pb origin, generally Pb is known to substitute in the apatite crystal structure and even to form an own apatite family (e.g. Baikie et al. 2008). Figure 1.13e illustrates Mn vs. As/U behaviour, supporting the finding of significantly different Mn (francolite) and As (hematite) hosting mechanisms. One sample point from the yellow leached rim containing highly elevated Mn (6 wt.%) and high concentrations of Ni, Zn and Pb, but low As, U, REE, Ca and P, is interpreted to represent a secondary matrix with micro-concretional metal accumulation formed after mobilization from the core material. Thus, both relic primary (see above) and post-alterational secondary matrices exist in the leached rim.

The common occurrence of metals from different primary matrix sources (Mn and Pb from francolite, Ni from clay minerals, Zn from hematite) argues for a “trash bin” function of the described secondary matrix, collecting mobilized constituents from all parts of the original material. The fact that As and U collection does not seem to occur here suggests these trace elements’ loss to solution during alteration processes.

Few single spot measurements in a second “active arkose” sample (three in reddish-purple matrix, one in grey apatite matrix) from a strongly weathered outcrop in the vicinity of the freshly exposed, zoned specimen’s sampling site, were also implemented in Fig. 1.13 diagrams. Uranium concentrations in these spots are lower, compared to related material in the fresh sample (offset of the reddish-purple matrix from the trendline in Fig. 1.13a, grey matrix spot with $505 \mu\text{g g}^{-1}$ U, compared to $\emptyset 784 \mu\text{g g}^{-1}$). Also As content is decreased with $\emptyset 28 \mu\text{g g}^{-1}$ in the reddish-purple matrix ($\emptyset 52 \mu\text{g g}^{-1}$ in the fresh sample) and $17 \mu\text{g g}^{-1}$ compared to $\emptyset 33 \mu\text{g g}^{-1}$ in the grey apatite matrix. The distributional trends are thus the same as in the freshly exposed specimen, though with lower absolute concentrations. In the As-U diagram (Fig. 1.13f), these samples plot between the unaltered arkose and its leached rim, indicating alteration in progress which leads to As and U loss. This is underlined in the case of U by the clearly lower Mn concentrations (Fig. 1.13e) when additionally considering the highly Mn-enriched secondary matrix described above: Mn, originally residing with apatite and obviously being prone to mobilization, is depleted in the weathered arkose.

All these observations argue for significant U and As occurrence in “active arkoses”, though preferentially in different host phases, and their loss from the sediments during weathering. Dimension and potential mechanisms behind the latter will be discussed in the following chapter.

As a final remark on the genesis of the differentiated sample core (red-purple, Fig. 1.12a), it can be said that probably, accretive crystallization of francolite is responsible for this phenomenon. Progressively purer apatites develop from the very fine-grained precipitated hematite-francolite mixture, thereby pushing aside the Fe oxide which then accumulates in free pore space of the arkose. This mechanism was described for other samples by Abele et al. (1962) and explains the occurrence of relatively pure, greyish apatite bands in the purple outer core on the one hand, and the relatively pure hematite in the red inner core on the other hand. Furthermore, this process accounts for the development of As and U concentrations in the LA-ICP-MS profile (Fig. 1.12d): the As (but not U) carrier hematite is successively displaced towards the concretion centre, gradual increase of U towards the outer parts of the core follows enhanced apatite abundance and reaches peak values in accretively crystallized pure apatite. This genetic model allows for the description of the geochemical profile in terms of a separation line between hematite and francolite.

1.4.2.4 Trace element fractionation and remobilization potential

Mineralogical fractionation and remobilization behaviour of As and U were assessed in a sequential extraction procedure (SEP) which will be described in the following. Subsequently, vulnerability to weathering and dissolution of the studied francolite will be discussed to evaluate the role of a major player in geogenic As and U dynamics of the study area in terms of trace element hosting and release potential to groundwater.

Sequential Extraction Procedure (SEP)

Results of the SEP for As and U are presented in Figs. 1.14 and 1.15, respectively. Readily (CH_3COOH -) soluble As is of minor importance in the analyzed sedimentites (sandstones, clay band and “active arkoses”), accounting for max. 5 % As_{tot} which corresponds to $0.9 \mu\text{g g}^{-1}$. Similarly, in the extraction step targeting the reducible As fraction ($\text{NH}_2\text{OH-HCl}$), low As mobilization of max. 5 % As_{tot} was achieved. Iron concentrations were photometrically determined in all SEP solutions to check the success of selective target phase extraction. Results show that only ~0.1 to 0.9 % of the total Fe content of the samples was mobilized during extraction with $\text{NH}_2\text{OH-HCl}$. This observation supports the findings of Pickering (1981): the extraction solution is not suitable for dissolution of crystalline Fe oxides like hematite which was shown to be the main host of As in the analyzed rocks (cf. chapter 1.4.2.3). Therefore, this trace element fraction does not fully represent the portion bound to Fe oxides in the conducted procedure. Nevertheless, when comparing As/Fe ratios in the $\text{NH}_2\text{OH-HCl}$ leachates to bulk sample As/Fe ratios, an As selectivity becomes obvious indicated by a mean ($\text{As/Fe}_{\text{leachate}} : \text{As/Fe}_{\text{bulk rock}}$) of 35. This implies that Fe oxides indeed play a significant role in As occurrence and behaviour, even though obviously, only Fe oxide surfaces were etched in the reducing extraction step.

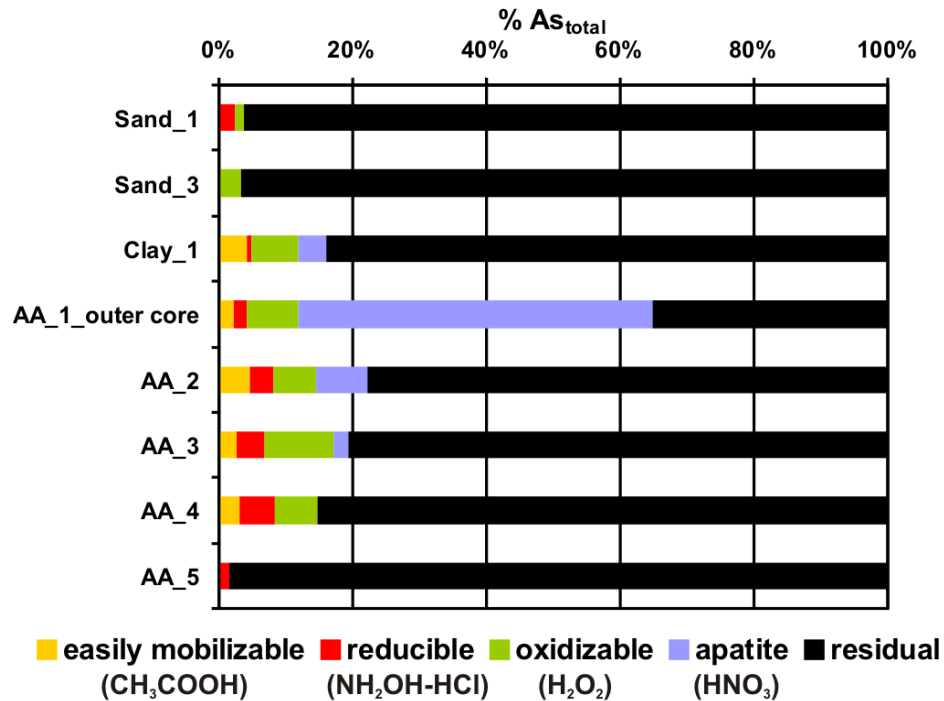


Fig. 1.14: Results of the sequential extraction procedure (SEP) for As, cf. Tab. 1.4 for sample allocation.

The oxidizable (H₂O₂-soluble) As fraction accounts for a maximum proportion of 10 % As_{tot} and an absolute amount of max. 1.4 $\mu\text{g g}^{-1}$. Sulphide-S in the addressed samples is broadly <0.01 wt.% and hardly any Fe was dissolved in this step, making sulphide hosted As unlikely. It may be speculated that dispersed relic organic matter is responsible for this signal. Extraction with HNO₃, targeting the apatite-bound trace element fraction, yielded insignificant As portions in sandstones and clay, but a maximum of 53 % As_{tot} in one “active arkose” sample, the purple outer core of the specimen analyzed in detail (cf. chapter 1.4.2.3). Other “active arkose” samples showed varying As proportions in this step which will be discussed later on. Concentrations of Fe released by this solution, which can be suspected to attack the undissolved Fe oxides (Dües 1989), yielded low values again, accounting for 0.01 to 2.8 % of sample Fe_{tot} . The residual As fraction was the dominant one in this SEP which, nevertheless, supposedly includes most of the As bound to hematite (see above).

Easily mobilizable U represents Ø 7 % of the total U pool in “active arkoses”, accounting for up to 12.8 g g^{-1} . Abele et al. (1962) discuss the speciation of U in the “active arkose” samples and declared that U is partly sorbed as U(VI)O₂HPO₄ on the apatite surface (in addition to U(IV) present in the apatite crystal structure). This proportion may have been partly dissolved during CH₃COOH-extraction.

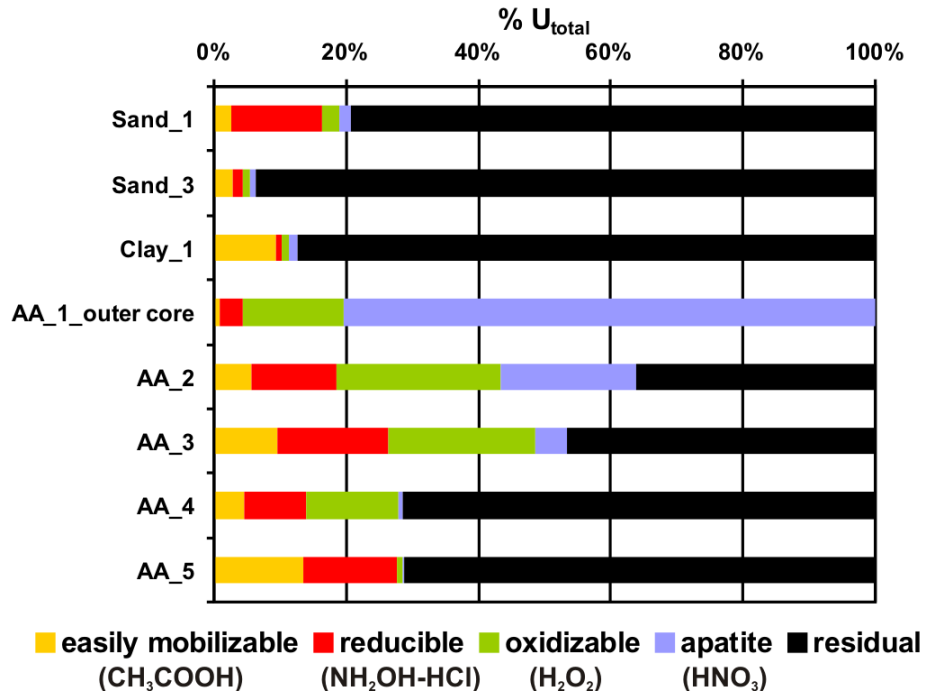


Fig. 1.15: Results of the sequential extraction procedure (SEP) for U, cf. Tab. 1.4 for sample allocation.

Interestingly, the freshly exposed sample AA_1_outer core hardly yields any readily mobilizable U (1 % U_{tot}). Secondary alteration during weathering is thus likely to lead to U oxidation, redistribution and transformation into significantly better soluble species. This would argue for successively elevated U mobility in “active arkoses” in the course of weathering. Reducible U accounts for up to 14 % U_{tot} in sandstones and Ø 12 % U_{tot} in “active arkoses”, corresponding to up to $24.7 \mu\text{g g}^{-1}$. Again, lowest values are reached for AA_1_outer core, making a further dissolution of surface-bound U more probable than a mobilization from oxides (cf. Fig. 1.13c). An average of 17 % oxidizable U is present in “active arkoses” (insignificant values for other sample types). Likewise for As, dispersed organic matter might be an explanation. Nevertheless, this was neither observed under the microscope nor described by Abele et al. (1962). It seems more plausible to assume that structural U(IV) near apatite crystal surfaces is oxidized to U(VI) by H_2O_2 , resulting in mobilization. This mechanism may, on the other hand, lead to the assumption that structural apatite-As is simultaneously mobilized which is supported by a positive trend between dissolved As and U in this step. Like for As, dissolved U concentrations in the apatite-targeting extraction step are unimportant for sandstones and clay, and vary widely in “active arkoses” (<1 to >80 % U_{tot}) which will be discussed in the following. In contrast to the findings for As, a significant overestimation of the residual U fraction is rather unlikely. Concluding from the previous correlation analysis (Fig. 1.10b), U in sandstones is present in zircon and thus immobile. Residual U in “active arkoses” is probably not to be sought in undissolved hematite regarding the clearly negative trend between U and Fe (Fig. 1.13c), but may reside in relictic

apatite, insoluble in 1 M HNO_3 , as concluded from non-existence of a residual in the freshest sample and Fig. 1.16 which compares dissolved As and U during the apatite (HNO_3) step.

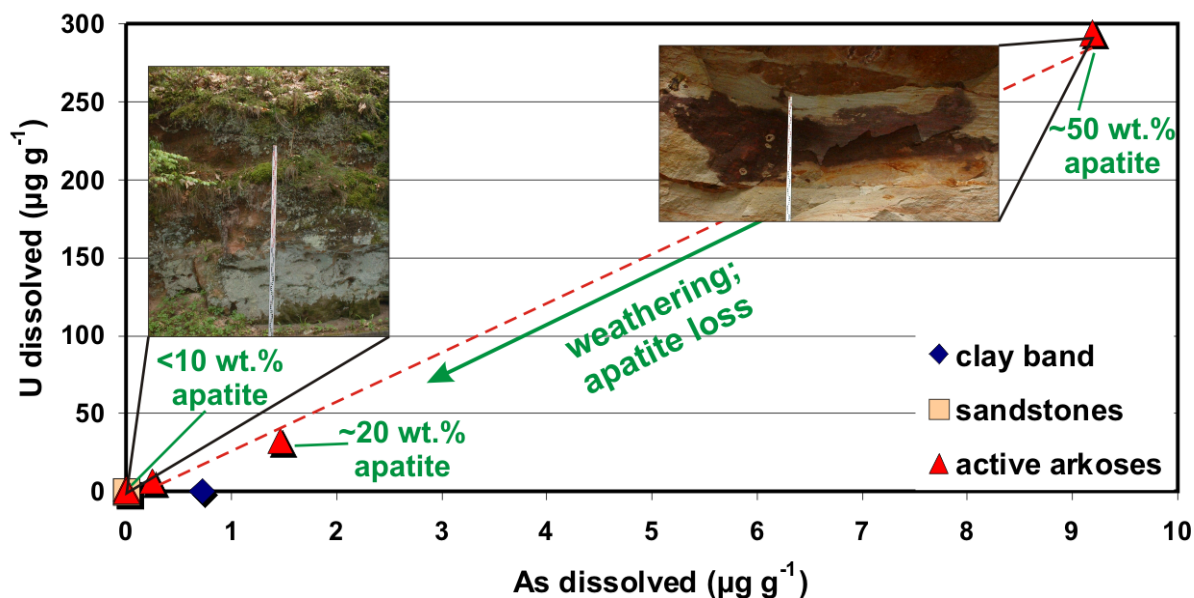


Fig. 1.16: Apatite-step (1 M HNO_3 -) soluble As vs. U with bulk rock fluorapatite contents derived from XRD analysis, and images of a freshly outcropping sample (right picture) and a strongly weathered “active arkose” outcrop (left picture).

It becomes obvious from Fig. 1.16 that apatite is insignificant as As and U host in sandstone samples and clay bands (albeit little As was dissolved in this step from the clay sample). This finding is supported by low median Ca (0.06 wt.% and 0.04 wt.%, respectively) and P (0.03 wt.% and 0.02 wt.%, respectively) concentrations in these sample groups and non-existing correlations towards As and U. “Active arkoses” show a more differentiated behaviour during 1 M HNO_3 extraction: 294 $\mu\text{g g}^{-1}$ U and 9.2 $\mu\text{g g}^{-1}$ As were dissolved from the sample taken in the freshly exposed outcrop containing ~50 wt.% fluorapatite (determined by XRD following Rietveld analysis). Samples from older, more weathered outcrops follow a trend towards lower apatite content and simultaneously decreasing U and As dissolution. From the sample with the second highest apatite proportion (~20 wt.%), 33 $\mu\text{g g}^{-1}$ U and 1.5 $\mu\text{g g}^{-1}$ As were mobilized, the following sample (~12 wt.% apatite) lost 6.5 $\mu\text{g g}^{-1}$ U and 0.2 $\mu\text{g g}^{-1}$ As to solution. No As and very low U (0.1 and 1.8 $\mu\text{g g}^{-1}$) mobilization was detected for samples with less than 10 wt.% fluorapatite although these samples contain significant bulk U concentrations. The simultaneous As and U dissolution trend supports the conclusion developed earlier of francolite being both a major U carrier and at least one important As host (besides hematite, see chapter 1.4.2.3). It is concluded that this decreasing trend represents a line of weathering including successive mobilization and loss of apatite and resulting in decreasing “active arkose” reactivity in terms of potential U and As

dissolution. Relic (1 M HNO₃-insoluble) U remains in the “active arkoses” after weathering, probably in more resistant apatites, explaining large residual U fractions for highly weathered samples (Fig. 1.15).

In consequence from SEP results, together with the data on mineralogical composition and trace element distribution in “active arkoses” (chapters 1.4.2.2 and 1.4.2.3), it is shown that francolite, hosting both U and As and being attacked during weathering, is capable of losing large amounts of U and also significant As concentrations to solution under natural conditions in the study area. Therefore, it represents a common source for both trace elements’ occurrence in groundwater. Presumably, considerably higher As concentrations adsorbed in the hematitic matrix are potentially mobilized from “active arkoses” when reducing conditions arise in the course of water-rock-interaction. It was shown in chapter 1.4.1 that this is the case in parts of the Burgsandstein aquifer, partly exhibiting Fe^{III}/SO₄-reducing groundwater milieus capable of As(V) reduction to As(III) and thus, of mobilization. Indeed, these anoxic groundwater samples contain elevated As concentrations (Fig. 1.7).

As a final remark, it must be acknowledged that the applied SEP is only partially suitable for the given samples – while the extractions of readily soluble and apatite-bound fractions yielded good results, the reducing step did not release hematite-As quantitatively, as described above, and the oxidizing step is rather redundant, regarding the lack of sulfides and organic matter, and may even be misleading as it seems to attack apatite. Retrospectively, taking the obtained geochemical and mineralogical data into account (which was not completely available when the SEP was designed), the following sequence would be more promising: Readily soluble fraction (CH₃COOH, Ure et al. 1993) – Apatite-bound fraction (HNO₃, Nezat et al. 2007) – Fraction bound to crystalline Fe oxides (NH₄-oxalate + ascorbic acid in a hot water bath, Wenzel et al. 2001). This order should be followed as it was shown here that 1 M HNO₃ did not significantly attack hematite but conversely, the hot acid oxalate extraction is very likely to partially dissolve apatite (Cervini-Silva et al. 2005), especially U-rich francolite which is considerably more sensitive to alteration than “classical” apatite as will be discussed in the following.

Enhanced solubility of analyzed francolite

Apatite is generally considered a mineral of low solubility – Valsami-Jones et al. (1998) cite a thermodynamic solubility product of 10^{-60.6} for fluorapatite – although it was shown to be the least stable member of the heavy mineral group (Lång 2000) and dissolves several orders of magnitude faster than e.g. plagioclase (Nezat et al. 2008). Steady-state congruent dissolution of apatite was observed after preferential Ca release in early stages (Guidry and Mackenzie 2003). Jahnke (1984) as well as Valsami-Jones et al. (1998) observed stoichiometric dissolution at near neutral pH with rates increasing with decreasing pH. Dissolution rates for natural apatites are faster than for synthetic samples, proba-

bly due to higher chemical heterogeneity (Valsami-Jones et al. 1998). The dissolution – and thus the weathering – rate of apatite is further controlled by temperature and surface area. Guidry and Mackenzie (2000) state that weathering of apatite as the primary P sink in the exosphere controls P fluxes and availability and thus biological productivity on geological time scales.

Solubility and vulnerability to weathering and thus, trace element mobilization potential of the francolites analyzed in this study are likely to be significantly enhanced, compared to standard apatites in laboratory studies, for three reasons – (1) influence of plants and microorganisms, (2) high degree of CO_3^{2-} -substitution in the crystal structure and (3) impact of radiation deriving from high U concentrations in the minerals.

In the following, the mentioned arguments [(1)-(3)] will be assessed in more detail in terms of a short discussion of relevant literature and transferability of the findings to the present study.

- (1) Apatite represents the dominant primary source of natural P in soils and is thus a limiting factor for the nutrient supply of vegetational colonization (Cervini-Silva et al. 2005). Moreover, it may be a major Ca source in non-carbonate or decarbonatized sites as its weatherability plots between that of Ca carbonates and that of Ca silicates; it therefore counteracts Ca depletion in soils (Nezat et al. 2008). Blum et al. (2002) showed that ectomycorrhizal fungi associated with conifer roots are able to use apatite as a direct source of Ca and P and thus to effectively weather the mineral. This is supported by Wallander (2000) who supplied pine tree seedlings with apatite as the only P source. He calculated a P budget and found that up to 0.9 % of the added apatite had been weathered by the plants after 210 days. The release mechanism behind this phenomenon is the attack of organic acids known to considerably enhance apatite dissolution kinetics (Valsami-Jones et al. 1998, Cervini-Silva et al. 2005). Coniferous forest represents the characteristic vegetation on the relatively acid soils developed on the Burgsandstein sedimentites in Franconia. Additionally, numerous bacteria and algae are able to mobilize apatite, also at neutral pH (Smith et al. 1978), some of which are even applied for U extraction from apatite-hosted deposits (Abhilash et al. 2009). Mailloux et al. (2009) found that bacterial utilization of As-bearing apatite for nutrient acquisition releases significant As concentrations to solution. The authors postulate that this mechanism may be one of the main processes leading to the widespread occurrence of high As groundwater in Bangladesh. It is conceivable that also U, if present in the mineral, will be released from apatite during microbial attack. Though not quantifiable, as no analysis in this direction have been carried out, it seems highly probable that microbiology and/or botany may play a major role in apatite weathering in the present study area as well.

- (2) The substitution of $\text{CO}_3^{2-}/\text{F}^-$ for PO_4^{3-} into the fluorapatite structure alters the mineral's chemical stability significantly. Jahnke (1984) reports that “the solubility of apatite increases dramatically with increasing carbonate content”, an enhanced chemical reactivity following this substitution was already observed by Smith and Lehr (1966). The destabilizing effect is due to distortion of the crystal structure caused by coupled substitution (cf. chapter 1.4.2.2). Regnier et al. (1994) ascribe this effect to the interstitial position of substituted F^- ions in the mineral structure and associated breakdown of crystal symmetry. Their conclusions are based on studying a francolite specimen with ~1 wt.% structural CO_2 . As described in chapter 1.4.2.2, the francolites studied here contain ~4.5 wt.% CO_2 , greatly enhanced solubility compared to carbonate-free fluorapatite is thus expectable.
- (3) Radiation derived from U decay in minerals of sufficient U concentration and/or age can greatly increase these minerals' dissolution rates due to α -recoil damage in the crystals (Petit et al. 1985). These authors found that a critical dose of radiation has to be exceeded in certain minerals in order to drastically enhance their solubility in an aqueous solution of typical groundwater composition. Apatite is such a mineral sensitive to radiation-enhanced dissolution, whereas e.g. uraninite and zircon do not show significant reactions to this effect (Petit et al. 1985). In their work, these authors give a set of equations to calculate radioactive element concentrations or mineral ages necessary to reach the critical dose of α -recoil, which was applied for the francolites subjected to the present study:

$$N_c = T * n_i * \lambda_i * C_i$$

where

N_c is the critical dose of α -recoil [cm^{-3}]

T is the mineral age [a]

n_i is the number of α -decays in the disintegration chain of a radioactive element [-]

λ_i is the decay constant of the radioactive element [a^{-1}]

C_i is the concentration of the radioactive element in the mineral [atoms g^{-1}]

Calculations were performed for U only as it represents the only relevant radioactive component in the analyzed francolites, Th radiation is negligible (Abele et al. 1962), i.e. $n_i = 8$ and $\lambda_i = 1.53 * 10^{-10} \text{ a}^{-1}$. N_c is given as $2.5 * 10^{18} \text{ cm}^{-3}$ (Petit et al. 1985), T was set to 210 Ma accounting for the syngenetic formation of the francolites in Norian times (age taken from ICS 2009). With the given data, it is possible to calculate the minimum U concentration necessary to exceed the critical dose of α -decay reached after mineral formation, and evaluate if the U contents measured in the francolites are sufficient to account for significantly radiation-

enhanced apatite solubility. With a mineral density of 3.12 g cm^{-3} for carbonate fluorapatite (Barthelmy 2011), the result of the calculation is $\sim 370 \text{ } \mu\text{g g}^{-1} \text{ U}$. Regarding U concentrations determined in this study (chapters 1.4.2.1 and 1.4.2.3), together with the results of Abele et al. (1962, cf. chapter 1.4.2.2), it is concluded that a very high percentage of the francolites occurring in Triassic “active arkoses” clearly exceed the critical dose value, thus exhibiting radiation-enhanced solubility and a significantly increased tendency to lose incorporated U and As to solution and therefore, to groundwater of the study area.

Another potentially important factor for especially As release from Fe oxides is inorganic anion concurrence leading to desorption from host mineral surfaces. Casentini et al. (2010) showed that the presence of bicarbonate and fluoride strongly enhances the mobilization of metal-(hydr)oxide hosted As from volcanic rocks at near neutral pH. Due to its chemical similarity to AsO_4^{3-} , phosphate is known to compete for sorption sites and thus to affect As mobility (e.g. Jain and Loeppert 2000). Possible anion exchange processes are currently studied for Burgsandstein aquifer samples. First results (Rubinos et al. 2011) indicate that HCO_3^- present in groundwater of the study area does obviously not promote As and U mobility. Nevertheless, the dissolution of carbonate fluorapatite is likely to release phosphate and fluoride to solution. With regard to the observed proximity of U-(and As-) bearing francolite and As-bearing hematite, together forming large parts of the “active arkose” matrix material, it can be speculated that released PO_4^{3-} and/or F^- may trigger *in situ* desorption of near-surface As from hematite. The As fraction extracted by $\text{NH}_2\text{OH-HCl}$ in the SEP (see above) allows for a quantity estimation of the latter: an average of 5 % As_{tot} was released from “active arkoses” in this step, thus doubling the easily mobilizable fraction and enhancing the overall mobilization potential of the studied sediments. Consequently, both As source phases (francolite and hematite) might be activated in the course of francolite dissolution. This question is planned to be assessed in future laboratory experiments.

1.5 Conclusions

In groundwater extracted from an Upper Triassic sandstone aquifer (Burgsandstein) in Franconia/Northern Bavaria, elevated concentrations of both As and U, partly in excess of drinking water limitations, were identified in recent years. Nevertheless, the mechanisms responsible for the creation of this hydrochemical signature are only partly understood in the case of As, and are discussed here for the first time in the case of U. This study gives evidence for the major role of abundant syngenetic intercalations within the terrestrial facies of the aquifer sandstones, so-called “active arkoses”. These exhibit a carbonate fluorapatite (francolite)-hematite matrix containing high U contents attached to the francolite and elevated As concentrations prevailing in both Fe oxidic and Ca phosphatic components. Arguments include spatial patterns of trace elements in groundwater and aquifer material, paleo-

geographical/depositional conditions, rock geochemical and mineralogical composition, U and As distribution on a microscale in “active arkoses” as well as their mineralogical fractionation and mobilization behaviour during weathering. It was further shown that the studied francolite is highly susceptible to alteration and thus, loss of trace elements to solution. In consequence, “active arkoses” were identified as most likely source for groundwater U and As in the study area with subsequent separation of both elements following heterogeneous redox conditions in the aquifer.

While elevated As seems to be restricted to the area studied here, high groundwater U also occurs further northwards, in an area exhibiting uraniferous dolomitic intercalations (calcretes) within the aquifer. In spite of lower bulk U concentrations as compared to “active arkoses”, these may represent an effective source due to high solubility of the U carrier phases, and also concluded from spatial distribution patterns of their depositional facies and groundwater U. Consequently, uraniferous inclusions in Triassic aquifer sandstones possibly control the occurrence of the geogenic U problem in Northern Bavaria as a whole. Further characterization of the dolomitic calcretes would, of course, be necessary to support this hypothesis.

This study underlines the crucial relevance of paleoenvironmental processes for the understanding of present-day distribution and behaviour of potentially hazardous geogenic trace elements. It tries to shed light not only on the hydrogeochemical background of Germany’s most significant groundwater U and As problem area identified so far, but also on the probably underestimated importance of apatite as a player in the structure of trace element sources and sinks in many affected areas worldwide. It is shown here that this is the case for As, but appears to be especially true for U, an element which increasingly finds itself in the focus of hydrogeochemical and health-related research.

Part 2 – Jurassic: Evolution, scale and impact of arsenic accumulations in ooidic iron ores from southwestern Germany

This study was published in modified form as one part of the following peer-reviewed article:

Banning, A., Rüde, T.R., 2010. Enrichment processes of arsenic in oxidic sedimentary rocks – from geochemical and genetic characterization to potential mobility. *Water Research* 44(19), 5512-5531.

It was extended and rewritten (including modified and new figures) for this dissertation.

Some preliminary results from this study were presented in modified form in the following conference contributions:

Banning, A., Rüde, T.R., 2009. Natürliche Arsenvorkommen in eisenoxidreichen Sedimentgesteinen Deutschlands – Charakterisierung und Akkumulationsprozesse. *Arsen 2009 – Verhalten von Arsen in geologischen, hydrologischen und biologischen Systemen*, September 23-24, 2009, Leipzig/Germany.

Banning, A., Rüde, T.R., 2008. Geogenic enrichment and behaviour of arsenic in iron oxides containing sedimentary rocks in Germany. 2nd International Congress on Arsenic in the Environment – Arsenic from nature to humans (As2008), May 21-23, 2008, Valencia/Spain.

Key questions

Do ooidic Fe ores show a potential for As accumulation?

Which depositional processes led to As enrichment?

What is the scale of accumulation, in absolute terms and compared to other trace elements?

Are findings concerning As distribution comparable on macro- and microscale?

Do mineralogical fractionation and present-day conditions allow for As remobilization?

2.1 Background and study area

Ooidic ores represent widespread Fe accumulations of enormous economic and scientific interest. The literature about this mainly Phanerozoic Fe ore type is extensive, well characterized occurrences are found in many parts of Europe and elsewhere, including Germany, France, Switzerland, Luxembourg, Great Britain, Czech Republic, U.S.A., Egypt, Algeria, Lybia, Nigeria, Ivory Coast, Colombia and India (Maynard 1983, Young and Taylor 1989, Schneiderhöhn 1964, James and Van Houten 1979,

Pfeifer et al. 2002, Dahayanake and Krumbein 1986, Mücke and Farshad 2005, Nahon et al. 1980, Taylor et al. 2002, Taylor 1996, Van Houten 1990, Van Houten 1992, Burkhalter 1995, Salama et al. 2008, Siehl and Thein 1978). Accordingly, much is known about ore genesis and development, mineralogical and major element composition. Nevertheless, information on trace element behaviour is scarce, the only published study (to the author's knowledge) including As determination (Siehl and Thein 1978) found partly high concentrations of up to $435 \mu\text{g g}^{-1}$ As in western European Minette-type ores (cf. chapter 2.4.1). Pfeifer et al. (2002) mention "elevated amounts" of As in Jurassic ores from Switzerland. The As enrichment mechanisms and fractionation in the rocks as well as potential environmental impact remain widely unknown which gave rise to the present study.

A prominent Middle Jurassic sedimentary profile from the Upper Rhine Graben (URG) in southwestern Germany was selected for sampling. 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. 2.1).

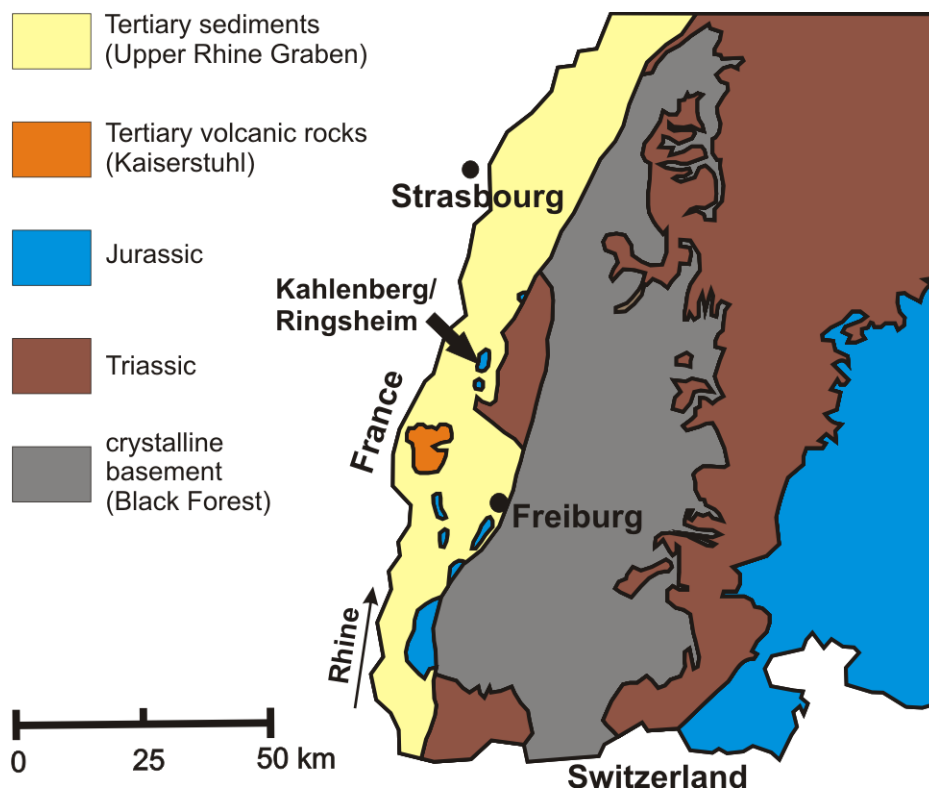


Fig. 2.1: Location and geology (modified after LGRB 1998) of the study area in southwestern Germany (Baden-Wuerttemberg, cf. Fig. 1).

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 early Tertiary and being active to date, steep marginal faults developed and the Jurassic sediments disrupted. Nowadays, they 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 near Ringsheim (~30 km north of Freiburg, mined until 1969 and today serving as a waste disposal site, Fig. 2.1), represents a prominent outcrop of the Aalenian ooidic Fe ores and was therefore chosen for sampling. Figure 2.2 shows the general and regional stratigraphic position of the sampled profile.

General stratigraphy		Regional units and thicknesses	Regional index fossils
MIDDLE JURASSIC	BAJOCCIAN	Coronaten-Schichten ~20 m	
		Sonninien-Schichten ~30 m	<i>Sonninia sowerbyi</i> <i>Hyperlioceras discites</i>
	AALENIAN	Ludwigien-Schichten ~40 m	<i>Graphoceras concavum</i> <i>Ludwigia murchinsonae</i>
LOWER JURASSIC	TOARCICAN	Opalinus-Ton ~80 m	

Fig. 2.2: Jurassic stratigraphy of the study area with the approximate position of the sampled profile highlighted by hachures, approximate unit thicknesses and index fossils relevant for regional biozone stratigraphy (cf. chapter 2.2.1) (figure produced after information from Bayer 1970, DSK 2002 and Geyer and Gwinner 2011).

2.2 Materials and methods

2.2.1 Profile description

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 and Bajocian (Figs. 2.2, 2.3). 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 (cf. Fig. 2.2).

The strata underlying the profile include clays (Opalinus-Ton containing the Toarcian-Aalenian boundary, Fig. 2.2) 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 (cf. Fig. 2.3). The ore consists of different 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 Variscan Rhenish Massif in the north (Sauer and Simon 1975). In their top part, the Ludwigen-Schichten (cf. Fig. 2.2) containing the *murchinsonae* ore include 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) (cf. Fig. 2.3). 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) (cf. Fig. 2.3) belong to the *hyperlioceras* and the *sowerbyi* zone (cf. Fig. 2.2). The Jurassic rocks in the area are covered by Pleistocene loess with a thickness of up to 10 m.

2.2.2 Methods

Bulk rock major and trace element geochemistry was assessed for all samples using 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) and total digestion ($\text{HClO}_4\text{-HNO}_3\text{-HCl-HF}$ at 240°C)

followed by analysis with ICP-OES (Varian 735ES; execution: Activation Laboratories Ltd., Ontario/Canada).

Five ore samples were ground to powder grain size in a McCrone corundum mill and their mineralogical composition was determined using a Bruker AXS D8 Advance X-ray diffractometer (XRD; operational adjustments: 40 kV, 40 mA; $2\theta=2-92^\circ$; measurements conducted at the Institute of Clay and Interface Mineralogy, RWTH Aachen University). Quantitative mineral phase analysis was accomplished applying Rietveld peak profile modelling with the software BGMN 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) at the Institute of Structural Geology – Tectonics – Geomechanics, RWTH Aachen University. 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 μm ; measurements conducted at the Institute of Mineralogy and Mineral Deposits, RWTH Aachen University). 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, cf. chapter 2.3.1. Altogether, the applied procedure consisted of six steps (Tab. 2.1). Eight samples from the sedimentary profile were involved in the sequence. The pulverized (agate mortar) solid sample (2 g) was placed in a centrifugation tube. Successively, 50 mL of each extraction reagent was added and the respective extraction procedure 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; execution: Institute of Mineralogy and Mineral Deposits, RWTH Aachen University).

Tab. 2.1: Sequential Extraction Procedure.

Fraction no.	Targeted As fraction	Extractant	Procedure	Reference
1	Exchangeable	$\text{NH}_4\text{H}_2\text{PO}_4$ (0.05 M)	16 h shaking	Wenzel et al. 2001
2	Bound to Mn-(hydr)oxides	$\text{NH}_2\text{OH-HCl}$ (0.1 M) + NH_4OAc (1 M, pH 6)	30 min shaking; wash step: NH_4OAc (1 M, pH 6), 10 min shaking	Zeien and Brümmer 1989
3	Bound to amorphous Fe-(hydr)oxides	NH_4 -oxalate (0.2 M, pH 3.25)	4 h shaking in the dark; wash step: NH_4 -oxalate (0.2 M, pH 3.25), 10 min shaking in the dark	Wenzel et al. 2001
4	Bound to crystalline Fe-(hydr)oxides	NH_4 -oxalate (0.2 M) + ascorbic acid (0.1 M), pH 3.25	30 min in a water bath (96 °C); wash step: NH_4 -oxalate (0.2 M, pH 3.25), 10 min shaking in the dark	Wenzel et al. 2001
5	Bound to sulphides	H_2O_2 (30 %) + NH_4OAc (1 M, pH 2)	3 h in a water basin (85 °C) with H_2O_2 ; subsequently 30 min shaking with NH_4OAc	Tessier et al. 1979
6	Residual	As (total) – As (sum steps 1-5)		

2.3 Results

2.3.1 Bulk rock geochemistry and mineralogy

Contents of selected elements in the sampled rocks as determined from INAA/TD-ICP analysis as well as MUNSELL sample colour characterization are shown in Tab. 2.2. Figure 2.3 illustrates the development of Fe and As as well as Fe phase fractionation in the sediment profile at the Kahlenberg.

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 ± 48.5 $\mu\text{g g}^{-1}$ (UOL: 131 ± 21 $\mu\text{g g}^{-1}$; LOL: 97 ± 11 $\mu\text{g g}^{-1}$; HEL: 133 ± 59 $\mu\text{g g}^{-1}$), in the remaining sediments at 18.0 ± 7.8 $\mu\text{g g}^{-1}$. Iron and As development with depths exhibit a close positive correlation (Fig. 2.3). Trace metals contents in the single samples are shown in Tab. 2.2.

Tab. 2.2: Whole rock geochemical results and MUNSELL colour 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 highlighted in grey were analyzed with XRD.

Layer	DL	Sample code	Fe	Ca	Al	S	As	Mn	Pb	Zn	Cu	Co	Cr	Cd	Ni	Colour
			wt.%	wt.%	wt.%	wt.%	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	MUNSELL
			0.01	0.01	0.01	0.01	0.5	1	3	1	1	1	2	0.3	1	
HK		MK_0101	1.12	9.24	3.28	<DL	19.6	325	6	47	3	7	67	<DL	17	10 YR 7/6
		MK_0102	1.16	21.5	1.71	0.02	20.1	257	6	31	3	2	39	0.4	8	10 YR 7/6
		MK_0103	1.21	27.9	1.37	0.02	10.3	413	6	10	2	<DL	21	<DL	4	10 YR 6/6
RT		MK_0201	3.34	3.15	9.76	1.39	39.9	191	15	51	23	23	106	0.4	64	N3
		MK_0202	5.20	3.15	8.62	0.54	26.2	508	12	69	19	20	98	0.5	54	5 PB 4/2
UOL		MK_0301	16.2	19.5	1.89	0.58	146	2460	17	65	11	30	93	1.6	84	10 YR 5/2
		MK_0302	11.9	21.0	2.19	0.14	116	2840	15	54	10	15	98	1.2	49	5 Y 4/2
LOL		MK_0303	11.3	17.9	3.55	0.02	107	953	13	61	8	19	136	1.1	59	5 R 3/4
		MK_0305	10.2	21.9	2.89	0.02	91.8	1100	11	59	7	19	114	1.4	50	5 R 3/2
		MK_0307	13.2	10.2	5.12	0.02	101	956	11	85	26	36	163	1.4	78	10 R 4/4
		MK_0308	12.2	13.7	3.47	0.02	103	1260	11	79	16	28	153	1.3	77	5 R 4/4
		MK_0310	10.9	19.6	2.72	0.03	79.6	1360	9	68	21	32	104	0.9	65	10 R 4/2
WS		MK_0401	2.16	5.01	3.81	<DL	18.3	560	10	25	3	8	83	0.3	22	10 YR 7/6
		MK_0403	2.17	4.34	3.73	<DL	17.9	371	9	33	2	7	85	<DL	20	10 YR 7/6
		MK_0405	1.92	3.96	4.24	<DL	14.4	575	13	66	2	8	96	<DL	22	10 YR 8/6
		MK_0408	2.59	0.57	4.77	<DL	21.3	374	32	71	3	15	93	<DL	37	10 YR 7/6
		MK_0411	2.12	3.47	3.90	0.38	14.7	487	13	31	3	9	85	0.3	20	5 Y 4/2
		MK_0412	1.55	9.60	3.90	0.32	11.1	554	17	28	3	10	82	<DL	22	10 Y 5/2
		MK_0413	1.55	12.4	3.23	0.02	10.5	515	15	20	3	3	71	<DL	10	5 Y 5/2
GM		MK_0501	2.10	2.66	4.75	0.33	11.8	365	11	39	4	7	95	0.3	24	5 B 6/1
		MK_0502	2.66	0.30	3.92	<DL	16.3	442	12	43	3	8	105	0.3	25	10 YR 7/6
HEL		MK_0601	10.5	25.0	1.27	0.03	71.7	1780	11	54	4	10	136	1.2	33	10 R 4/4
		MK_0602	16.1	19.8	1.46	0.02	97.8	1440	17	68	<DL	16	212	1.3	40	5 R 4/4
		MK_0603	19.7	12.4	1.98	0.02	103	1190	12	80	<DL	20	243	1.4	53	10 R 3/4
		MK_0604	15.6	7.01	2.54	0.02	99.8	1180	14	126	2	42	228	1.7	114	10 R 3/4
		MK_0605	28.5	6.55	3.00	0.03	212	1040	29	142	2	31	315	2.2	84	5 R 3/4
		MK_0606	13.8	23.3	1.18	0.02	63.8	1520	11	54	<DL	15	66	1.2	41	5 R 3/4
		MK_0607	20.0	20.0	1.08	0.02	78.1	1300	12	51	<DL	15	96	1.4	37	10 R 4/6
		MK_0608	25.9	11.2	2.52	0.03	173	1020	22	132	<DL	34	355	2.0	96	10 R 3/4
		MK_0609	26.6	13.5	1.98	0.03	188	1190	24	107	<DL	27	277	1.8	64	5 R 3/4
		MK_0610	32.2	5.95	2.87	0.02	223	1020	29	161	1	42	336	2.0	107	5 R 3/2
		MK_0611	25.0	14.2	2.42	0.02	156	1280	21	124	1	33	274	1.8	89	10 R 3/4

The mineralogical composition of the ooidic Fe ores was deduced from X-ray diffractograms using Rietveld analysis, Fe phase fractionation is indicated in Fig. 2.3.

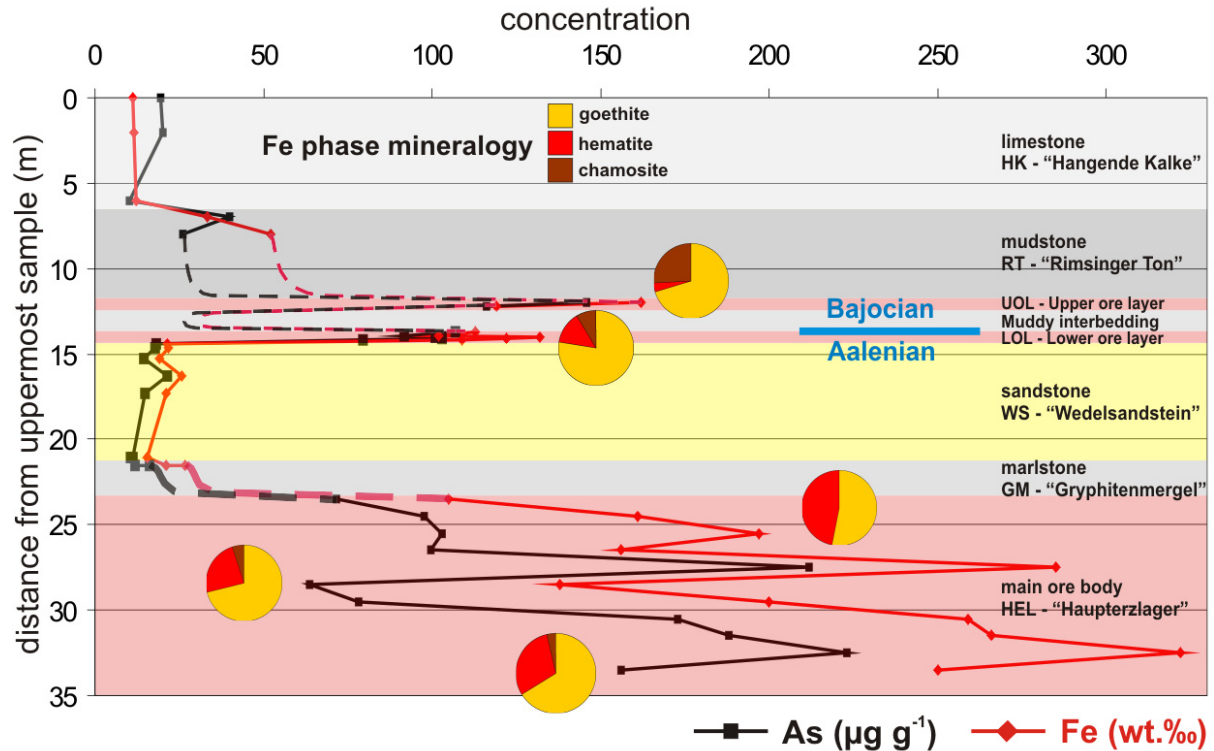


Fig. 2.3: Lithology, Fe and As contents development and Fe phase fractionation of the Jurassic profile, former quarry Kahlenberg. Dashed lines: assumed concentration curves.

Goethite (α -FeOOH) is the most important Fe host mineral in the ore layers, accounting for $67 \pm 9 \%$ 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 (α -Fe₂O₃; $23.8 \pm 16 \%$) and the Fe silicate mineral chamosite ($(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5 \text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$; $8.8 \pm 10 \%$), show much higher variabilities. Hematite is more abundant in the main ore body, while chamosite reaches significant amounts in the ore layers only (Fig. 2.3). Besides Fe host minerals, bulk ore samples contain calcite (CaCO₃) as the main matrix mineral, detrital quartz (SiO₂) and minor amounts of muscovite (KAl₂(Si₃Al)O₁₀(OH,F)₂) and microcline (KAlSi₃O₈). Dolomite (CaMg(CO₃)₂) is partly detectable, pyrite (FeS₂) is present in trace amounts in the two thinner ore layers only.

In all Fe ore thin sections, oval to nearly spherical 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 (Fig. 2.4). Sub-rounded detrital quartz grains and bioclasts are further components.

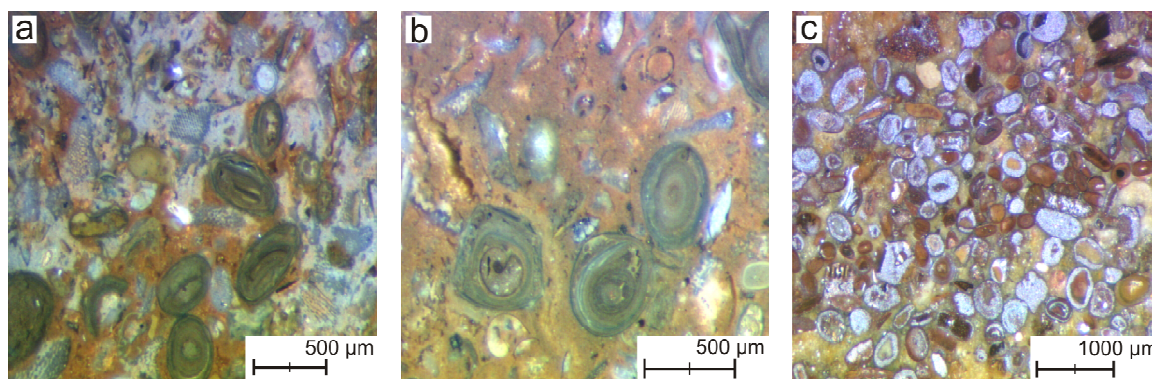


Fig. 2.4: Microscopy photographs of Jurassic Fe ores from (a) the upper ore layer, (b) the lower ore layer, (c) the main ore body.

Among the fossils found in the samples, echinoderms, especially crinoids, are most abundant (Fig. 2.4a). Additionally, gastropoda, bivalvia, bryozoa, foraminifera and one calcite-filled belemnite rostrum were observed. 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 (Fig. 2.4b). 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 (Fig. 2.4), 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 primal goethite or its precursor phases (Maynard 1983, Schwertmann et al. 1999) in HEL, compared to the thinner ore layers.

2.3.2 Electron microprobe results

Results of the chemical mapping of an ooid grain from the upper part of the main ore body conducted with energy-dispersive microprobe analysis are shown in Fig. 2.5. The general detection limit for this method is ~0.5 wt.%. The mapping area was chosen to contain all important sediment components (Fe ooids, carbonate matrix, clastic grains). For As, the resulting map was homogeneous, thus not showing any differences in As distribution. This suggests that As is present in contents <0.5 wt.% in all rock compounds.

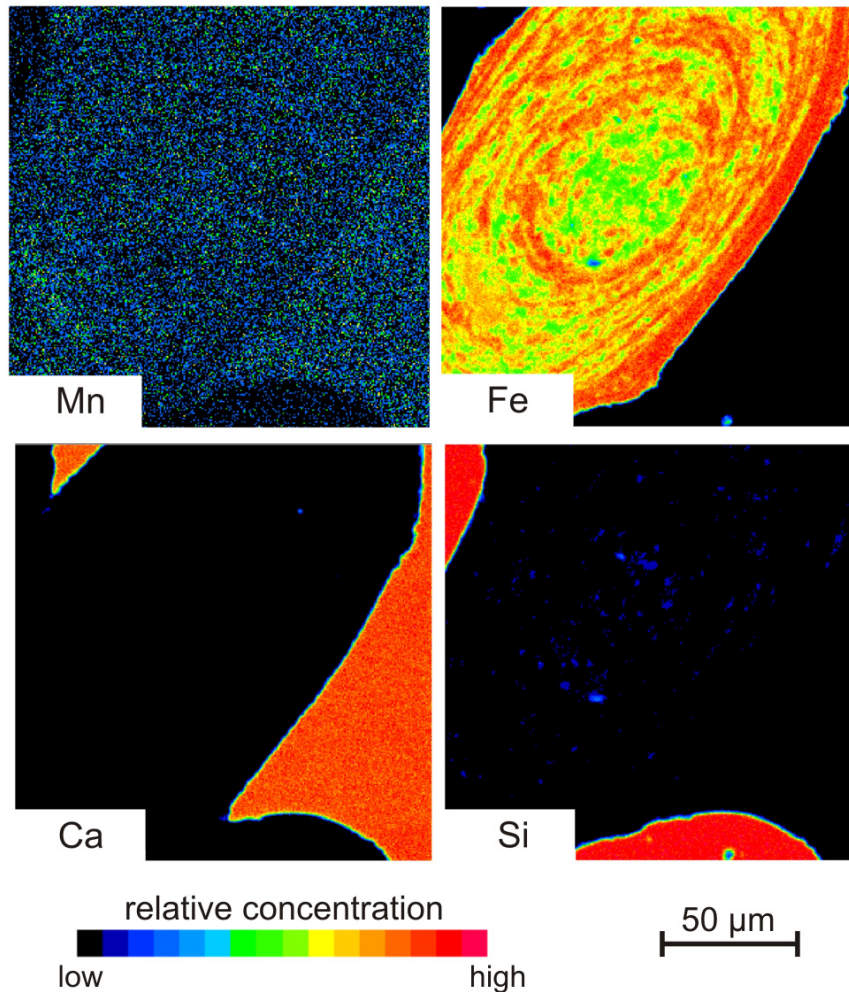


Fig. 2.5: Electron microprobe elemental mapping of an ooid in calcitic matrix (qualitative) for Mn, Fe, Ca and Si.

Element distribution maps (Fig. 2.5, cf. chapter 2.2.2) show a well-defined oval Fe ooid (Fe map) from the HEL, together with matrix material and margins of two silicate grains (Si map). Calcium is present in the matrix only. Besides the detrital grains, Si occurs in smaller amounts in some areas within the ooid. The distribution of Mn indicates its preferential presence in the matrix rather than in the ooid. Iron distribution within the ooid is not even, differences correspond to different layers of the cortex, the ooid rim seems to be particularly enriched. In the case of Fig. 2.5, 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.

To assess As contents in the ooid grains, a traverse of quantitative wavelength-dispersive single spot measurements was carried out (Fig. 2.6). Detection limit for As in this procedure was determined as $117 \mu\text{g g}^{-1}$.

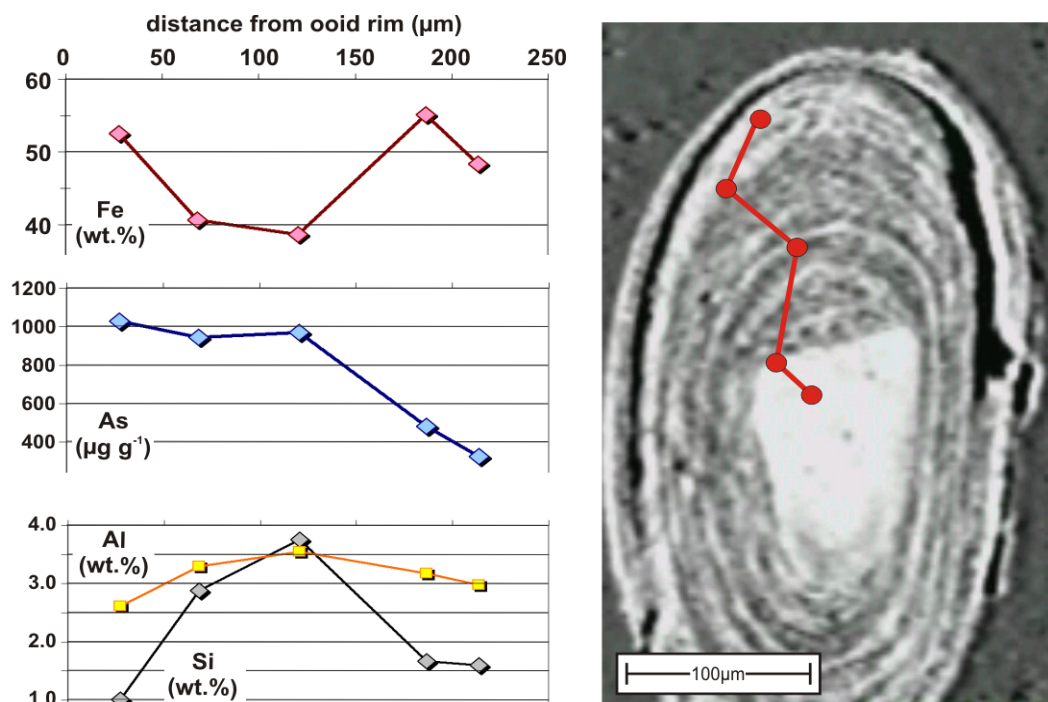


Fig. 2.6: Traverse (profile indicated in backscattered light image) of microprobe single spot chemical measurements through cortex and nucleus of an ooid with contents of Fe, As, Al and Si.

The point profile supports the findings from Fig. 2.5. 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. 2.3), As contents do not necessarily follow Fe in the grain scale. While, independent from Fe, As 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.

2.3.3 Sequential extraction results

Results of As fractionation determined by SEP are shown in Fig. 2.7.

An average proportion of $3.64 \pm 1.9\%$ As_{tot} is exchangeable (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 show similar relative proportions of 3.7 %, but absolute As amounts of only 0.8-1.5 $\mu\text{g g}^{-1}$ soluble in step 1.

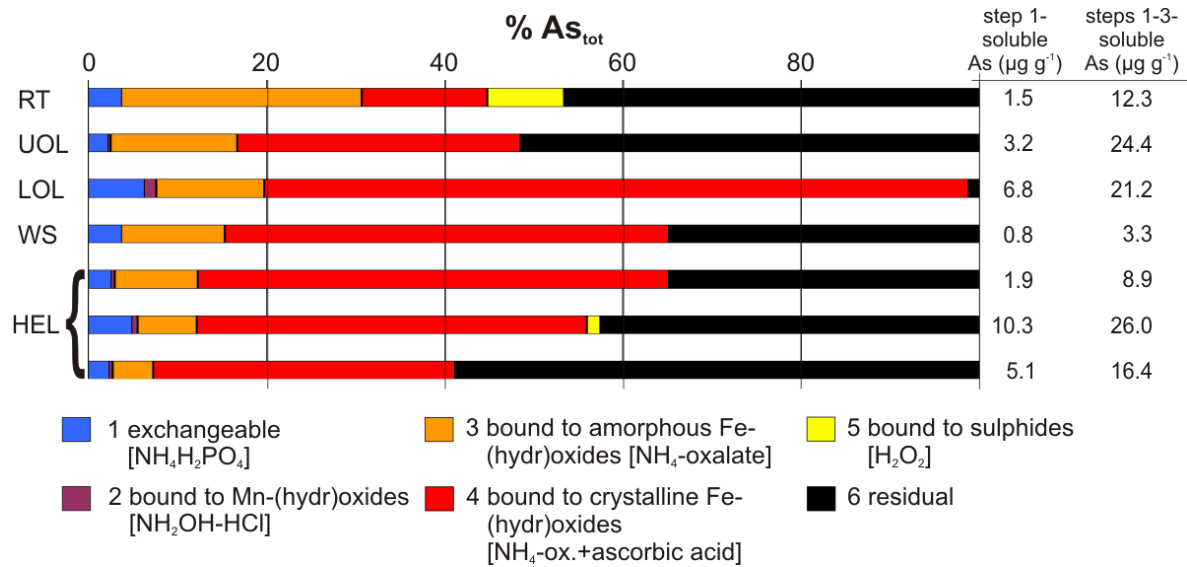


Fig. 2.7: Sequential extraction results, cf. Fig. 2.3 for layer allocation.

Arsenic bound to Mn (hydr)oxides, targeted with NH₂OH-HCl (step 2), is of minor importance (0.7 ± 0.4 % in ore layers). NH₄-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. 2.7).

2.4 Discussion

2.4.1 Geochemical characterization and timing of As accumulation

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. Overall average in 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 2.4.2.

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 Fig. 2.8 whereby the data was not normalized. Optical checks were performed for trend linearity and to eliminate extreme outliers.

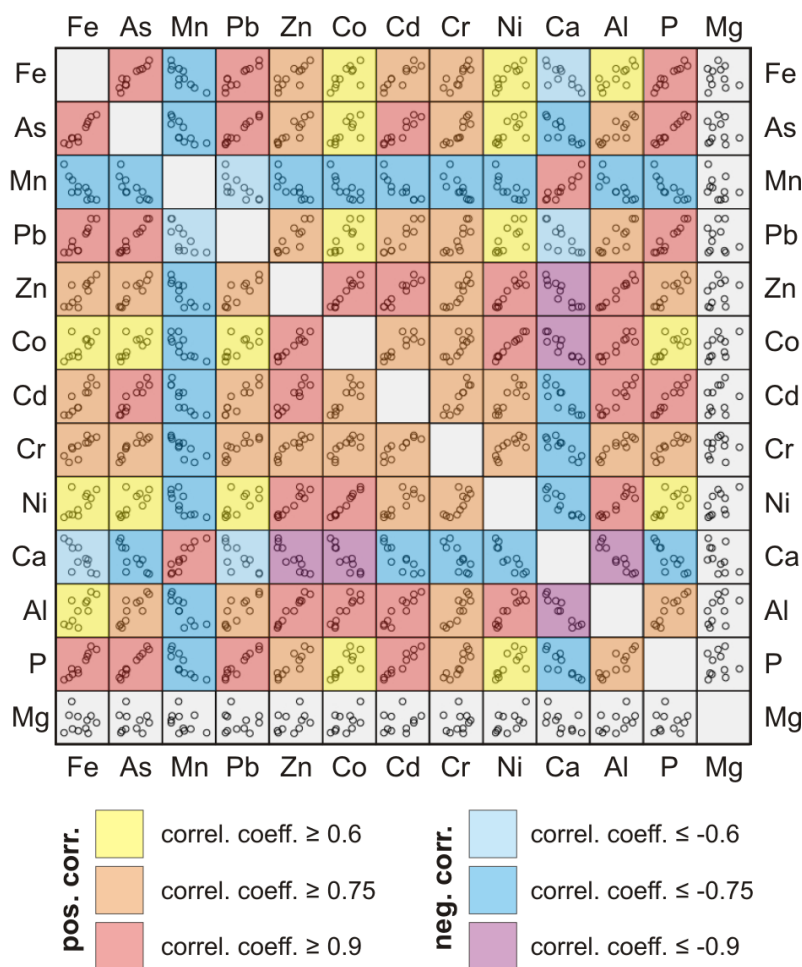


Fig. 2.8: Pearson element correlation matrix for samples from the HEL.

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. 2.8). 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 de-

grees 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. 2.5), Al and Si enrichment in the “darker” layers of the cortex (Fig. 2.6) as well as a positive Fe-Al correlation (Fig. 2.8). 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. 2.8), 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. 2.5) and the lack of As bound to Mn (hydr)oxides as suggested by SEP (Fig. 2.7). 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. 2.3).

Contrary to manganese, 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. 2.6). 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 2.3.1; 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.

2.4.2 Scale of accumulation

In order to assess the degree of As accumulation in the ooidic Fe ores 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:

$$EF = \frac{C_{sam}}{C_{ref}} \bigg/ \frac{B_{sam}}{B_{ref}}$$

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

whereby $EF < 2$ 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 (Fig. 2.8). The reference environment was defined as the average of non-ore sediments in the sedimentary profile, weighed according to their thicknesses.

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):

$$CF = \frac{C_{av}}{C_0}$$

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 Kahlenberg profile were defined as reference environment. 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.

Results for EF and CF calculations are shown in Fig. 2.9. Enrichment factors are presented for all Fe ore samples and the six most enriched trace elements, contamination 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.

With average EF of 0.8 and 1.4, respectively, Cu and Pb show no enrichment in the Fe ores. Cadmium was 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 (2.1), Ni (2.2), Co (2.3) and Cr (2.4) 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=3.9), highest values are reached in the UOL. However, As is the most enriched element, yielding an average EF of 6.4 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 ($\emptyset$ UOL=7.5, $\emptyset$ LOL=5.0), 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 2.4.1), and thus only regarding elements hosted in Fe ooids, As 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. 2.9, pie chart).

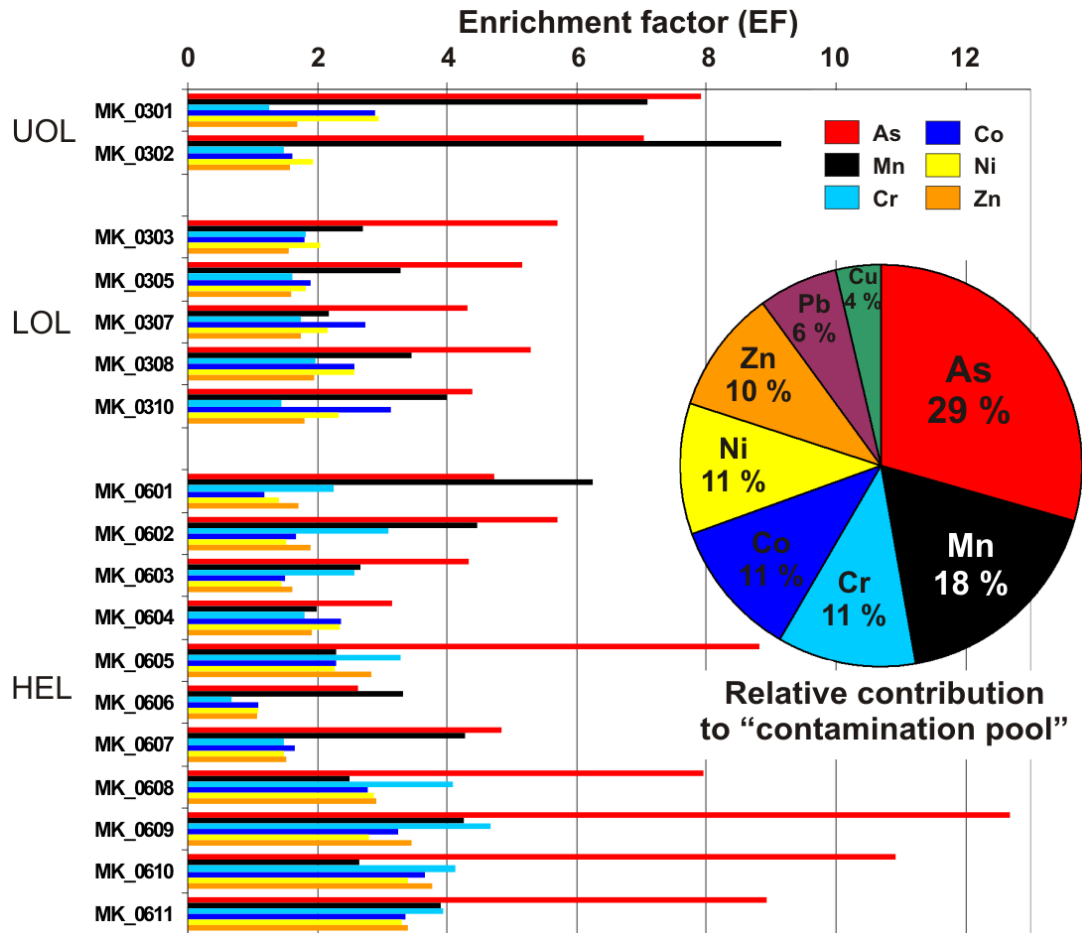


Fig. 2.9: Enrichment Factors of 6 elements for Jurassic Fe ore samples. Pie chart: single element contribution to total "contamination pool" (cf. Fig. 2.3 for layer allocation).

2.4.3 Implications for potential As remobilization

Presently, groundwater milieu around the former quarry Kahlenberg is oxidizing and circumneutral in pH (~ 7.2). The Ca-HCO_3 type groundwater exhibits background Fe and As concentrations of $\sim 0.01 \text{ mg L}^{-1}$ and $\sim 0.2 \text{ } \mu\text{g L}^{-1}$, respectively (LGRB 2001, LGRB 2009). An artificial lake, located $\sim 1 \text{ km}$ downstream of the quarry in highly conductive Quaternary gravels ($K = 1 \cdot 10^{-2} - 1 \cdot 10^{-3} \text{ m/s}$) is in proven hydraulic contact with the Jurassic Fe ores. Nevertheless, transport of As or other potential 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. Average exchangeable ($\text{NH}_4\text{H}_2\text{PO}_4$ -soluble) As was calculated for UOL, LOL and HEL, applying thickness-weighted mean values, to be $4.8 \text{ } \mu\text{g g}^{-1}$ and thus plotting in an inconspicuous range. Assuming a change to reducing redox conditions, the average short- to medium-term mobilizable As amount (steps 1-3) would be $15.9 \text{ } \mu\text{g g}^{-1}$. With an average density of 3.3 g cm^{-3} (calculated for 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 2.4.1), 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 (see above). 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.

2.5 Conclusions

A syndepositional and therefore primary As accumulation process has been identified in Jurassic shallow marine ooidic Fe ores (Aalenian/Bajocian) of the Upper Rhine Graben, southwestern Germany. The primal As input into the study area occurred during terrestrial weathering of Variscan mainlands (first-order source) whereby As supply and/or degree of enrichment favourability varied in time on both outcrop and single grain scales.

Elevated As contents developed in mainly goethite ooids slowly forming during condensed sedimentation under mainly oxidic conditions, thereby continually offering reactive surfaces for accumulation. These ooids represent first-order As sinks and at the same time, potential second-order sources. The accumulation process favoured As enrichment over other contaminants, underlining preferential As sorption on Fe hydroxides. In spite of high bulk As in ooidic ores, the potential for remobilization and output into groundwater is considered to be rather limited.

The obtained results and interpretations are of global relevance as this study represents the first detailed geochemical and genetic characterization of As occurrence in ooidic Fe ores which exhibit enormous abundance worldwide.

Part 3 – Cretaceous: Arsenic in paleo redox events, case I – Münsterland Cretaceous Basin

Some preliminary results from this study were presented in modified form in the following conference contribution:

Banning, A., Rüde, T.R., 2010. Impact of paleo redox processes on arsenic distribution and mobility in sediments. 3rd International Congress on Arsenic in the Environment – Arsenic in geosphere and human diseases (As2010), May 17-21, 2010, Tainan/Taiwan.

Key questions

Which processes lead to the extremely heterogeneous As distribution in near-surface sediments?

Which carrier phases control As distribution below and above the paleo redox boundary?

What happens in the zone of redox transition in terms of As occurrence and reactivity?

Which role do siderite concretions play for As dynamics in the given geo-environment?

Is As remobilization potential comparable in different redox facies and positions in the basin?

3.1 Introduction and study area

Elevated As concentrations are known in gleys from the western Münsterland. Included in these soils, Peronne (2003) found up to 565 $\mu\text{g g}^{-1}$ As in subrecent limonitic bog iron ores formed through groundwater oscillation. Banning et al. (2009) identified hydroxidic Fe concretions occurring within the unconsolidated upper part of the Santonian Haltern-Schichten as the geogenic sources of As in the area. These concretions formed during terrestrial weathering processes under tropical-warm and wet conditions in late Tertiary times (Braun 1969, GLA NRW 1995) leading to the oxidative mobilization of Fe from primarily reduced phases and its accumulation in the oxidized near-surface section. Dahm-Arens (1972) suggested the latter to take place in oxidizing groundwater, making the concretions representatives of paleo groundwater tables. This was supported by Banning (2008) by geochemical, mineralogical and genetic comparison to recent bog iron ore environments. Based on the results of the mentioned study and those of Banning et al. (2009), the name “paleo bog iron ores” (PBIOs) was suggested for the concretions which were subdivided into 5 types depending on differences in mineralogy, geochemistry and Fe hydroxide ageing level. Selected PBIO samples and their As concentrations are shown in Fig. 3.1 (cf. also Fig. 3.4 for PBIO spatial distribution in the area).

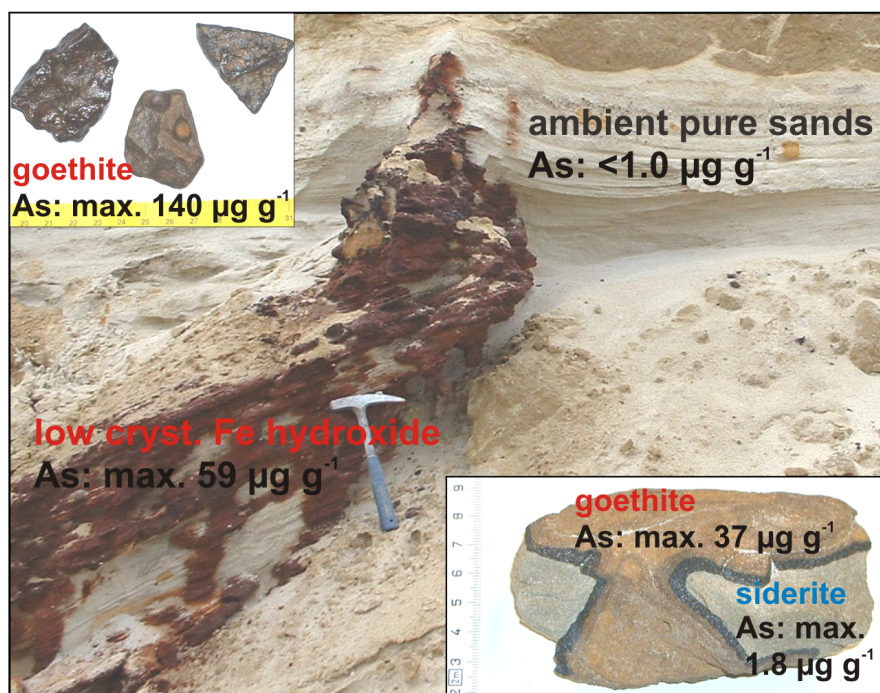


Fig. 3.1: Different types of oxidic Fe concretions (PBIOS) occurring in otherwise pure quartz sand of the Haltern-Schichten with respective Fe phase mineralogy and maximum As concentrations (modified after Banning 2008 and Banning et al. 2009).

Iron hydroxide PBIOS exhibit distinct enrichment of Fe (up to 29.5 wt.%) and As (up to $140 \mu\text{g g}^{-1}$), compared to ambient quartz sands while siderite concretions (up to 14.1 wt.% Fe) do not appear as As hosts (Fig. 3.1, Banning et al. 2009). It was speculated in this earlier study that As in PBIOS, likewise Fe, originally derived from reduced mineral phases of the primary calcitic and glauconitic facies of the Haltern-Schichten in the subsurface (the so-called Wulfen Facies) and was mobilized, transported and accumulated in the course of the paleo redox event, i.e. the Tertiary oxidative weathering process. To assess this hypothesis, a characterization of the reduced facies and especially the paleo redox boundary would be necessary. Nevertheless, at that time, no sample material was available for analysis since outcrops of the Wulfen Facies are not known and the depth of the paleo redox boundary was described as 60-70 m below ground surface (Braun 1969) leading to dependence from boreholes to obtain these sediments. Recently, it was possible to take samples from a 128 m deep research borehole constructed by the Geological Survey of North Rhine-Westphalia near the municipality of Nordvelen, ~10 km southeast of Stadtlohn (Figs. 3.2, 3.4). Furthermore, two boreholes from the vicinity of Flaesheim, ~10 km southeast of Haltern (Figs. 3.2, 3.4), containing the paleo redox boundary within the Haltern-Schichten, could be sampled by courtesy of Quarzwerke Frechen. It was then possible to characterize the primary reduced facies of the Santonian sediments, study As occurrence and behaviour, and derive possible mobilization and reaccumulation mechanisms.

The study area is located in the western part of the Münsterland Cretaceous Basin, a syncline structure filled with marine Cretaceous sediments on Variscan basement, north of the Rhenish Massif. The sampled Haltern-Schichten of Santonian age cover an area of $\sim 770 \text{ km}^2$ with a thickness of up to 300 m (GLA NRW 1995, Grabert 1998, Voigt et al. 2007; Fig. 3.2).

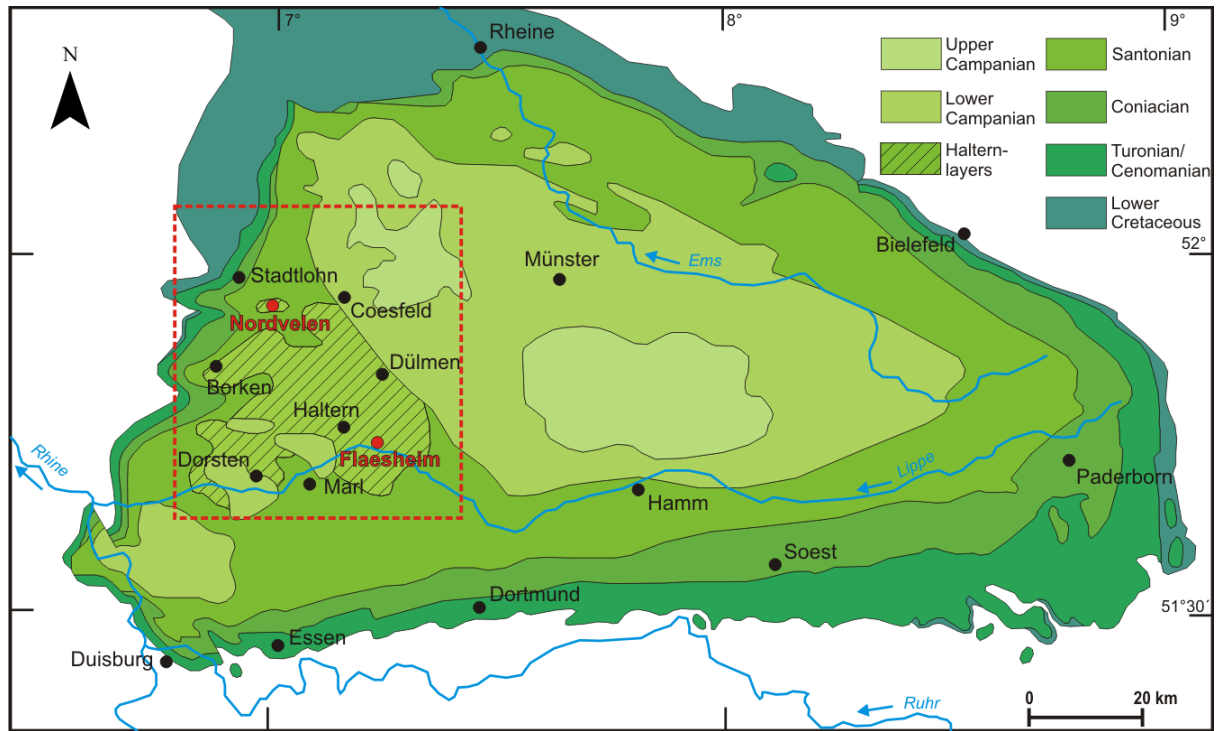


Fig. 3.2: Geology of the Münsterland Cretaceous Basin (modified after GLA NRW 1995), distribution of the Haltern-Schichten (after M. Hiss, GLA NRW, pers. comm.), location of the studied boreholes (red dots) and location of the area shown in Fig. 3.4 (red dotted rectangle). See Fig. 3.3 for stratigraphical allocation of the illustrated units.

The Haltern-Schichten were deposited under shallow marine conditions (water depths: 40 to 60 m, cf. chapter 3.3.1), their sandy character documents proximity to the provenance area, probably Variscan mainlands in the northwest, e.g. the Winterswijk anticline (Kaeffer and Lommerzheim 1991). This marginal character is in contrast to the otherwise widely carbonatic succession in the basin (Arnold 1964). The secondary alteration of the primary reduced facies under terrestrial conditions during the Tertiary is described above, it left the near-surface oxidized section as rather unconsolidated, pure quartz sands. Figure 3.3 illustrates the stratigraphical position of the Haltern-Schichten in the context of the Upper Cretaceous geology in the southwestern Münsterland.

General stratigraphy		Regional units
UPPER CRETACEOUS	CAMPANIAN	Baumberge-Schichten
		Coesfeld-Schichten
		Holtwick-Schichten
		Dülmen-Schichten
	SANTONIAN	Haltern-Schichten
		Recklinghausen-Schichten
	CONIACIAN	Emscher-Mergel
	TURONIAN	Soest-Grünsand
		Bochum-Grünsand
	CENOMANIAN	Essen-Grünsand

Fig. 3.3: Upper Cretaceous stratigraphy of the study area with the sampled unit highlighted by hachures (figure produced after information in GLA NRW 1995).

The distribution of the Haltern-Schichten and the PBIOS occurring therein after Dahm-Arens (1972) is illustrated in Fig. 3.4. Due to their hardness in comparison to the unconsolidated ambient sands, the abundant Fe concretions shape the region's morphology and are responsible for the naming of some locations therein, e.g. the city of Borken received its name from the German word "Borke" (meaning bark or crust), referring to the Fe crusts in the sediments.

The pure quartz sands are in demand by especially the glass industry and therefore excavated in several locations. Nevertheless, the Haltern-Schichten also play a major role in the drinking water supply of a large area in western North Rhine-Westphalia, they represent the most important groundwater reservoir in Westphalian Cretaceous sediments (Birk 1981). Hydrochemically, this groundwater is widely characterized as Ca-HCO_3 or $\text{Ca-HCO}_3\text{-SO}_4$ type (Birk 1981). It is generally oxidizing and circumneutral in pH, although reducing and acid groundwater with high Fe content occurs locally (Banning 2008). Also heavy temporal fluctuations of the groundwater redox milieu in the area were observed (Banning et al. 2009). Groundwater As concentrations exceeding $10 \mu\text{g L}^{-1}$ are not documented for this aquifer. Nevertheless, Heinrichs and Udluft (1996) reviewed As contents in German groundwater and found that values $>5 \mu\text{g L}^{-1}$ in Cretaceous sediments from North Rhine-Westphalia mainly occur in the Haltern-Schichten. Banning et al. (2009) detected a maximum of $8 \mu\text{g L}^{-1}$ As.

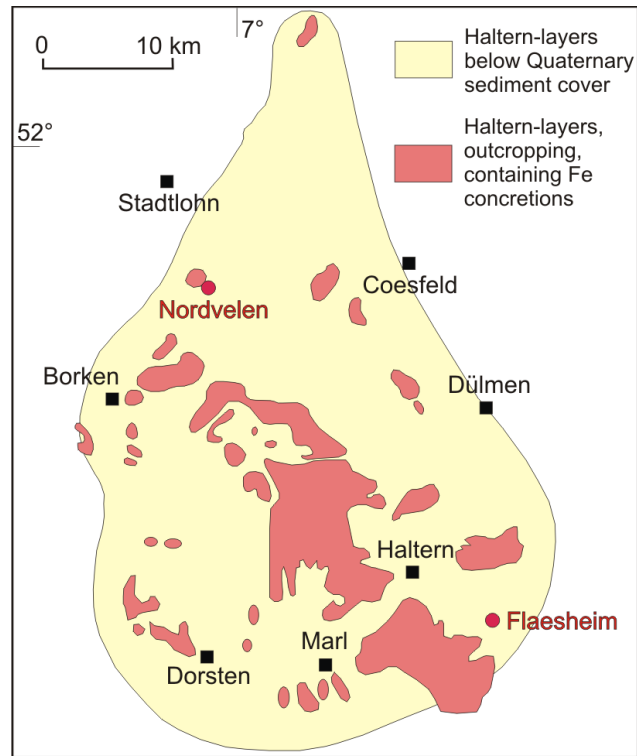


Fig. 3.4: Distribution area of the Haltern-Schichten, and oxidic Fe concretions included therein, in the western Münsterland Cretaceous Basin (modified after Dahm-Arens 1972), and location of the studied boreholes (red dots).

These findings – major importance of the aquifer for water supply and elevated groundwater As contents therein (though not observed in excess of the standard value until now) and in soils, abundant high-As Fe concretions within the aquifer as well as its heterogeneity in physico-chemical conditions arguing for the possibility of temporal As release – underline the necessity of understanding the structure of As sources and sinks in the area.

3.2 Materials and methods

From the borehole near Nordvelen in the northwestern distribution area of the Haltern-Schichten (Figs. 3.2, 3.4), a total of 23 samples were included in this study covering a depth range from 5.5 to 127.6 m below ground surface (cf. Fig. 3.5). Greyish reduced (9 samples) and yellowish oxidized (4 samples) sands were considered as well as eye-catching concretionary sections, obviously rich in Fe(II) mineral phases whose surfaces altered very rapidly in contact with air, resulting in a colour change from greyish-greenish to orange which indicates oxidation to Fe(III) (7 samples) (cf. Fig. 3.6b). Three samples were taken from around the optical transition from reduced to oxidized conditions (cf. Fig. 3.6a). The material was sealed in gastight PE bags and stored in the dark until analysis.

Two additional boreholes near Flaesheim in the southeastern distribution area of the Haltern-Schichten (Figs. 3.2, 3.4) were sampled, a total of 15 samples were obtained. The boreholes were constructed in a distance of around 500 m from each other in the vicinity of an active sand pit. The aim was to meet the paleo redox boundary in these boreholes. Therefore, sampling was arranged around a distinct sediment colour change in the first borehole (Flaesheim 1), 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 material was also sealed and stored likewise the Nordvelen borehole. Nevertheless, it must be acknowledged that long-term storage of the samples (archived by Quarzwerke Frechen) was rather not under air exclusion such that partly oxidation of primarily reduced material cannot be ruled out.

Bulk rock geochemistry was assessed for all sediment samples using INAA/ICP-OES (execution: Activation Laboratories Ltd., Ontario/Canada). Six samples from the Nordvelen borehole were selected for XRD measurement (conducted at the Institute of Clay and Interface Mineralogy, RWTH Aachen University) followed by Rietveld analysis for phase quantification. Instrumentation, sample preparation and procedure were according to the description in part 2 of this work. A sequential extraction procedure (SEP) was carried out for eight samples (six from the borehole Nordvelen, two from one of the Flaesheim boreholes). Step compilation, sample preparation and processing were similar to the procedure developed for the samples described in part 2 of this work, unless in the present study, the step targeting Mn-(hydr)oxides was omitted, only 1 g of sample instead of 2 g were used (nevertheless, a solid-solution ratio of 1:25 was maintained), and no wash steps were included after steps 2 and 3. Arsenic determination (graphite furnace AAS) in extraction solutions was performed at the Institute of Mineralogy and Mineral Deposits, RWTH Aachen University. The applied SEP is summarized in Tab. 3.1.

Tab. 3.1: Applied sequential extraction procedure (SEP).

Fraction no.	Targeted As fraction	Extractant	Procedure	Reference
1	Surface-bound	NH ₄ H ₂ PO ₄ (0.05 M)	16 h shaking, 20 °C	Wenzel et al. 2001
2	Bound to amorphous Fe-(hydr)oxides	NH ₄ -oxalate (0.2 M, pH 3.25)	4 h shaking in the dark	Wenzel et al. 2001
3	Bound to crystalline Fe-(hydr)oxides	NH ₄ -oxalate (0.2 M) + ascorbic acid (0.1 M), pH 3.25	30 min in a water bath (96 °C)	Wenzel et al. 2001
4	Bound to sulphides	H ₂ O ₂ (30 %) + NH ₄ OAc (1 M, pH 2)	3 h in a water basin (85 °C) with H ₂ O ₂ ; subsequently 30 min shaking with NH ₄ OAc	Tessier et al. 1979
5	Residual		As (total) – As (sum steps 1-4)	

3.3 Results and discussion

3.3.1 Northwestern Santonian sediments (Nordvelen borehole)

A summary of Fe and trace element concentrations for the Nordvelen borehole, distinguished by sample groups, is given in Tab. 3.2.

Tab. 3.2: Statistics on Fe and selected trace element concentrations in the studied sediments from the borehole near Nordvelen.

	Fe wt. %	As µg g ⁻¹	Mn µg g ⁻¹	Pb µg g ⁻¹	Zn µg g ⁻¹	Cr µg g ⁻¹	Ni µg g ⁻¹	U µg g ⁻¹	V µg g ⁻¹
DL	0.01	0.5	1	3	1	2	1	0.5	2
Oxidized sands (n=4)									
min	0.37	3	8	3	7	15	2	<DL	29
max	0.71	10	26	5	11	72	4	1	51
mean	0.58	5	14	4	9	32	3		37
median	0.61	4	12	4	9	21	3		33
Redox transition zone (n=3)									
min	0.86	61	16	10	11	27	4	0.8	69
max	1.64	73	26	16	32	83	14	1.6	150
mean	1.14	68	21	13	24	49	9	1.2	110
median	0.93	70	21	12	30	37	8	1.3	110
Reduced sands (n=9)									
min	0.25	5	14	<DL	9	15	3	<DL	31
max	1.30	39	38	9	78	117	15	1.6	65
mean	0.74	15	19	5	29	39	8	0.8	50
median	0.60	8	16	4	19	29	7	0.8	50
Siderite concretions (n=7)									
min	5.75	8	474	<DL	11	34	5	1.4	33
max	19.4	19	1360	15	62	66	20	7.5	94
mean	12.4	13	974	8	27	51	11	4.0	56
median	12.4	12	1020	10	22	51	9	3.8	56

Figure 3.5 illustrates a simplified lithological profile of the Nordvelen borehole and development of Fe, As and S concentrations with depth. Iron phase mineralogy as obtained from XRD analysis is also presented.

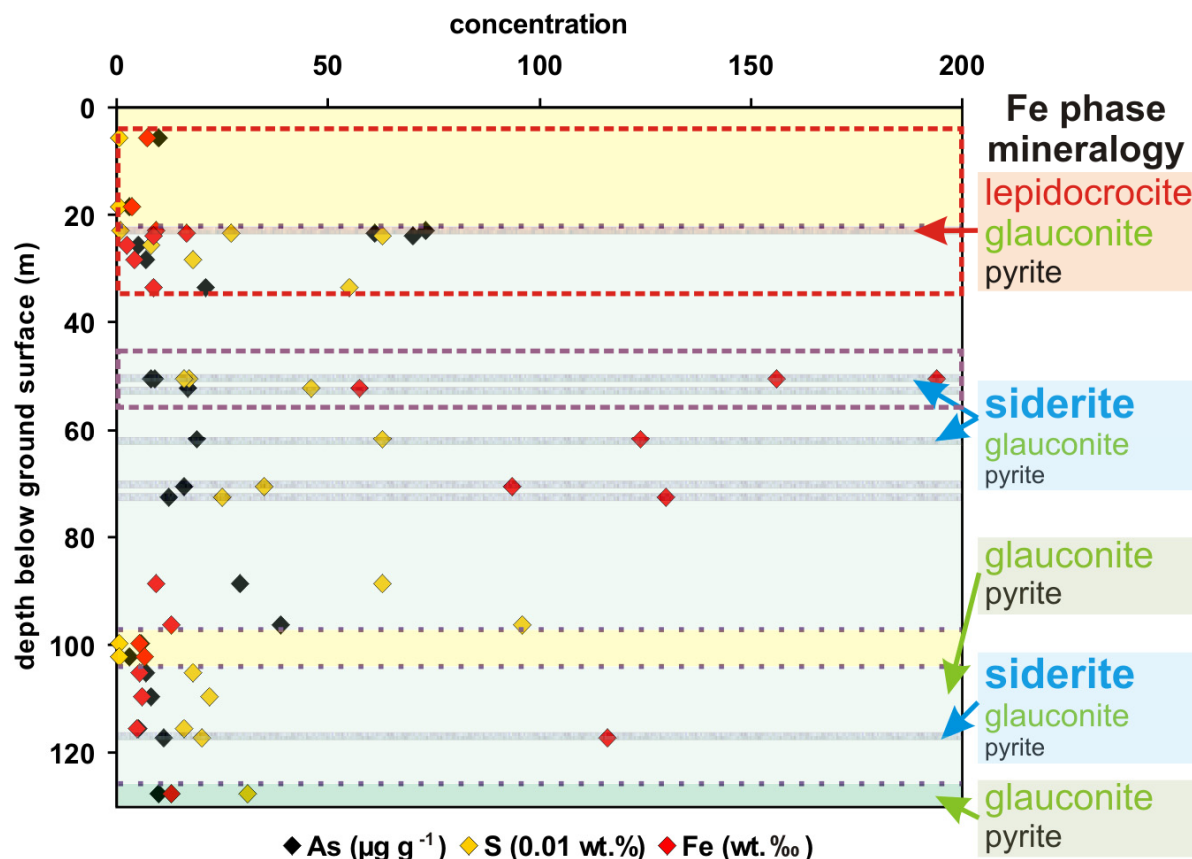


Fig. 3.5: Lithological and geochemical (As, S, Fe) profile of the borehole from Nordvelen (cf. Fig. 3.2) where yellowish and light bluish colours indicate oxidized and reduced sections, respectively, while light green represents glauconitic bottom sands, darker bluish layers the positions of siderite concretions and the reddish one that of a Fe hydroxides containing layer. Locations of the more detailed Figs. 3.6a and 3.6b are indicated by red and purple dotted rectangles, respectively. Iron phase mineralogy is shown on the right side with minerals ordered by abundance obtained from Rietveld analysis following XRD.

Iron(II) concretions with median Fe concentration of 12.4 wt.% occurring within the reduced sands of the profile turned out to be mainly composed of siderite [FeCO_3] with an average proportion of 27.2 wt.%. Like Jurassic marine siderite concretions studied by Hounslow (2001), these are likely to have developed during burial and compaction, i.e. 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 Santonian sediments described by Banning (2008) (cf. Fig. 3.1). While no siderite was detected in the other reduced samples, the presence of glauconite $[(\text{K},\text{Na})(\text{Fe},\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2]$ 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 (2001). Concerning As uptake potential, each of the three identified reduced Fe phases is a candidate. A literature discussion on this topic is given in part 4, chapter 4.4.1, of the present work. Besides glauconite and pyrite, the Fe oxyhydroxide

lepidocrocite [γ -FeOOH] was detected in an orange sample from the zone of redox transition from reducing to oxidizing at 23.5 m below ground surface (cf. Figs. 3.5, 3.6a). The presence of lepidocrocite is associated with temporally changing redox conditions in the subsurface, the mineral occurs as weathering product of pyrite (Smeck et al. 2002). Lepidocrocite is known as an effective As adsorbent, especially in slightly acid to circumneutral conditions (Bowell 1994). 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, lithologically representing the largest part of the profile (Fig. 3.5), an As concentration of $15 \pm 12 \mu\text{g g}^{-1}$ with a maximum of $39 \mu\text{g g}^{-1}$ was detected. Compared to that, the siderite concretions ($13 \pm 4 \mu\text{g g}^{-1}$) do not show any tendency towards As accumulation while mean values of Fe and Mn are enriched by factor 17 and 50, respectively. Like for As, no significant enrichment of other trace elements was observed with the exceptions of Mn and U (factor 5) (Tab. 3.2). While high Mn contents in siderite concretions are attributable to a significant proportion of MnCO_3 in these inclusions (Hounslow 2001), U(VI) can be immobilized at the siderite surface by incorporation in Fe precipitates with subsequent reduction to U(IV) (Ithurbide et al. 2009). 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). High As contents ($61\text{-}73 \mu\text{g g}^{-1}$) 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. 3.6a). Oxidized yellowish sands in the profile are depleted in Fe and all trace elements (As: $5 \pm 3 \mu\text{g g}^{-1}$) in comparison to the reduced section and especially the redox transition zone (Tab. 3.2, Fig. 3.5), S is generally below the detection limit, i.e. <0.01 wt.%. This observation argues for component mobilization and evacuation processes during the paleo redox event. It is noteworthy that the homogeneous oxidized sandy horizon occurring at around 100 m depth below ground surface (Fig. 3.5), being hardly explainable by the paleo redox model developed here, turned out to represent subaerial (beach facies) deposits (B. Dölling, GLA NRW, pers. comm.). These 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, indicating paleo sea level variations and further supporting the paleogeographical configuration described in chapter 3.1.

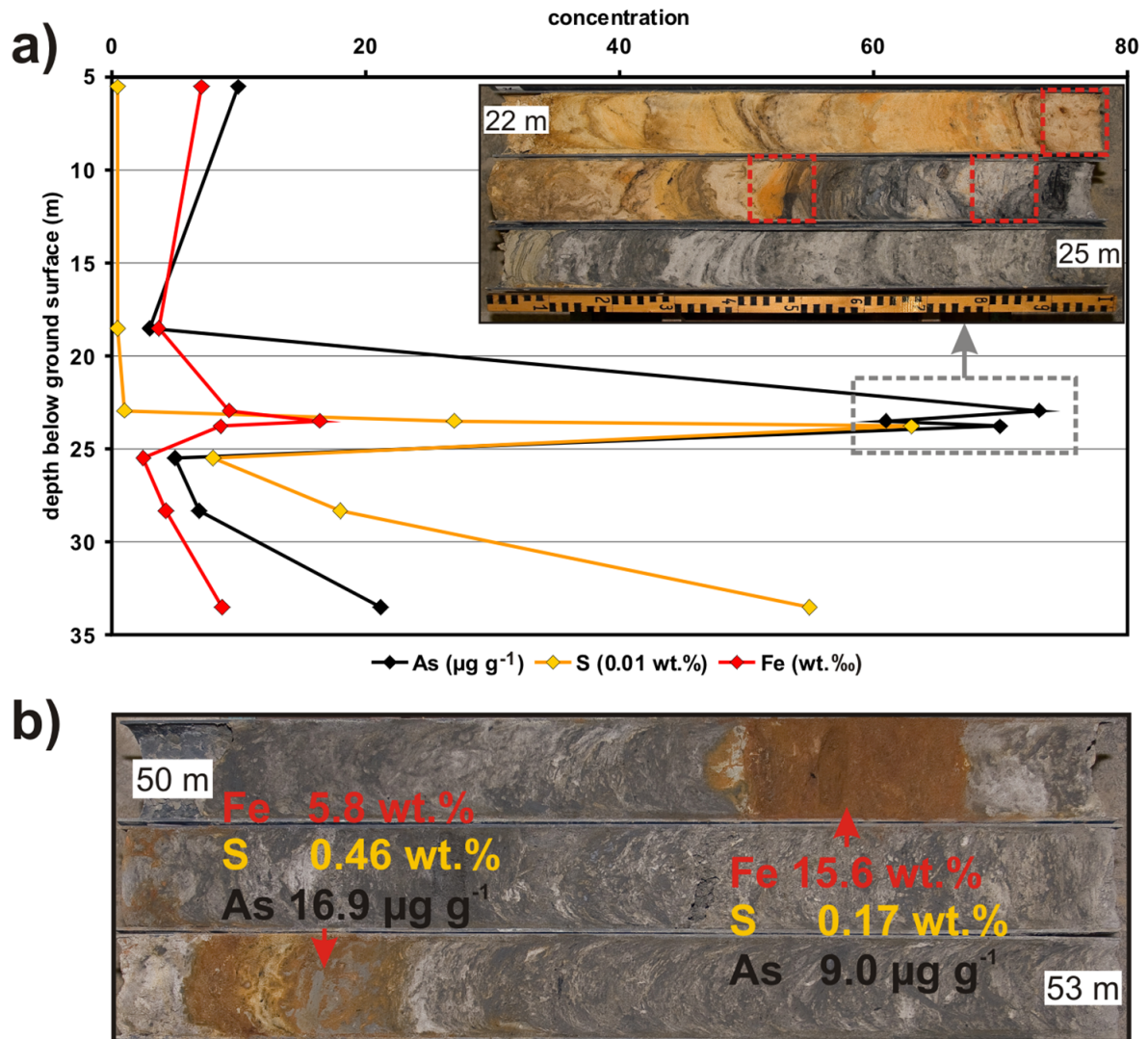


Fig. 3.6: Detail sections from the Nordvelen borehole (cf. Fig. 3.5). (a) Geochemical profile (As, S, Fe) around the redox transition zone, inset upper right side: core photograph of the redox transition zone with red dotted rectangles indicating the position of analyzed samples in the profile (grey dotted rectangle). (b) core photograph from 50-53 m below ground surface, containing two siderite concretions (rapidly oxidized) with respective concentrations of Fe, S and As therein (photographs: Geological Survey of North Rhine-Westphalia).

The optically sharp redox boundary between greyish and yellowish fine sands (Fig. 3.6a, photograph inset) is also expressed in the geochemical profile (Fig. 3.6a, diagram). Concentrations of As, S and Fe develop parallelly in the reduced sediments, As and S reach peak values ~30 cm below the optical 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 lepidocrocite formation and Fe_{tot} accumulation, whereby the majority of As is probably retained by the Fe hydroxide. Its coexistence with pyrite and glauconite

(Fig. 3.5) indicates that sediment oxidation at this point is incomplete. Sulfur content 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 parallelly to Fe (Fig. 3.6a) while S is <0.01 wt.%. Obviously, a change of As-controlling host phases from Fe sulfides 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 may 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 *in situ* Fe hydroxide formation (“autochthonous” concretions) can be considered in addition to the precipitation of “allochthonous” Fe hydroxides from groundwater (PBIOS). With respect to the generally considerably 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.

Comparison of two of these concretions between 50 and 53 m below ground surface (Fig. 3.6b) illustrates that higher As concentrations prevail in the lower Fe concretion, together with higher S content, indicating sulfide-controlled rather than carbonate-controlled As behaviour. To check this assumption for the whole reduced section (accounting for more than $\frac{3}{4}$ of the total profile, Fig. 3.5), correlation analysis of As vs. S and Fe were conducted for greyish fine sands and siderite concretions (Fig. 3.7).

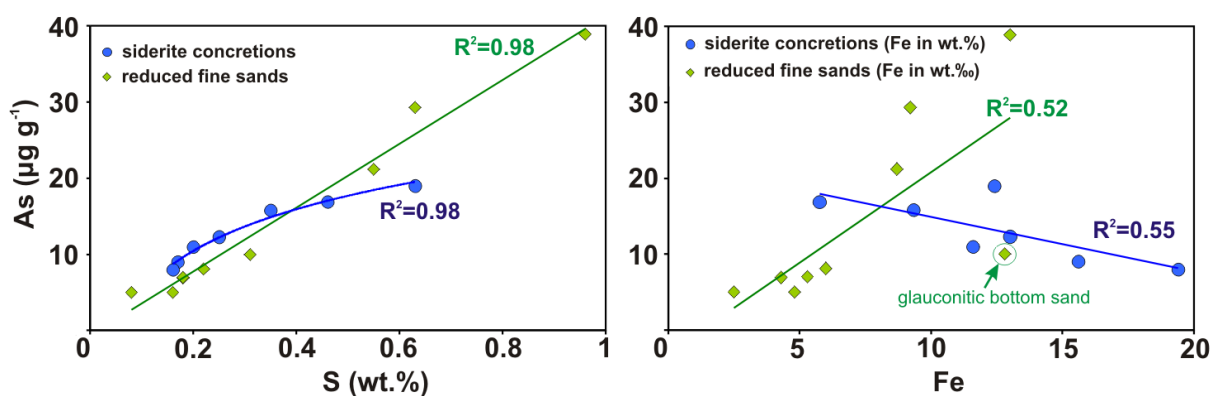


Fig. 3.7: Scatter plots of S vs. As (left side) and Fe vs. As (right side) for reduced sands and siderite concretions from the Nordvelen borehole. Note differing Fe units in the right diagram (see legend).

Both the reduced fine sands and the siderite concretions therein exhibit a close positive correlation between As and S (each $R^2=0.98$) 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. Especially the glauconitic sand at the bottom of the profile (cf. Fig. 3.5) represents an outlier with excess Fe (Fig. 3.7). 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 the by far dominant Fe carrier in the concretions, siderite obscures a visible $\text{Fe}_{\text{pyrite}}$ -As interrelation. Assuming bulk As hosting in pyrite, average $\text{As}_{\text{pyrite}}$ 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.

3.3.2 Southeastern Santonian sediments (Flaesheim boreholes)

A summary of Fe and trace element concentrations for the Flaesheim boreholes, differentiated by redox milieu, is given in Tab. 3.3.

Tab. 3.3: Statistics on Fe and selected trace element concentrations in the studied sediments from the two Flaesheim boreholes.

	Fe wt. %	As $\mu\text{g g}^{-1}$	Mn $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	Cr $\mu\text{g g}^{-1}$	Ni $\mu\text{g g}^{-1}$	U $\mu\text{g g}^{-1}$	V $\mu\text{g g}^{-1}$
DL	0.01	0.5	1	3	1	2	1	0.5	2
Oxidized sands (n=11)									
min	0.14	0.8	19	<DL	5	25	1	<DL	18
max	0.49	10.3	36	4	15	33	4	0.8	47
mean	0.33	4.3	27	3	10	30	3	0.5	27
median	0.37	4.0	26	3	10	30	2	0.5	24
Reduced sands (n=4)									
min	0.36	6.3	26	4	8	27	3	<DL	19
max	0.44	14.3	38	4	17	32	4	0.6	24
mean	0.40	8.5	32	4	11	30	4	0.5	22
median	0.40	6.7	31	4	10	30	4	0.5	22

A relatively homogeneous Fe and trace element distribution is observable in the reduced layers. However, As shows a significant range (6.3-14.3 $\mu\text{g g}^{-1}$). The values are well comparable to those from the reduced zone of the Nordvelen borehole (Tab. 3.2), albeit generally slightly lower. Trace element and Fe concentrations in the oxidized sands are very similar to the reduced material on average but exhibit higher variability. Only As is significantly depleted (factor 2) which is in agreement with the findings from Nordvelen. Therefore, apart from the absence of concretionary sections and a high-As redox transition zone in Flaesheim, a rather homogeneous Fe and trace element distribution can be assumed in non-concretionary sections of the Santonian sediments. Higher concentrations and variabilities in

Nordvelen can be explained by a more proximal position with regard to the paleo coastline in the northwest (cf. chapter 3.1), leading to fluctuating terrestrial input and changing trace element incorporation into the sediments, while the more distal area around Flaesheim rather received a more stable “background” amount of trace elements which were not immobilized in the shallower facies.

Figure 3.8 illustrates a geochemical profile of the borehole Flaesheim 1 with development of As, S, Fe and Ca concentrations with depth and an impression of sediment appearance.

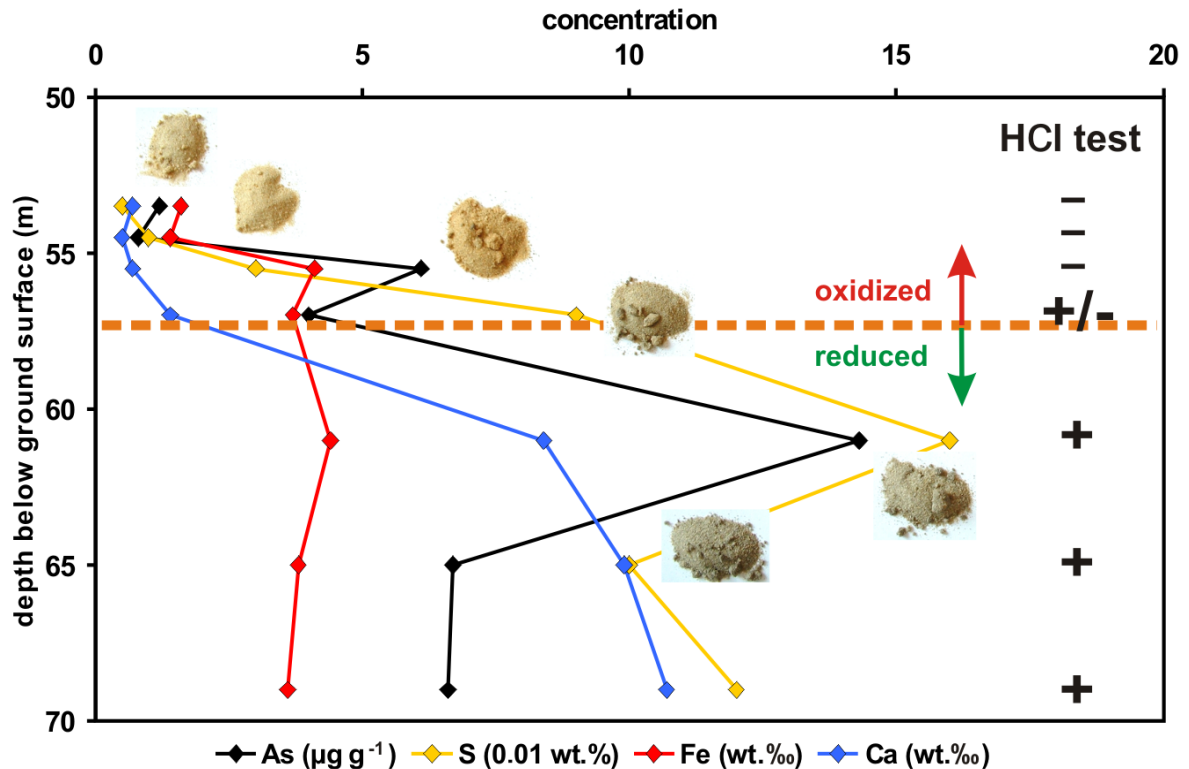


Fig. 3.8: Geochemical profile (As, S, Fe, Ca) and estimated position of the redox boundary in the borehole Flaesheim 1. Included photographs show sample appearance from the respective depths. “HCl test” indicates reaction of the samples towards treatment with 10 % HCl, with + strong reaction, +/- weak reaction, - no reaction.

Sediment colouration changes significantly within the sampled profile. Greenish to greyish colours dominate below a depth of ~57 m. The sample taken from 57 m below ground surface exhibits several orange fragments, obviously Fe hydroxides, indicating proximity to the redox boundary. Further upwards, strongly orange coloured sands are observed at ~55 m (Fig. 3.8), followed by light yellowish sands containing single Fe hydroxide fragments. Calcium content in the sediment decreases sharply between 61 and 57 m below ground surface, reaction intensity on 10 % HCl treatment weakens accordingly. The calcitic cement of the deeper reduced layers was obviously evacuated during the paleo redox process, suggesting that not only oxidation but also material loss occurs. This observation ex-

plains the unconsolidated status of the pure near-surface oxidized Santonian quartz sands. Sulfur and As concentrations develop parallelly 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 sulfide oxidation. Sulfur values fall to <0.01 wt.% within a few meters (Fig. 3.8) while As shows another smaller peak shortly above the redox boundary (in the orange sample), together with Fe, indicating the potential for *in situ* accumulation of As after mobilization during the paleo redox process. In conclusion, As behaviour appears to be Fe sulfide-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 very similar to what was described for the northwestern distribution area (cf. chapter 3.3.1), albeit at a lower concentration scale.

Commonalities and differences are documented in the profile of the second Flaesheim borehole (Flaesheim 2, Fig. 3.9).

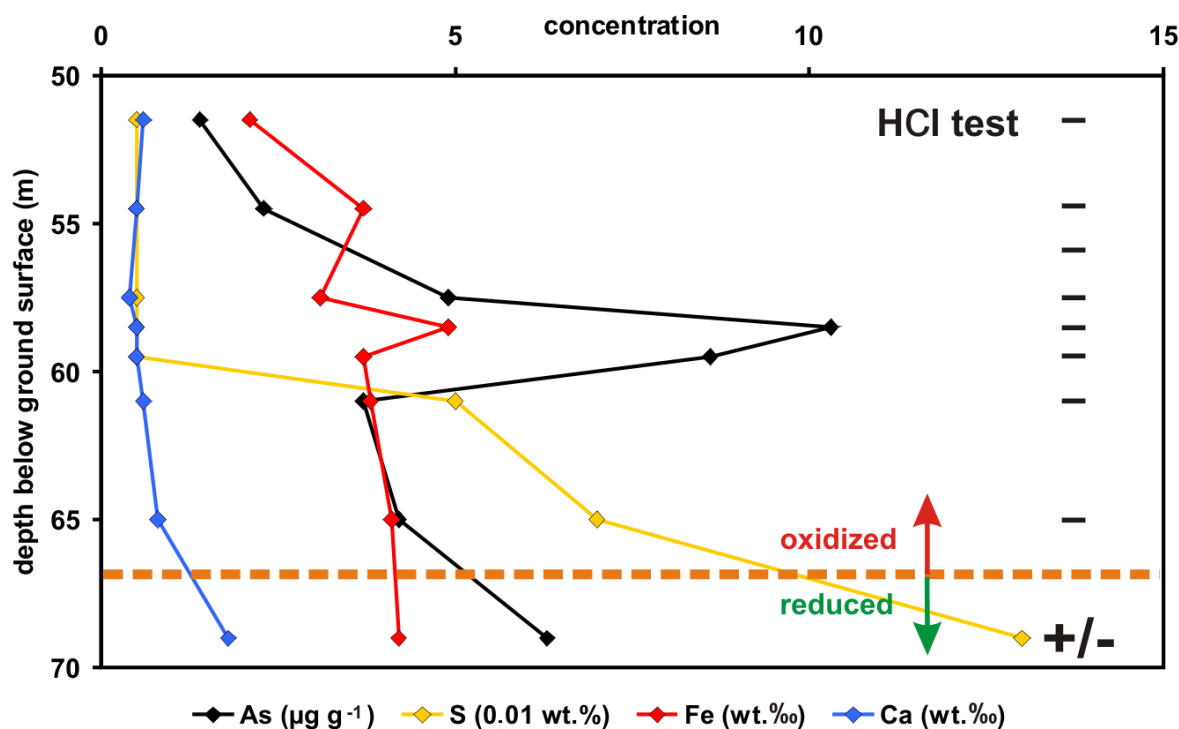


Fig. 3.9: Geochemical profile (As, S, Fe, Ca) and estimated position of the redox boundary in the borehole Flaesheim 2. “HCl test” indicates reaction of the samples towards treatment with 10 % HCl, with +/- weak reaction, - no reaction.

Taken from the same depth interval as in the first borehole, geochemical proxies in Flaesheim 2 exhibit partly different behaviour. Calcium content is universally low with a maximum in the bottommost sample which exclusively shows a reaction with HCl (Fig. 3.9). The paleo redox bound-

ary 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 (estimated) depth of the paleo redox boundary varies by ~10 m within a distance of only ~500 m between the two boreholes, arguing for a rather heterogeneous depth influence of the terrestrial weathering process.

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 in pyrite. The result is an average of 0.21 wt.% As_{pyrite} which is in good agreement with the values determined for Nordvelen reduced sands and siderite concretions (0.20 and 0.18 wt.%, respectively). It is concluded that in spite of lower Fe and As amounts reaching the more distal parts through terrigenous input, the incorporation potential of As in pyrite is rather homogeneous within the Santonian shallow marine system.

3.3.3 Arsenic fractionation and remobilization potential

Results of mineralogical As fractionation as determined by SEP are presented in Fig. 3.10.

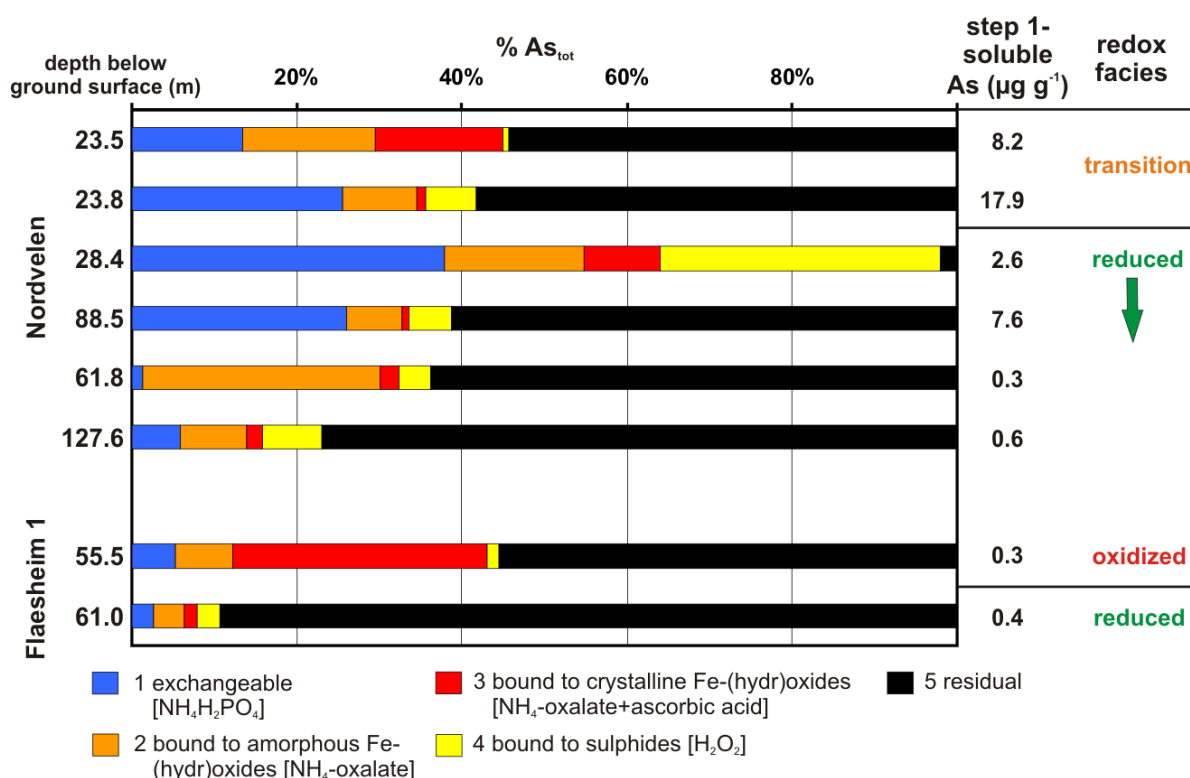


Fig. 3.10: SEP results for samples from the boreholes Nordvelen (top) and Flaesheim 1 (bottom, cf. Fig. 3.8) with absolute NH₄H₂PO₄-soluble As concentrations, ordered by redox facies. Nordvelen borehole: samples at 23.5 and 23.8 m are from the redox transition zone (cf. Fig. 3.6a), those from 28.4 and 88.5 m represent reduced sands, that from 61.8 m a siderite concretion and that from 127.6 m the glauconitic bottom sand.

Exchangeable (step 1-soluble) As shows highest relative proportions in reduced sands (26–38 % $A_{s_{tot}}$) but most significant absolute values of up to $17.9 \mu\text{g g}^{-1}$ dissolvable in the redox transition zone, indicating high reactivity and remobilization potential in this sector. In contrast, siderite concretion and bottom sand as well as the Flaesheim samples (both redox facies) are negligible in this respect. The fraction of As bound to amorphous Fe (hydr)oxides (step 2-soluble) is much larger than that prevailing in crystalline phases (step 3-soluble) within all reduced samples. This may partly be explainable by rather subrecent oxidation of reduced Fe phases, probably via air contact during sampling and storage, especially the siderite concretions were observed to oxidize within minutes (cf. chapter 3.2). 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, crystalline Fe hydroxide presence was approved, indicated As hosting is thus interpreted to be a primary signal. Sulfide-bound (step 4-soluble) As is likely to be generally underestimated in the reduced samples due to artificially induced oxidation described above. Nevertheless, trends are clearly visible. Between 4 and 34 % $A_{s_{tot}}$ are dissolvable in this step in the reduced layers while <1.5 % $A_{s_{tot}}$ are detected in the rather oxidized samples. In the redox transition zone, the proportion of this step decreases by factor 10 within 30 cm depth between the sample from directly below the paleo redox boundary, and the lepidocrocite-bearing layer marking it (cf. Fig. 3.6a), while 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. 3.10). These results clearly support the aforementioned decoupling of As from sulfide control and the uptake by Fe hydroxides in the course of the redox event.

In comparison to the paleo bog Fe ores (PBIOS) in the near-surface oxidized section of the Santonian sediments studied by Banning et al. (2009), a higher degree of exchangeable As is evident in the redox transition zone, i.e. in the precursor material of PBIOS. On average, only 2.8 % $A_{s_{tot}}$ was dissolvable by $\text{NH}_4\text{H}_2\text{PO}_4$ from the consolidated, mainly goethitic Fe crusts (cf. Figs. 3.1, 3.4) while this proportion is elevated by factor 10 at 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 and thus, to decreasing remobilization potential, while bulk As concentrations in precursor material ($\bar{O}$ $68 \mu\text{g g}^{-1}$) and PBIOS ($\bar{O}$ $44 \mu\text{g g}^{-1}$) are in the same order of magnitude. With respect to the reduced layers, the Tertiary paleo redox process led to extremely heterogeneous redistribution of As and Fe in the oxidized sediments.

3.4 Conclusions

Upper Cretaceous shallow marine sediments (Haltern-Schichten) from the western Münsterland were affected by deep terrestrial weathering in Tertiary times, leading to loss of carbonatic cement and oxi-

dation of Fe(II) mineral phases. Distinct boundaries of sediment colour and geochemical changes witness this paleo redox process, leaving a lower reduced and an upper oxidized section (oxidized layers occurring at greater depths in boreholes proximal to the provenance area represent beach facies deposits and thus primarily oxidized sediments). 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.

Early stages of concretionary accumulations of Fe and As in this section are interpreted as precursors of mainly goethitic high-As Fe concretions widespread in the near-surface oxidized part of the sediments. The structure model of As sources and sinks in the western Münsterland set up by Banning et al. (2009) is therefore completed by the present study – the unaltered Santonian sediments represent the primary source of As in the area, heterogeneous redistribution in the course of the paleo redox process led to abundant concretionary accumulation in PBIOs known to be partly exposed to hydrochemical conditions enabling remobilization of As which is finally found in soils and groundwater of the region.

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 distribution area of the Santonian sediments. 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 As. Knowledge of the paleo redox boundary position and monitoring of As concentrations as well as physico-chemical conditions are thus essential before and during groundwater extraction.

Part 4 – Paleogene: Arsenic in paleo redox events, case II – Lower Rhine Embayment

This study was published in modified form as one part of the following peer-reviewed article:

Banning, A., Rüde, T.R., 2010. Enrichment processes of arsenic in oxidic sedimentary rocks – from geochemical and genetic characterization to potential mobility. *Water Research* 44(19), 5512-5531.

It was extended and rewritten (including modified and new figures) for this dissertation.

Some preliminary results from this study were presented in modified form in the following conference contributions:

Banning, A., Rüde, T.R., 2010. Impact of paleo redox processes on arsenic distribution and mobility in sediments. 3rd International Congress on Arsenic in the Environment – Arsenic in geosphere and human diseases (As2010), May 17-21, 2010, Tainan/Taiwan.

Hümpel, E., Banning, A., Rüde, T.R., 2009. Heterogene Arsenverteilung in Sedimenten als Folge der Arsenanreicherung an sekundären Eisenkonkretionen. *Arsen 2009 – Verhalten von Arsen in geologischen, hydrologischen und biologischen Systemen*, September 23-24, 2009, Leipzig/Germany.

Banning, A., Rüde, T.R., 2009. Natürliche Arsenvorkommen in eisenoxidreichen Sedimentgesteinen Deutschlands – Charakterisierung und Akkumulationsprozesse. *Arsen 2009 – Verhalten von Arsen in geologischen, hydrologischen und biologischen Systemen*, September 23-24, 2009, Leipzig/Germany.

Banning, A., Rüde, T.R., 2008. Geogenic enrichment and behaviour of arsenic in iron oxides containing sedimentary rocks in Germany. 2nd International Congress on Arsenic in the Environment – Arsenic from nature to humans (As2008), May 21-23, 2008, Valencia/Spain.

Key questions

Does a second paleo redox-affected area support the findings from the first study (Part 3)?

What is the extent of secondary As accumulation, also in comparison to other trace elements?

What can be learned from trace element signatures about the development of the actual situation?

Which role does glauconite play in As and Fe dynamics in the given geo-environment?

Is a risk for As release into groundwater derivable from the obtained results?

4.1 Study area and objectives

The Lower Rhine Embayment (LRE) is part of the North-West European Tertiary Basin ranging from the British Isles to Poland. Similar to, and in continuance of, the URG (part 2 of this work), it represents a rift structure starting its break-in in middle Tertiary. It is mainly filled with Tertiary marine sediments derived from the uplift and subsequent erosion of the Variscan Rhenish Massif (Fig. 4.1).

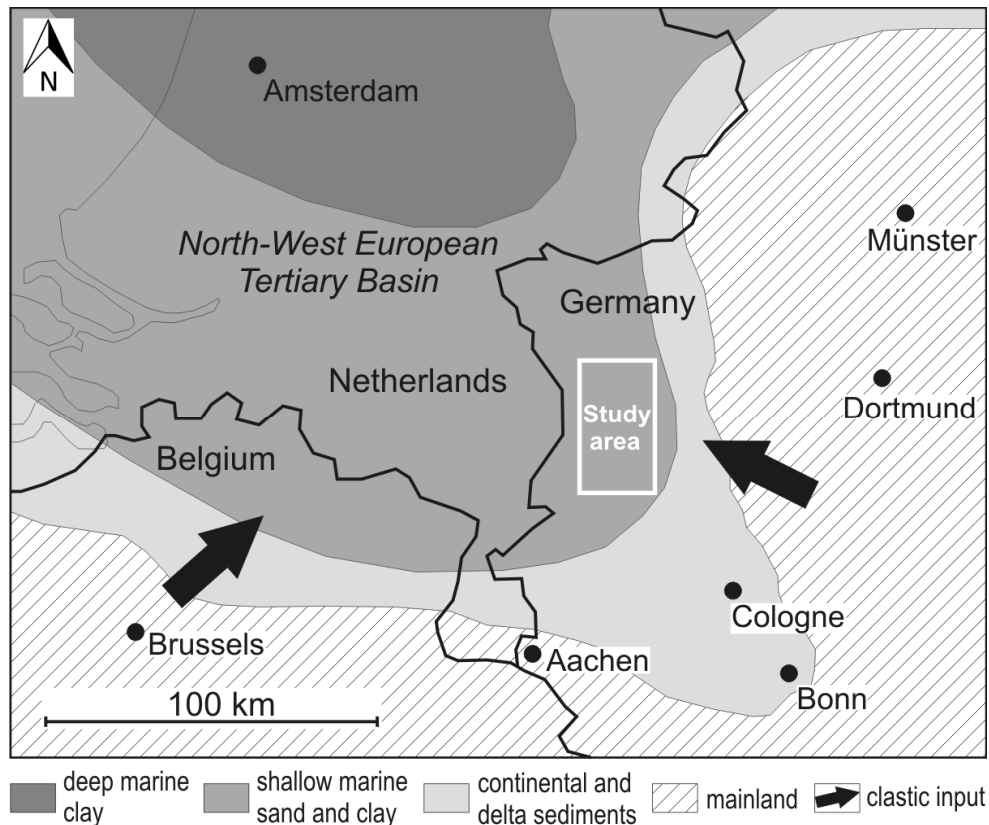


Fig. 4.1: Oligocene paleogeographical situation of the study area (modified after Vinken 1988 and Ziegler 1990).

The graben basin strikes NNW-SSE, its filling comprises a relatively complete succession of Oligocene, Miocene and Pliocene sediments with variable thicknesses due to extensional fault tectonics and the crust breaking apart into several blocks (cf. Fig. 4.3). The Grafenberg-Schichten of the Upper Oligocene (Chattian) are 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 stratigraphical position of the sampled strata in and around the study area is shown in Fig. 4.2.

General stratigraphy		Regional units
MIOCENE	LANG-HIAN	Schichten von Breda
	BURDIGALIAN	<i>hiatus</i>
	AQUITANIAN	
OLIGOCENE	CHATTIAN	Grafenberg-Schichten
		<i>hiatus</i>
	RUPELIAN	Lintfort-Schichten Ratingen-Schichten Walsum-Schichten
EOCENE		<i>hiatus</i>

Fig. 4.2: Tertiary stratigraphy of the study area with the sampled unit highlighted by hachures (figure produced after information in GLA NRW 1988).

The primary calcareous and glauconitic Grafenberg-Schichten underwent deep terrestrial weathering in Neogene times. 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 paleo 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 reduced lower part of the Grafenberg-Schichten was sampled from boreholes near Willich and Hamminkeln. Being mostly covered by younger sediments, the near-surface oxidized section was assessed from two outcrops near Süchteln. Here, tectonic activity related to a major regional normal fault (“Viersener Sprung”) resulted in a narrow area of Oligocene outcropping at ground surface on the boundary between the Venlo Block and the Krefeld Block (Fig. 4.3).

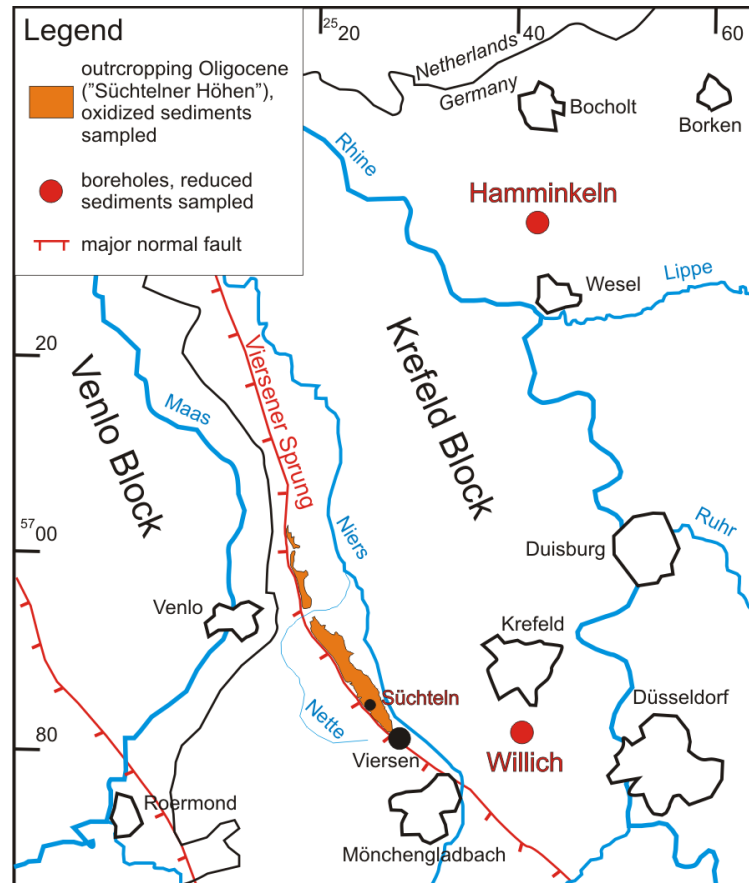


Fig. 4.3: Sampling locations and regional tectonics of the study area (modified after GLA NRW 1984 and GLA NRW 1988).

The geological background, postdepositional redox history and present situation is well comparable to the one described for the southwestern Münsterland Cretaceous Basin (part 3 of this work). This study assesses the question if this is also valid for As dynamics in paleo redox processes and thus, if a generalization and transfer of the obtained results to other geologically similar areas is possible. The detection of partly high As concentrations (up to $150 \mu\text{g g}^{-1}$) in Fe hydroxidic layers in outcrops from the southern part of the Chattian sediments distribution area (Jansen 2006) supports the area selection for this comparative approach.

4.2 Materials and methods

A total number of 36 sediment samples were obtained, 16 of which stem from the reduced lower section and were sampled from cores of up to 182 m deep boreholes near Willich and Hamminkeln (cf. Fig. 4.3; 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-Schichten (“Süchtelner Höhen”, cf. Fig. 4.3).

The reduced lower facies of the Grafenberg-Schichten comprises quite homogeneous marine fine sands 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 study area derived from the weathering of mainly Variscan mainlands to the southeast of the LRE (Fig. 4.1).

Resulting from the paleo-redox process mentioned in the previous chapter, the oxidized upper facies of the Grafenberg-Schichten 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 Neogene weathering precipitated in the upper part, forming Fe(III) hydroxide coatings around quartz grains. In outcrops, Fe(III) concretions are observable with orange to dark red colours and significantly more consolidated than the ambient sands. Special attention was paid to these concretions during sampling.

Bulk rock geochemistry for all samples, quantitative mineralogy (twelve samples, five from the reduced part of the Grafenberg-Schichten, seven from the respective oxidized part) and As fractionation and mobilization potential (sequential extraction of twelve samples, four from the reduced section, eight from the oxidized facies) were assessed as described in part 2 of this work. Some pyrite and glauconite grains were separated by hand-picking under the binocular after pre-enrichment using the density separation fluid sodium polytungstate ($\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$). Mineral shapes and habits were microscopically studied and photographed.

4.3 Results

Table 4.1 shows the geochemical composition of sediments from the Grafenberg-Schichten. A concentration profile indicates geochemical development of As, Fe and S, and Fe phase fractionation dependent upon depth in the borehole (Fig. 4.4).

next page:

Tab. 4.1: Whole rock geochemical results for selected elements and MUNSELL colour of the Paleogene sediments (DL: detection limit; Ox_G: oxidized Grafenberg-Schichten; QC_G: Quaternary cover sediment; Red_G: reduced Grafenberg-Schichten from the borehole near Willich; Red_H: reduced Grafenberg-Schichten from the borehole near Hamminkeln). Samples highlighted in grey were analyzed with XRD.

		Fe	Ca	Al	S	As	Mn	Pb	Zn	Cu	Co	Cr	Cd	Ni	Colour
		wt.%	wt.%	wt.%	wt.%	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹	MUNSELL
	DL	0.01	0.01	0.01	0.01	0.5	1	3	1	1	1	2	0.3	1	
Layer	Sample code														
Ox_G	GS_0101	4.44	0.18	3.59	0.02	26.6	86	10	36	6	5	130	0.5	12	10 YR 7/8 – 10 YR 8/3
	GS_0102	6.61	0.17	3.51	0.03	25.8	103	11	78	7	6	140	1.0	15	10 YR 7/8 – 10 YR 8/3
	GS_0103	8.06	0.15	3.08	0.03	20.0	213	12	126	4	14	143	0.8	24	10 YR 5/8
	GS_0104	6.08	0.14	3.02	0.04	57.8	90	15	74	9	5	120	0.8	12	5 YR 4/4 – 5 YR 5/6
	GS_0105	3.19	0.17	2.87	0.10	28.9	101	9	28	4	3	130	0.4	9	10 YR 8/3 – 10 YR 7/8
	GS_0106	4.76	0.16	2.97	0.02	31.7	116	12	41	4	6	110	0.5	6	10 YR 8/8 – 10 YR 8/1
	GS_0107	6.45	0.15	2.96	0.01	19.0	188	9	157	3	25	110	0.7	27	10 R 4/6
	GS_0108	10.5	0.12	2.72	0.03	18.0	258	12	326	5	18	100	1.3	24	5 R 2/6 – 10 R 3/4
	GS_0109	3.90	0.17	3.30	<DL	10.4	152	8	95	3	15	96	0.5	23	10 YR 7/8 – 10 YR 8/1
	GS_0110	5.90	0.20	4.10	0.04	22.9	551	11	67	4	38	95	0.8	80	10 YR 4/6
	GS_0111	4.03	0.17	3.34	0.01	13.2	259	9	125	4	20	98	0.4	27	10 YR 8/3
	GS_0112	5.60	0.16	3.38	0.02	31.8	533	12	139	4	47	96	0.7	60	5 R 2/8
	GS_0113	4.53	0.16	3.14	<DL	15.0	607	11	132	3	46	95	0.5	101	10 YR 7/8 – 10 YR 8/2
	GS_0114	12.3	0.16	2.81	0.03	36.0	105	13	149	11	6	196	1.1	18	10 YR 7/8
	GG_0101	1.41	0.21	3.86	0.05	8.9	75	13	37	4	6	91	<DL	14	5 YR 4/6
	GG_0102	2.91	0.18	3.56	<DL	48.7	64	6	55	7	8	120	<DL	20	10 YR 8/3
	GG_0103	23.4	0.09	2.28	0.02	1860	1200	84	309	113	219	800	1.5	65	5 R 2/6 – 5R 2/2
	GG_0104	0.94	0.09	2.37	<DL	9.3	79	7	20	7	3	34	<DL	16	10 YR 8/1 – 10 YR 7/8
	GG_0105	0.90	0.08	2.27	<DL	6.6	82	13	19	6	3	24	<DL	10	10 YR 8/1 – 10 YR 7/8
	GG_0106	1.29	0.17	4.02	<DL	9.0	49	10	27	9	3	73	<DL	16	10 YR 8/1 – 10 YR 7/8
QC_G	GW_0101	0.74	3.37	3.37	0.01	3.2	180	20	23	6	5	31	<DL	20	10 YR 7/4
Red_G	GW_0201	5.71	0.67	2.32	0.33	21.2	348	9	32	3	6	82	0.5	14	5 YR 3/2
	GW_0202	1.55	3.45	2.47	0.14	8.5	122	9	36	7	5	73	<DL	12	5 G 5/1
	GW_0203	1.52	3.18	2.58	0.22	9.7	145	19	42	4	5	106	<DL	14	5 B 6/1
	GW_0204	1.13	2.70	2.28	0.12	6.9	94	10	37	4	5	64	<DL	11	5 GY 3/1
	GW_0205	1.39	2.72	1.62	0.2	9.4	107	7	31	2	5	76	<DL	6	5 Y 6/1
	GW_0206	1.67	1.02	2.51	0.11	7.2	126	9	37	3	5	69	<DL	11	5 Y 6/1
	GW_0207	1.75	1.81	2.67	0.29	13.1	147	9	36	4	5	101	0.3	13	5 Y 5/2
	GW_0208	2.37	3.05	2.33	0.15	10.0	187	9	32	3	5	130	<DL	11	5 GY 6/1
	GW_0209	1.55	1.70	2.79	0.24	13.1	139	10	33	3	5	88	<DL	11	5 Y 7/1
	GW_0210	1.69	1.93	3.27	0.33	13.2	112	9	34	5	5	64	<DL	15	10 YR 6/2
	GW_0211	2.22	2.34	2.61	0.42	17.3	131	10	35	4	6	113	<DL	14	5 Y 6/2
	GW_0212	3.38	2.08	2.14	0.22	19.4	104	10	34	3	8	81	0.4	16	5 GY 4/1
	GW_0213	1.38	4.49	1.05	0.13	11.9	62	5	20	2	3	54	<DL	5	5 Y 6/1
	GW_0214	1.23	1.57	1.33	0.22	13.4	67	5	21	2	3	49	0.3	7	5 Y 5/1
	GW_0215	1.60	1.07	1.37	0.14	10.0	69	4	20	1	3	68	<DL	5	10 Y 6/2
Red_H	GH_0101	2.64	1.75	4.47	0.35	10.8	144	8	48	7	6	92	0.5	22	5 Y 6/2

The reduced lower part of the Grafenberg-Schichten contains relatively homogeneous 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. 4.4).

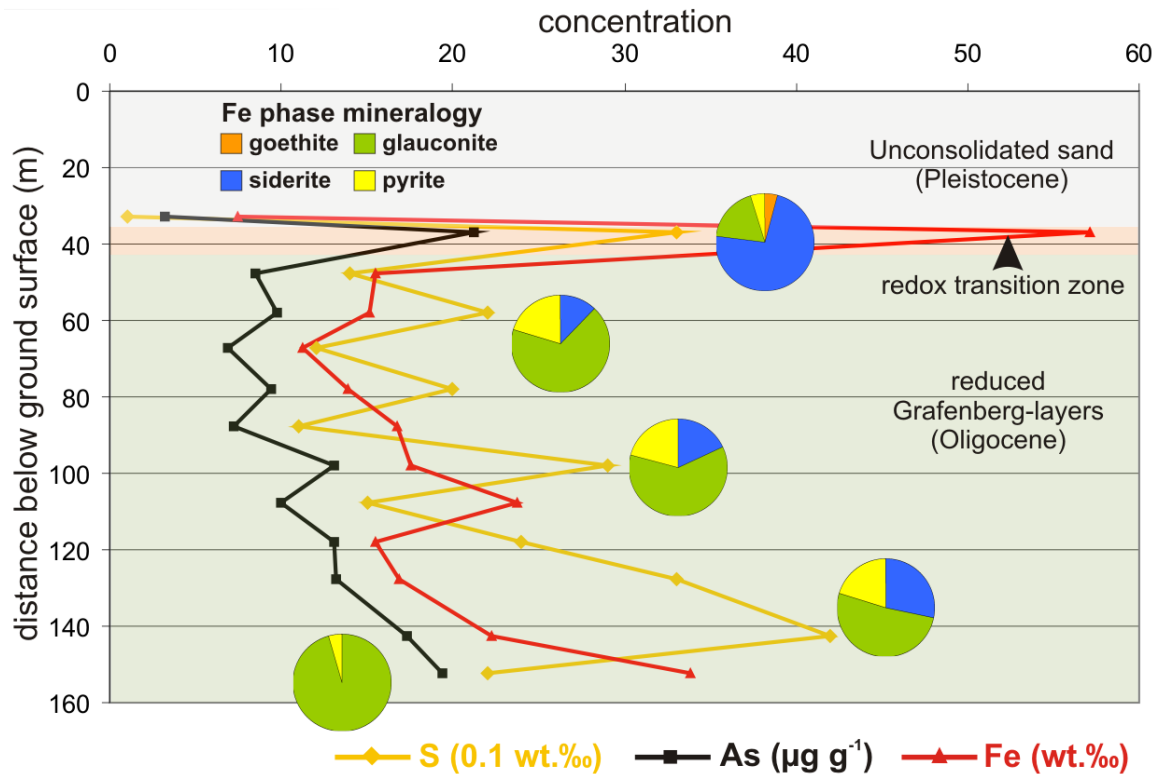


Fig. 4.4: Stratigraphical profile, Fe, As and S contents development and Fe phase fractionation of the Grafenberg-Schichten sampled from the borehole near Willich.

Iron phase fractionation in borehole samples is indicated in Fig. 4.4. XRD analysis identified several reduced Fe minerals, wherein glauconite ($(\text{K,Na})(\text{Fe,Al,Mg})_2[(\text{OH})_2(\text{Si,Al})_4\text{O}_{10}]$) is dominant (60 % of all Fe phases on average) over pyrite (FeS_2) and siderite (FeCO_3). Greenish to bluish glauconite and mainly framboidal pyrite grains were observable in the sediments under the microscope (Fig. 4.5). One layer at the bottom of the borehole contains a high glauconite proportion of 11.1 wt.% of the bulk sample (other reduced samples: 2.05 ± 0.10 wt.%) while the uppermost sample exhibits high siderite (8.5 wt.%, other reduced samples: 0.69 ± 0.39 wt.%). Pyrite distribution is relatively homogeneous in the whole profile (0.63 ± 0.11 wt.%; cf. chapter 4.4.1).

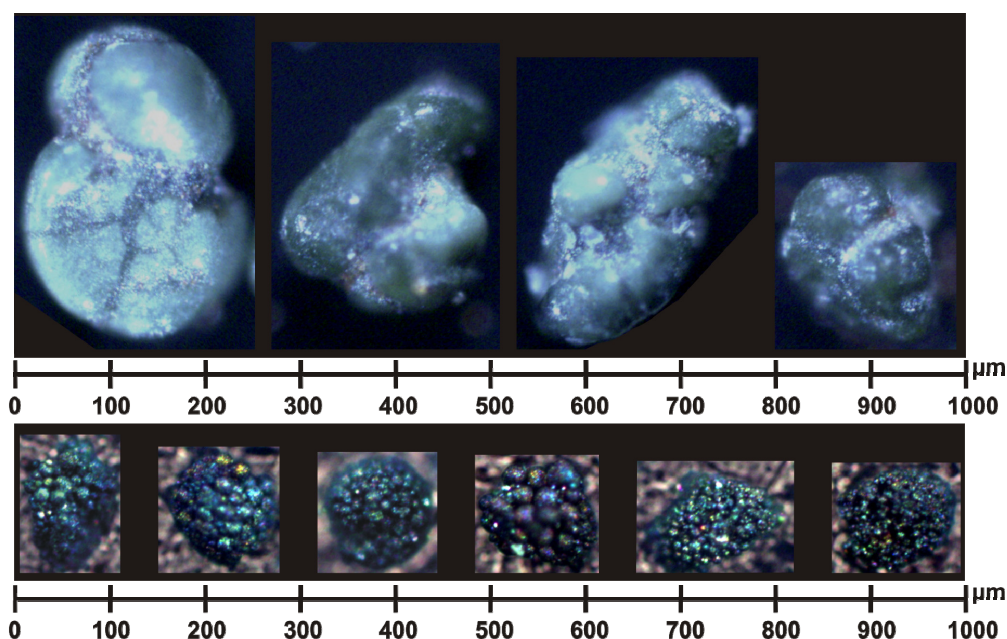


Fig. 4.5: Examples of reduced Fe phases under the microscope. Upper part: glauconite, lower part: framboidal pyrite.

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 wt.%) is depleted, compared to the deeper sediments (1.82 ± 0.79 wt.%); 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. 4.4). Besides quartz as the dominant mineral phase (83.8 ± 2.6 wt.%), calcite and the mentioned Fe phases, the samples contain minor amounts of muscovite, clay minerals and feldspar.

In comparison to the deep sediments, the upper oxidized facies of the Grafenberg-Schichten shows a very heterogeneous distribution of Fe, As and other trace elements. Iron content averages 3.93 ± 2.2 wt.% in the unconsolidated sands, but can be as high as 23.4 wt.% in concretions. All XRD-analyzed samples contain goethite whose proportion ranges from 1.04 to 34.5 wt.%. Lepidocrocite ($\gamma\text{-FeOOH}$) as a second Fe hydroxide was identified in two samples (1.88 and 11.4 wt.%). XRD analysis was additionally conducted for one sample in the grain fraction $<0.63 \mu\text{m}$ (obtained through wet sieving) indicating that Fe hydroxides are preferably present in the fine-grained sediment proportion (elevated abundance compared to bulk sample by factor 3.4 for goethite and factor 5.5 for lepidocrocite). Calcite was not detectable in any sample, the same is valid for pyrite, glauconite and siderite.

Arsenic contents average $20.3 \pm 11.8 \mu\text{g g}^{-1}$ in oxidized sands, but yield a peak value of $1860 \mu\text{g g}^{-1}$ in one Fe concretion, thus underlining the pronounced heterogeneity of element distribution in the oxidized facies, even at very close range (Fig. 4.6).

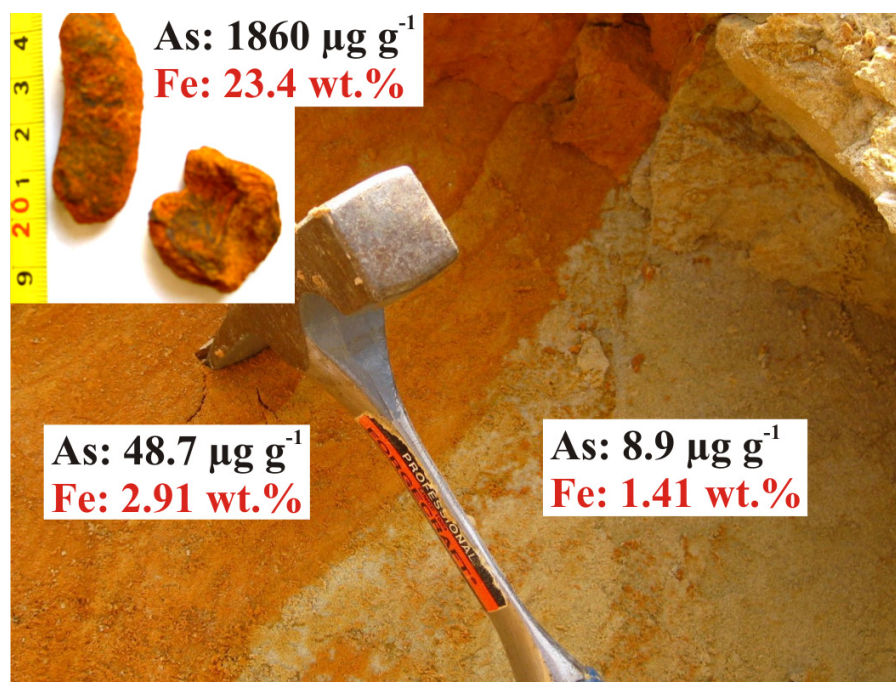


Fig. 4.6: Example of heterogeneous Fe and As distribution in the oxidized part of the Chattian sediments. The inset (upper left corner) shows Fe concretions found in the orange layer on the left side.

In the example shown in Fig. 4.6, Fe and As levels increase erratically from light coloured (right side) via bright orange sands (left side) to the very hard, dark reddish Fe concretions (inset) found within the latter. Approximate ratios in these three sediment zones for Fe are 1:2:17, for As 1:5:207. The different scales of enrichment, also for other trace elements, are discussed in chapter 4.4.2. Sharp redox-related sediment boundaries in outcrops like the one presented in Fig. 4.6 are typical relic features of pedogenesis and fluctuation of sediment saturation (McCarthy et al. 1998) under humid tropical conditions as described by Felix-Henningsen (1994) for paleo weathering of Paleozoic shales in the Hunsrück, ~150 km south of the present study area, during the same terrestrial Neogene redox event. The occurrence of mainly goethite Fe concretions within the oxidized zone (so-called “Hunsrück iron stones”, Felix-Henningsen 1994) and downward advancing leaching of soluble elements due to prevention of chemical equilibria during ongoing weathering are further common features of both studies confirming the wide influence of the Neogene event on terrestrial Central Europe. McSweeney and Fastovsky (1987) studied Cretaceous to Paleogene paleosols and found Fe(III) concretions derived from post-pedogenic precipitation. Thus, both paleo-pedogenic origin and formation in the zone of groundwater oscillation (as “paleo bog iron ores”, cf. part 3 of this work) are possible genetic mechanisms for concretions in the studied part of the Lower Rhine Embayment. Tuttle et al. (2009) observed general As depletion relative to Fe during pedogenesis of a shale containing As hosted by framboidal pyrite (cf. chapter 4.4.1) and attributed this to decreasing association between these elements in the course of soil formation. This cannot be fully supported in the present case regarding partly much

higher As enrichment, compared to that of Fe (Fig. 4.6). A model for As reaccumulation and an alternative approach to explain the low degree of Fe-As correlation in the oxidized sediments are presented in chapters 4.4.1 and 4.4.2 of this study.

Sequential extraction results for samples from the range of the Grafenberg-Schichten are illustrated in Fig. 4.7. The reduced lower part of the Grafenberg-Schichten comprises a relatively homogeneous As fractionation. Arsenic soluble in step 1 is 7.3 ± 0.4 %, 31.9 ± 2.1 % in step 3, 28.8 ± 5.2 % in step 4 and 27.5 ± 5.6 % in step 5. In the redox transition zone, H_2O_2 -soluble As decreases to 16 %. Potential mobilizability (extraction steps 1 to 3, cf. part 2 of this work, chapter 2.3.3) is similar in all samples (38.6 ± 2.3 % As_{tot}), but higher absolute amounts are found in the transition zone (Fig. 4.7).

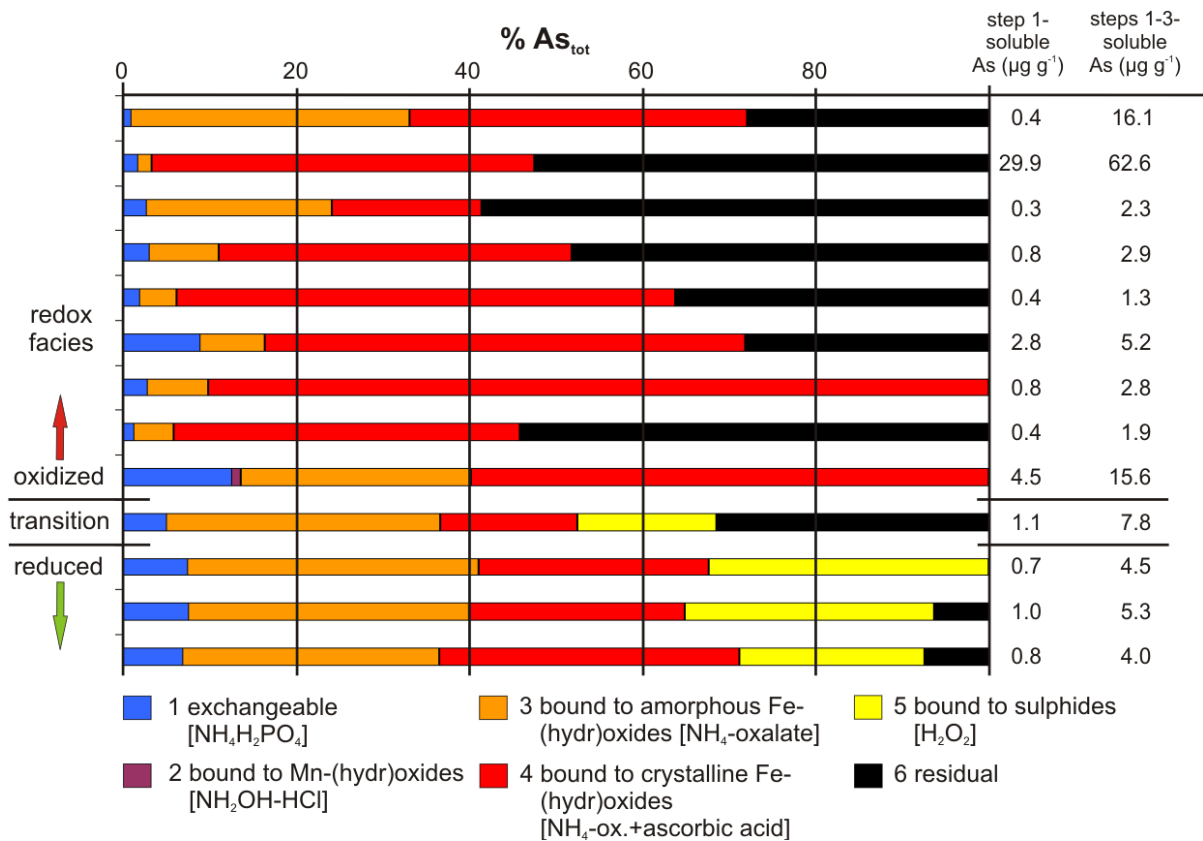


Fig. 4.7: Sequential extraction results for Paleogene sediment samples, ordered by redox facies.

Arsenic extractability in the oxidized facies is more heterogeneous. 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 $62.6 \mu\text{g g}^{-1}$ with a peak value for Fe concretion GG_0103 (second sample in Fig. 4.7, cf. Tab. 4.1).

4.4 Discussion

4.4.1 Geochemical characterization and timing of As accumulation

The oxidized upper part of the Grafenberg-Schichten, compared to the reduced lower part, is enriched in As by ~factor 2, considering average values. However, due to the extremely heterogeneous element distribution, the scale of enrichment has to be analyzed in more detail (chapter 4.4.2). Statistical analysis for the oxidized near-surface facies of the Grafenberg-Schichten was conducted using SPSS software. The Pearson element correlation matrix is shown in Fig. 4.8, whereby the data was not normalized, optical checks were performed for trend linearity and to eliminate extreme outliers: due to its partly extremely high concentrations, especially for Fe and As, concretion GG_0103 was not included in the calculations.

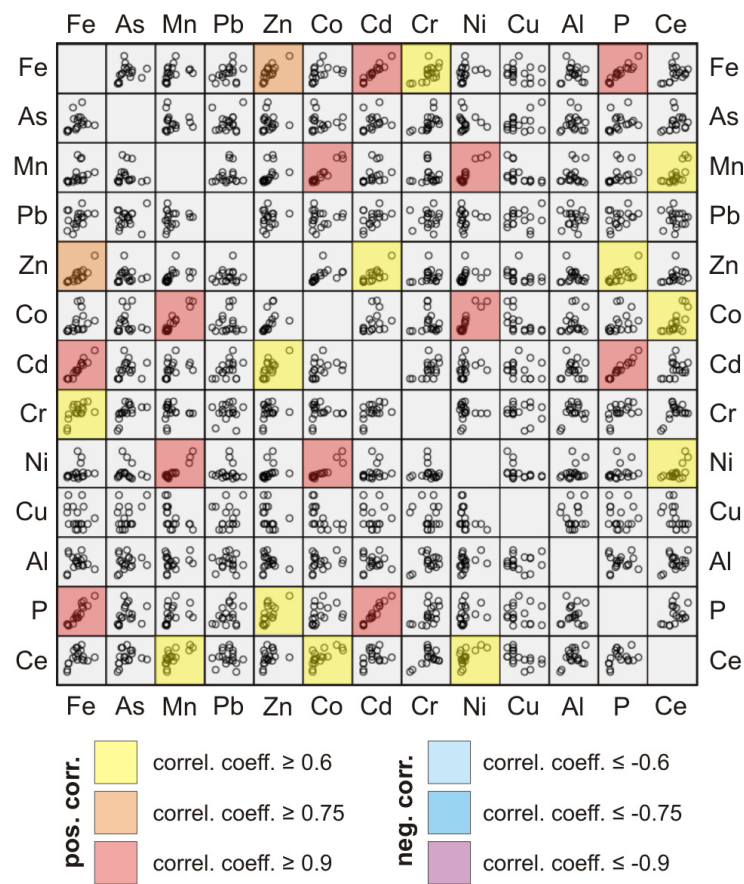


Fig. 4.8: Pearson element correlation matrix for samples from the oxidized facies of the Grafenberg-Schichten.

A striking positive correlation ($R^2=0.93$) between Fe and P is observable – P is obviously sorbed 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 extremely heterogeneous 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. 4.6). In a similar geological environment showing pronounced post paleo-redox elemental redistribution, the western Münsterland Cretaceous Basin, Banning et al. (2009) found As being accumulated in Fe hydroxide concretions without yielding any correlation with bulk Fe (cf. part 3 of this work).

The source of near-surface Fe and As is assumed 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 Paleogene sample, indicating a redox transition zone (chapter 4.3, Fig. 4.4). The potential role of the reduced Fe phases for As behaviour in the system 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. 4.4). 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. (2011) 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 author’s 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-Schichten is the major source for Fe accumulations in the oxidized near-surface part.

Siderite is mostly present as 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-Schichten 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 the Münsterland Cretaceous Basin also yielded low As contents (Banning et al. 2009, cf. part 3 of this work).

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 discussed before, As is incorporated into the pyrite structure by substitution for S. In particular, pyrite 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 disulfide 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 (cf. Fig. 4.5) is suspected to represent the main As host in the reduced deeper facies of the Grafenberg-Schichten 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. 4.9).

In the Fe-S scatter plot (Fig. 4.9a), the line of stoichiometric pyrite was implemented for comparison. Most samples plot along a line parallel to that. The offset 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 homogeneous concentrations in the reduced samples.

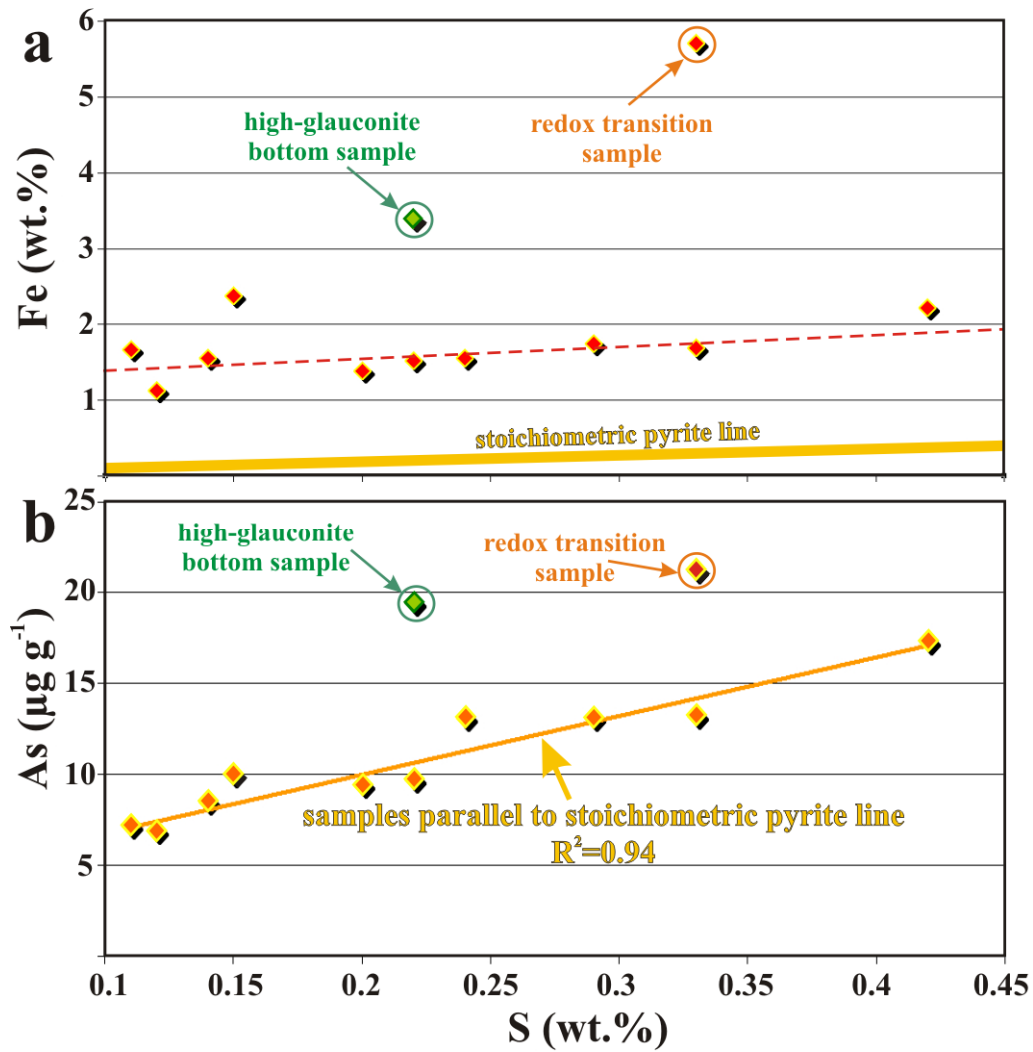


Fig. 4.9: Fe vs. S (a) and As vs. S (b) scatter plots for the reduced facies of the Grafenberg-Schichten.

Two distinct outliers from the pyrite line-parallel trend were identified: the only sample to contain goethite (redox transition zone), and the sample showing the by far highest glauconite content (11.1 wt.%, compared to an average of 2 wt.% in the other samples analyzed by XRD). These results were accounted for in the As-S scatter plot (Fig. 4.9b). Samples yielding a pyrite-like development in Fig. 4.9a showed a very close positive 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-Schichten. 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. Siderite is a rather unattractive host phase for As in the studied geo-environment as concluded from the findings here and in part 3 of this work. Obviously, the As-siderite affinity partly observed

under laboratory conditions (as discussed earlier in this chapter) does not apply for the natural system studied here.

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 of 0.21 ± 0.04 wt.% As_{pyr} results which plots in the range of As_{pyr} given by Abraitis et al. (2004) and is very similar to the average As_{pyr} value (0.23 wt.%) in a limestone aquifer studied by Price and Pichler (2006). Moreover, this result is in excellent agreement with As_{pyr} (~0.20 wt.%) determined for the reduced Cretaceous sediments studied in part 3 of this work.

All these considerations indicate a secondary As enrichment in the near-surface Grafenberg-Schichten, 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 4.1) 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 is likely to have caused the low degree 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 preferably enriched in glauconite (Dooley 1998) and like Fe, may have derived in largest part from the weathering of this mineral in the subsurface.

Consequently, heterogeneous 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.

4.4.2 Scale of accumulation

Enrichment Factor (EF) and cumulative Contamination Factor (CF) were calculated after Loska et al. (1997) and Loska et al. (2003), the approaches are described in part 2 of this work, chapter 2.4.2. Results of EF, ordered by Fe enrichment factor (values not shown) and CF calculations are shown in Fig. 4.10.

The pronounced heterogeneity in the oxidized sediments is underlined once more when regarding EF values, even if concretion GG_0103 (cf. Tab. 4.1) 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. Cadmium was not included in the calculations due to numerous samples in both redox facies showing contents below the detection limit.

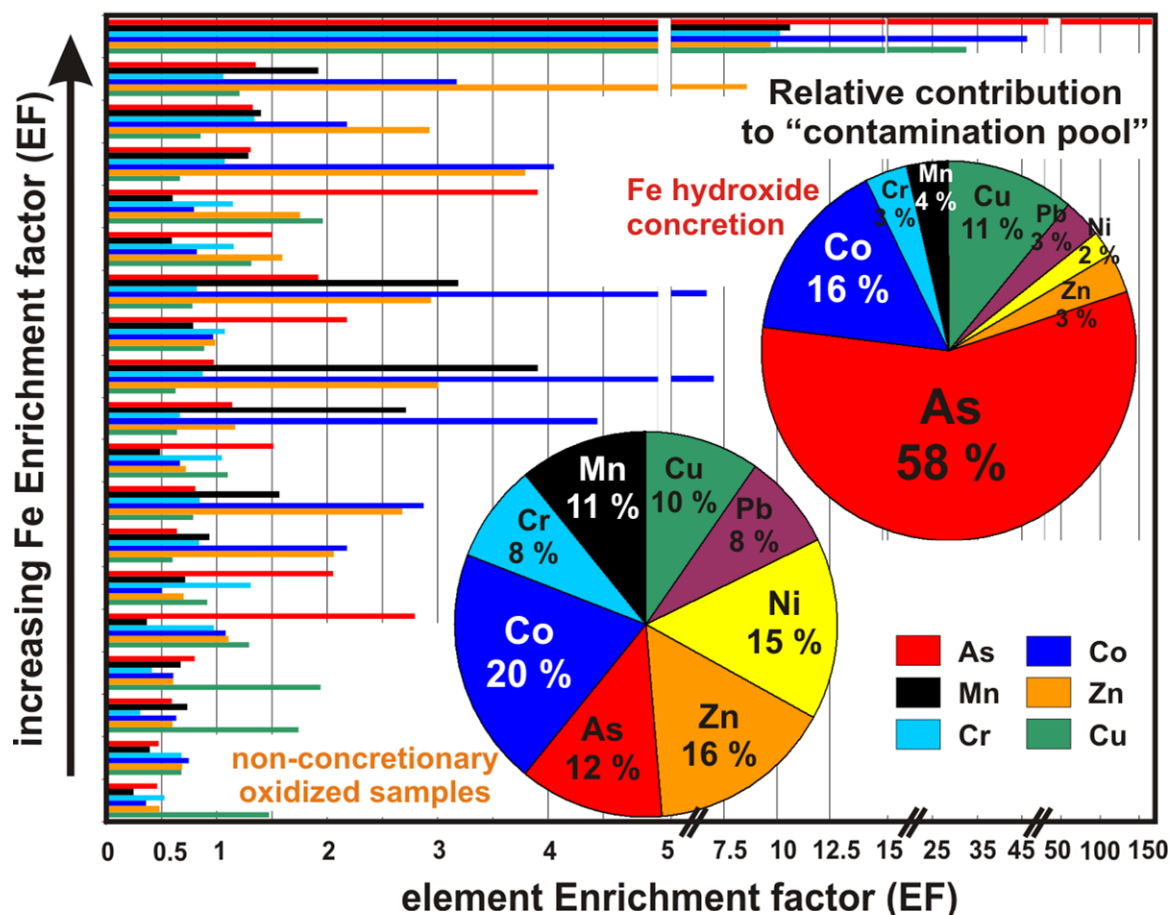


Fig. 4.10: Enrichment Factors (EF) of 6 elements for samples from the oxidized facies of the Grafenberg-Schichten. Upper pie chart: single elements' contribution to total "contamination pool" in one Fe hydroxide concretion, lower pie chart: single elements' contribution to total "contamination pool" of non-concretionary oxidized samples. Note changes of scale on the x-axis.

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 (Fig. 4.10). This situation results in relatively balanced contributions of single metals to the total "contamination pool" (Fig. 4.10, lower pie chart), where As has a proportion of 12 %. Calculating these percentages for the most Fe-rich concretion, the findings are completely different: here, As is by far the most important contributor, accounting for 58 % of the total contaminant pool (Fig. 4.10, 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-Schichten, also in larger sizes than the specimen analyzed in this study (Fig. 4.6). Quaas (1917) describes occurrences of banked "dark iron sandstone

containing hard Fe concretions” [citation translated from German] from several former quarries back-filled today and thus not accessible for sampling anymore.

From these findings, it can be concluded that during elemental redistribution after the paleo redox event, As 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 when the weathering front migrated further downwards. 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. 4.8). Moreover, it is known that rapidly formed Fe oxyhydroxides at $\text{pH} > 6.5$ precipitate without significant As adsorption to the fresh surfaces (Peters 2000). Relatively high pH is likely to have prevailed during weathering due to calcite dissolution from the original facies, leading to fast and ubiquitous precipitation of Fe coatings without elevated As around quartz grains. Nevertheless, when it came to formation of Fe concretions in voids in the course of ongoing oxidation, As was favoured for adsorption over other elements. Continuous replenishment of Fe made sure that freshly precipitating Fe hydroxides 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-concretionary sediments (Fig. 4.7). In this late stage of the weathering process, the pH buffer function of dissolving calcite probably became insignificant 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 can also provide CO_3^{2-} for the observed intensified siderite formation (Fig. 4.4). In consequence, large amounts of Fe and As would still have been available for precipitation after the period of pH buffering. This genetic model explains the heterogeneous As distribution in the sediments and allocates the formation of rather punctiform high As enrichments to a late stage of the paleo redox process.

4.4.3 Implications for potential As remobilization

Step 1-soluble As in the reduced facies of the Grafenberg-Schichten 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 4.4.1 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 stoichiometric pyrite, when significant As contents are present in the crystal structure (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 $\sim 35\text{--}40 \text{ m}$ 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 of the present study. 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 $4.2 \cdot 10^{-5} \text{ m/s}$ 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 operation. It was described in chapter 4.1 that the depth of the paleo redox boundary is variable in the study area, but mostly around $20\text{--}30 \text{ m}$ below ground surface. Therefore, groundwater extraction might change redox conditions to rather oxidizing in the top of the reduced primary facies, thus enabling $\text{Fe}(\text{II})$ 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^{2-} as well as a successive increase of both parameters in deep wells of one waterworks in the study area since the start of water extraction from the Grafenberg-Schichten (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 heterogeneous element distribution and limited number of samples in the shallow redox facies, calculations for potential As mobilization must be considered a rough estimate. In the oxidized section, unconsolidated sands show an average of $0.9 \mu\text{g g}^{-1}$ $\text{NH}_4\text{H}_2\text{PO}_4$ -soluble As, corre-

sponding to $\sim 2.2 \text{ g m}^{-3}$ 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 readily exchangeable As in bulk sediments is contributed by concretions. Conducting these calculations for potentially short- to medium-term (SEP step 1-3) 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 then exhibit 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 4.4.2. 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-Schichten 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 homogeneous 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). If we assume that this is caused by solution of exchangeable As from the Chattian rocks ($\sim 2 \text{ g m}^{-3}$), we can calculate that, referring to 1 m^3 of sediment (with a known effective drainage porosity of $n_f=0.13$; Mäurer and Wisotzky 2007), approximately 10,000 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 potential impact of changing redox conditions on As concentration in groundwater of the area.

4.5 Conclusions

Homogeneously distributed framboidal pyrite is the main As host phase in Paleogene (Chattian) shallow marine fine sands from the Lower Rhine Embayment. In the course of a Neogene terrestrial redox event, massive element redistribution occurred, leading to an extremely heterogeneous present day Fe and As arrangement in near-surface oxidized sediments (paleo regolith), whereby highest As concentrations are found in Fe hydroxide concretions. Associations with other trace elements suggest that these derive from pyrite oxidation while Fe is likely to mainly stem from glauconite weathering. The primary accumulation process (As immobilization in pyrite) is thus followed by a secondary, postdepositional event (As redistribution and enrichment in Fe hydroxide). During the latter, As gathering in concretionary sections was clearly favored over other trace elements. In spite of higher bulk As in the oxidic rocks, the reduced deeper part of the sediments was shown to be the most probable candidate for potentially creating elevated As concentrations in groundwater, especially if the present redox milieu is anthropogenically disturbed by groundwater extraction or input of oxidants like nitrate.

Depositional facies, geological development as well as geochemical and mineralogical composition of unaltered and oxidized layers of the studied sediments show significant similarities to the situation in the western Münsterland Cretaceous Basin (part 3 of this work). This is also valid for the deduced As dynamics before, during and after the paleo redox event and the associated change from sulfide- to hydroxide-control. Arsenic distribution and behaviour in sedimentary basins with a similar paleo weathering record – or a recent geological and climatological situation comparable to Central European Neogene conditions – is thus likely to follow the patterns established in this study and part 3 of this work.

Part 5 – Paleogene-Neogene: Arsenic and uranium signatures and evolution in a volcano-sedimentary basin in central Mexico

This study was published in modified form as the following peer-reviewed article:

Banning, A., Cardona, A., Rude, T.R. (2012): Uranium and arsenic dynamics in volcano-sedimentary basins – An exemplary study in North-Central Mexico. *Applied Geochemistry*, doi:10.1016/j.apgeochem.2012.01.001.

It was extended and rewritten for this dissertation.

Some preliminary results from this study were presented in modified form in the following conference contributions:

Banning, A., Cardona, A., Rude, T.R., 2011. Evolution of arsenic and uranium signatures in volcanic rocks, sediments and groundwater from San Luis Potosí, Mexico. 22nd Colloquium on Latin American Earth Sciences (LAK 2011), March 30-April 1, 2011, Heidelberg/Germany.

Banning, A., Rude, T.R., Cardona, A., Aguillón-Robles, A., Padilla-Sanchez, L., 2010. Uranium and arsenic in some aquifers from Mexico and Germany – a common geogenic development? 13th Water-Rock-Interaction conference (WRI-13), August 16-20, 2010, Guanajuato/Mexico.

Key questions

How is the U and As distribution in groundwater and solid reservoirs of the study area?

How does magmatic differentiation affect As and U occurrence?

How and with which consequences do As and U cross the magmatic-sedimentary interface?

Which geochemical proxies can be used to deduce primary trace element source signals?

Do the derived processes help explain similar observations in comparable study areas?

5.1 Introduction

5.1.1 Background and objectives

Recent studies in arid to semi-arid volcanic areas in Argentina (Nicolli et al. 2010, Bundschuh et al. 2004, Smedley et al. 2002) and Ethiopia (Rango et al. 2010) observed elevated As concentrations (several hundreds of ppb) in groundwater to be accompanied by high U. Distinct positive correlations between the two trace elements in both areas led to the interpretation of a potential common geogenic source for As and U.

Very similar climatic and geological conditions prevail in north-central Mexico, therefore San Luis Potosí was chosen as investigation area to study trace element dynamics and the structure of their sources and sinks on the interface between magmatic and sedimentary processes and examine the common occurrence of As and U despite their oppositional redox behaviour (As more mobile under reducing, U under oxic conditions). While groundwater quality problems in connection with As (Jiménez 1982, Landín 2006) and especially fluorine (F) (Carrillo-Rivera et al. 2002) in the study area have been recognized in the past (although information on the occurrence of As has not been published so far), this study is the first to report on elevated U concentrations in San Luis Potosí, thus adding another bullet point to the water supply problems as, like in most semi-arid zones of Mexico, groundwater is the main source for drinking, agricultural and industrial use.

5.1.2 Study area

The San Luis Potosí (SLP) study area is located in the north-central semi-arid part of Mexico, ~370 km northwest of Mexico City (Fig. 5.1a) and hosts around 1 million citizens. It is part of one of the several closed volcano-sedimentary basins on the western edge of the Sierra Madre Oriental.

The rather flat valley morphology of the Villa de Reyes Graben structure is bordered with abrupt relief by the surrounding mountains of the Sierra de San Miguelito (SSM) to the west, and the Sierra de San Pedro (SSP) to the east, being composed of Tertiary felsic volcanic and Cretaceous carbonatic rocks, respectively (Fig. 5.1a). Typical distensive features of a rift graben are documented (Fig. 5.1b). The normal faults partly served as conduits for volcanism and bound a regional horst and graben structure. The sierras elevate to more than +2300 m a.s.l. and steeply slope towards the plane of the drainage basin with an altitude of around +1900 m a.s.l. Annual precipitation is 386 mm, the medium temperature 17.5°C and potential evaporation around 2000 mm/a (Carrillo-Rivera et al. 2002). The following geological information is after Labarthe-Hernández et al. 1982, Tristán-Gonzalez 1986 and Aguillón et al. 1994.

The general geological situation is governed by a thick (up to >1500 m) sequence of Tertiary volcanic rocks, covered by alluvial sediments, and covering a Cretaceous mainly calcareous sequence outcropping in folded NW-SE structures in SSP. These conditions are comparable to a number of similar basins in the Sierra Madres Occidental and Oriental, and other regions of north-western Mexico and the south-western U.S.A. The Tertiary volcanics are dominantly felsic to intermediate in composition (cf. Fig. 5.2). They show porphyric textures dominated by glassy matrix (80-85 vol.%) with main phenocrysts being quartz, sanidine and plagioclase, and biotite, hematite and sericite as accessory minerals. Some high-K and F-rich lava flows show cavities and fractures partly filled with mainly quartz and topaz crystals (cf. Fig. 5.3b).

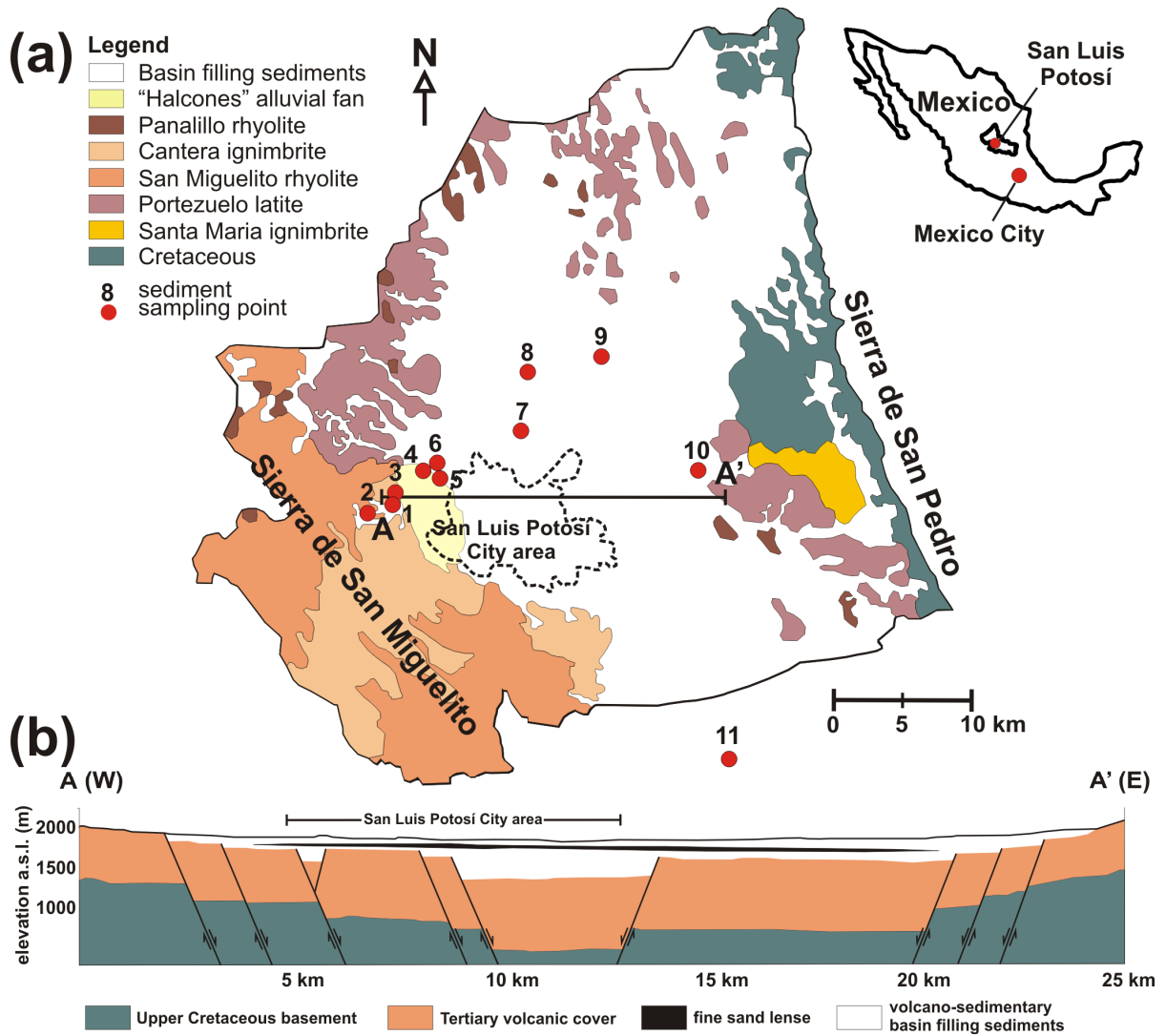


Fig. 5.1: (a) Geological map of the studied basin and location in Mexico (upper right corner) and (b) simplified stratigraphic-tectonic profile across the Villa de Reyes Graben (modified after Cardona et al. 2008, cf. Fig. 5.2).

The main phase of volcanic activity in the area was between 47 and 25 Ma BP with most abundant units (e.g. San Miguelito rhyolite) being formed during the Oligocene. Figure 5.2 offers a stratigraphical overview of the study area.

Volcano-clastic debris flow sediments resulting from erosion of the surrounding volcanics syn-tectonically filled the graben structure, the complete sequence is referred to as Tertiary Granular Undifferentiated (TGU). This basin filling consists of unconsolidated to moderately consolidated, well to poorly sorted beds of gravel, sand, silt, and clay deposited on alluvial fans (e.g. the "Halcones" alluvial fan, Fig. 5.1a), pediments, and playas, and comprises an average thickness of 250-300 m.

General stratigraphy		General regional lithologies		Units in Villa de Reyes Graben	Absolute age determinations (K-Ar)
		volcanic	sedimentary		
QUATERNARY	HOLOCENE		Alluvium		
	PLEISTOCENE	Basanites	Basin fill sediments (TGU+Quaternary)	Las Joyas basalt (sporadic)	
	PLIOCENE				
	MIOCENE	Andesites and basalts		Cabras basalt (sporadic)	8.1±0.8 Ma
TERTIARY	OLIGOCENE	Cover ignimbrites		Cantera ignimbrite Panalillo rhyolite El Zapote rhyolite Portezuelo latite	24.8±0.6 Ma to 29.0±1.5 Ma
		Rhyolitic domes		San Miguelito rhyolite Santa Maria ignimbrite Portezuelo latite	29.2±0.8 Ma to 32.0±1.0 Ma
	EOCENE	Heterogenous volcanism (andesitic to rhyolitic)		Casita Blanca andesite	37.0±3.0 Ma to 47.2±1.2 Ma
CRETACEOUS	ALBIAN - CENOMANIAN		carbonatic basement	El Doctor Fm.	

Fig. 5.2: Stratigraphy of the study area with the sampled units highlighted by hachures (figure produced after information from Cardona et al. 2008; TGU: Tertiary Granular Undifferentiated).

Fine-grained aeolian (loess-like) and flood plain deposits formed a 50 to 150 m thick layer, referred to as “fine sand lense” (Fig. 5.1b), fully enclosed in the TGU and being present in the largest part of the study area (except from the margins of the plain). This little permeable layer defines two main hydrogeological units, a shallow and a deep aquifer. The former is unconfined and consists of alluvium material with Ca-Cl-HCO₃-type groundwater. It shows heavy hydrochemical (e.g. nitrate) and microbiological (e.g. faecal coliforms) contamination. The heterogeneous deeper aquifer is confined below the fine-grained layer and hosted in both fractured volcanic rocks and granular material (TGU). Groundwater has a thermal character (T=30-40° C, partly up to 70° C determined by geothermometry (A. Cardona, UASLP, pers. comm.)) and slightly alkaline pH of 7.5 on average. It is HCO₃⁻-dominated exhibiting hydrochemical typification between Ca-HCO₃ and Na-HCO₃.

The deep aquifer has increasingly been subjected to intensive water extraction to supply SLP City, leading to a massive drawdown of the groundwater table in deep wells and the induction of regional old groundwater to the production wells. While agriculturally and industrially contaminated groundwater was successfully avoided by exploiting the deep aquifer, other water quality problems related to

high levels of F (up to 4 mg L^{-1}) and As (up to $65 \text{ } \mu\text{g L}^{-1}$) arose in some wells. Furthermore, significant concentrations of dissolved ^{222}Rn indicate a possible U source and thus an additional potential threat for the water supply. The previous hydrogeological and hydrochemical information is after Jiménez 1982, Carillo-Rivera 1992, Carillo-Rivera et al. 1996, Carillo-Rivera et al. 2002, Cardona and Carillo-Rivera 2006.

5.2 Materials and methods

To assess the different trace element reservoirs and interdependencies, the three compartments volcanic rocks, volcano-sedimentary basin fill sediments and groundwater were studied.

The volcanic rock database includes 40 samples (own outcrop sampling and analysis plus data from a previous local study, Rodríguez-Ríos 1997). Relevant units within the studied basin as well as some lithologies from its close surroundings were considered. Sample composition ranges from trachyandesitic to rhyolitic, whereby a focus was set on felsic volcanics accounting for their dominance in the study area (see chapter 5.3.1). The rocks are mainly of greyish to pinkish colour and exhibit different forms and grades of alteration, including devitrification, partly refilled irregularly shaped cavities suggesting glass dissolution, and oxidation of primary Fe phases to (hydr)oxides. Figure 5.3 gives an impression of some of these phenomena.

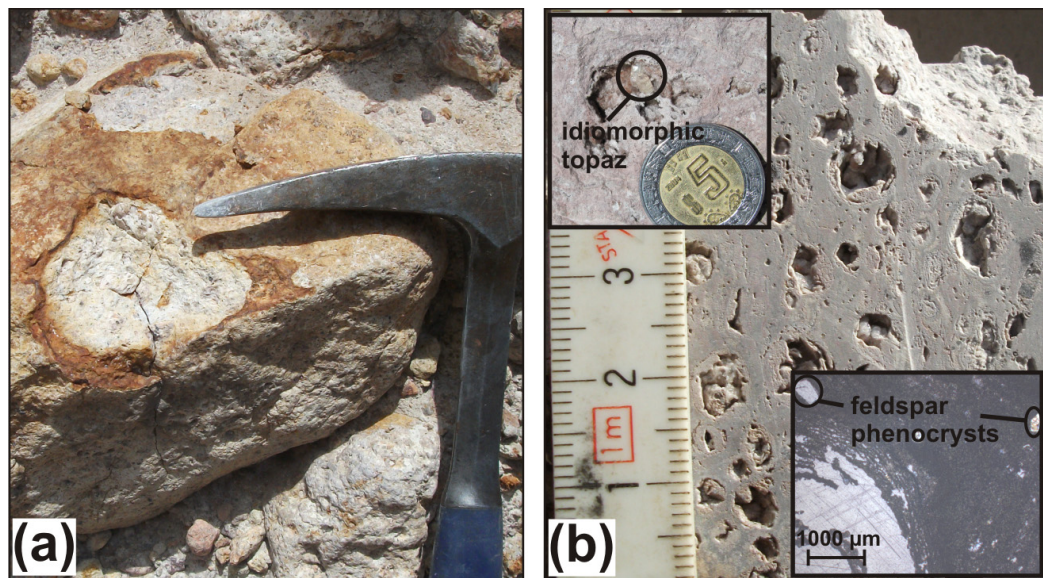


Fig. 5.3: Examples of volcanic rock appearance in the study area; (a) rhyolite block with reddish Fe oxide incrustation, (b) sawn rhyolite with irregular cavities deriving from glass dissolution (upper inset: rhyolite surface cavity with idiomorphic topaz crystal, lower inset: one cavity (light colour) in dense glassy matrix (dark colour) including few phenocrysts).

The basin filling sediments were sampled from outcrops (sand and gravel pits of the little consolidated material with a depth of up to 35 m below ground surface (Fig. 5.4a), also some shallower outcrops and river beds) at 11 locations (Fig. 5.1a), a total of 30 samples was obtained. These can be subdivided into two groups: (I) clastic sediments ranging in grain size from fine to coarse sand with differing portions of rounded rock pebbles, especially in proximity to the Sierra de San Miguelito. Samples of this type consist of material <2 mm only (obtained by sieving), rock pebbles were sorted out. In outcrops, dominant sediment colours are greyish to yellowish to dark orange indicating Fe-(hydr)oxides presence. (II) fine-grained light greyish to white sediments occurring as several meters thick banks or inter-bedded with the clastic sediments (Fig. 5.4b). These can be separated into two subgroups: (IIa) sediments showing a clear reaction to 10 % HCl treatment indicating the presence of a significant amount of calcite and (IIb) optically very similar whitish sediments (Fig. 5.4c) which do not react with HCl, in the following referred to as “pseudo-caliche”. Group IIa represents caliche crusts and banks which are interpreted as relicts of former ephemeral playa lakes in the valley. These secondary carbonates are a typical feature in semi-arid basins and were also identified in Argentinian As problem areas (Smedley et al. 2002). Group IIb is assumed to represent the alteration products of IIa following meteoric decarbonatization.

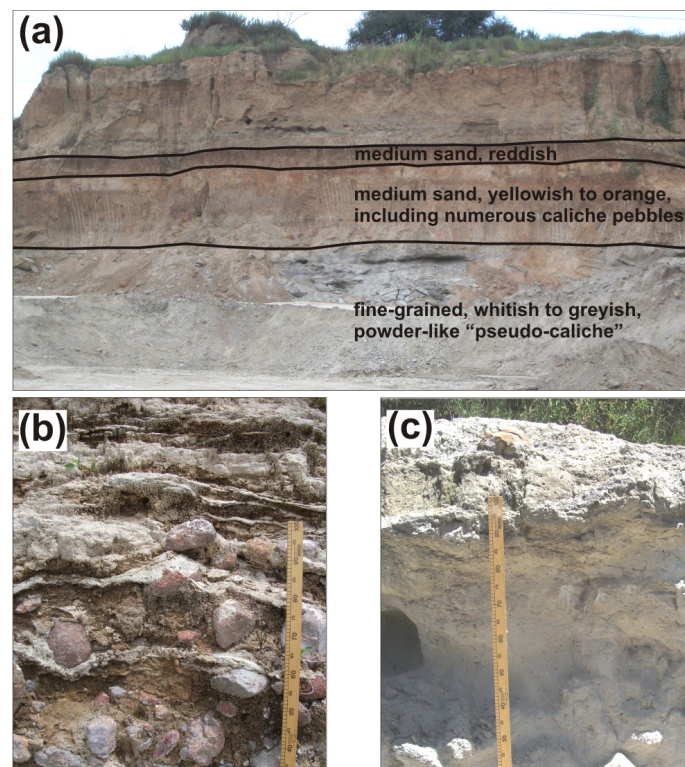


Fig. 5.4: Basin filling sediments in the study area; (a) outcrop 7, typical appearance of sediment outcropping in the central part of the basin (cf. Fig. 5.1a), no rock pebbles, (b) outcrop 1, caliche crusts inter-bedded with clastic material including numerous rhyolite boulders due to proximity to the Sierra de San Miguelito (cf. Fig. 5.1a), (c) outcrop 3, top of ~4 m thick “pseudo-caliche”, fine-grained, powder-like, little consolidated whitish sediment.

Groundwater samples were taken from wells extracting from the deep aquifer whereby a total of 61 samples (spatially representative for the aquifer extent) was obtained by pumping. An in-line flow cell was used to stabilize physico-chemical conditions during sampling. Groundwater samples were collected in double acid washed, low-density polyethylene bottles, filtered (0.45 μm) and stabilized to $\text{pH} < 2$ with 1 % ultrapure HNO_3 . Water samples were stored at 4° C until analysis. Trace element concentrations were determined by ICP-MS (Perkin Elmer ELAN 9000) (execution: Activation Laboratories Ltd., Ontario/Canada). The shallow aquifer was not sampled as this study does not deal with the evaporation effect on trace element concentrations, which surely is of importance for the shallow groundwater of the investigation area and has been well documented in climatically and geologically similar areas (e.g. Welch and Lico 1998, Smedley et al. 2002, Romero et al. 2003, Nicolli et al. 2010), but rather focuses on the impact of water-rock interaction processes leading to the hydrochemical signature of the groundwater, especially in terms of potentially hazardous trace elements like As and U. Moreover, the deep aquifer is of significantly higher importance for the water supply of San Luis Potosí, contributing 95 % of the total water usage (Carillo-Rivera et al. 1996).

For the volcanic rock samples taken for this study, whole rock samples were analyzed for major elements using a Siemens SRS 3000 X-ray wavelength dispersive spectrometer, a large suite of trace elements was quantified using ICP-MS (Perkin Elmer ELAN 9000) (execution: Ciencias de la Tierra, Universidad Autónoma de San Luis Potosí). Thin sections were produced from three rhyolite samples (San Miguelito rhyolite) and studied under the microscope (Olympus IX70).

Sampled basin filling sediments were sieved to < 2 mm grain size, ground in an agate mortar and analyzed for bulk rock geochemistry applying either Instrumental Neutron Activation Analysis or total digestion ($\text{HClO}_4\text{-HNO}_3\text{-HCl-HF}$ at 240°C) followed by ICP-OES analysis (Varian 735ES) (execution: Activation Laboratories Ltd., Ontario/Canada). Four sediment samples (1 from group I, 2 from group IIa, 1 from group IIb) were subjected to a four-step sequential extraction procedure (SEP, Tab. 5.1) to assess As and U fractionation and mobilization potential. Aliquots of the samples (1 g) were ground in an agate mortar and placed in 50 mL centrifugation tubes. Extraction solutions (25 mL) were added in each step and the respective treatment was conducted (Tab. 5.1). After centrifugation (15 min at 3000 rpm) and filtration (0.45 μm) of the supernatant solution, the remaining sediment was subjected to the subsequent step. The extracted solutions were analyzed for U and As using AAS (PerkinElmer AAnalyst 800), and for Ca and Fe with ICP-OES (PerkinElmer Optima 2000 DV) (execution: Institute of Mineralogy and Mineral Deposits, RWTH Aachen University).

Geochemical and hydrochemical results were statistically analyzed, especially for potential correlations of As and U, and trends with other elements. To assess the impact of rock alteration on trace element remobilization, the Chemical Index of Alteration (CIA) was calculated for the volcanic rocks after Nesbitt and Young (1982). Chondrite-normalized Rare Earth Elements (REE) patterns were pro-

duced and compared for the potential trace element reservoirs rock-sediment-groundwater. The data was compared to recent studies in geologically similar areas showing elevated trace element concentrations in groundwater (Nicolli et al. 2010; Rango et al. 2010).

Tab. 5.1: Applied sequential extraction procedure (SEP).

Step No.	Targeted fraction	Extractant	Procedure	Reference
1	Easily soluble	NH_4NO_3 (1 M, pH 7)	30 min shaking, 20° C	Han and Banin 1995
2	Bound to carbonates	NaOAc/HOAc (1 M, pH 5)	16 h shaking, 20° C	Han and Banin 1995
3	Bound to Fe-(hydr)oxides	NH_4 -oxalate (0.2 M) + ascorbic acid (0.1 M), pH 3.25	30 min in a water bath (96° C)	Wenzel et al. 2001
4	Residual	element (total) – element (sum steps 1-3)		

5.3 Results and Discussion

5.3.1 Volcanic rocks

To arrange sample groups for the following geochemical considerations, a petrographical classification of the studied volcanic rocks was conducted applying the approach of Le Bas and Streckeisen (1991) who defined lithological fields in a scatter plot of SiO_2 vs. $\text{Na}_2\text{O}+\text{K}_2\text{O}$ (TAS diagram, Fig. 5.5).

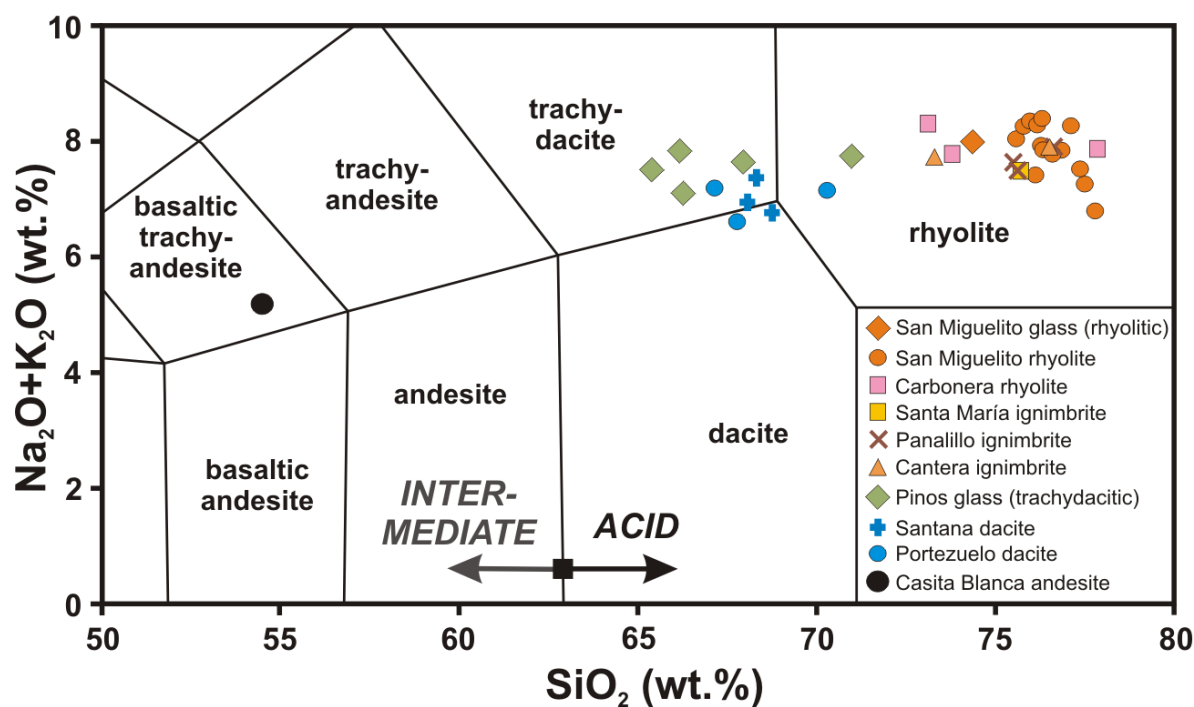


Fig. 5.5: Petrographical classification of the studied volcanic rock samples after Le Bas and Streckeisen 1991.

Except for one trachyandesite (Casita Blanca andesite), all samples can be classified as well differentiated, acid rocks (>63 wt.% SiO₂). The studied ignimbrites (Santa María ignimbrite, Panalillo ignimbrite and Cantera ignimbrite) all show rhyolitic composition. The Santana and Portezuelo units were combined as trachydacites, glass separates from the Pinos dome as trachydacitic glass (although in both groups, a slight overlap with the rhyolite field is observable). The San Miguelito and Carbonera units represent rhyolites (Fig. 5.5).

Concentrations of selected trace elements in the volcanic rocks, arranged according to the petrographical groups, are presented in Tab. 5.2. Furthermore, the chemical index of alteration (CIA) calculated as $CIA = Al_2O_3 / (Al_2O_3 + Na_2O + K_2O + CaO) * 100$ (Nesbitt and Young 1982) is implemented.

Tab. 5.2: Statistics on trace element concentration, As/U ratio and chemical index of alteration (CIA) for the volcanic rocks, and rhyolitic glass data from the Salí River Basin/Argentina (Nicolli et al. 2010).

	As μg g ⁻¹	U μg g ⁻¹	Th μg g ⁻¹	Pb μg g ⁻¹	Zn μg g ⁻¹	Cr μg g ⁻¹	Ni μg g ⁻¹	Cu μg g ⁻¹	V μg g ⁻¹	As/U -	CIA -
Trachyandesite (n=1)											
	2.50	1.26	6.00	18.0	123	68.0	27.0	<3	143	1.99	56.5
Trachydacite (n=6)											
mean	5.2	4.7	20.0	24.8	84.1	6.4	6.3	11.0	20.6	1.1	61.2
median	5.1	4.5	20.3	23.6	80.6	6.1	4.9	9.7	20.5	1.1	62.2
min	2.06	4.09	18.0	22.2	70.5	2.00	3.26	6.20	17.4	0.44	52.9
max	9.00	5.44	20.9	29.1	104	11.5	11.5	19.0	24.0	2.08	64.0
Rhyolitic ignimbrite (n=6)											
mean	11.9	4.2	29.9	34.3	92.7	2.0	10.7	22.4	23.3	2.9	58.3
median	11.7	4.1	25.6	32.0	91.2	1.9	13.0	28.5	28.8	2.9	58.6
min	7.47	3.23	24.0	26.1	58.0	1.00	1.48	4.21	12.0	1.64	57.0
max	18.2	5.38	40.0	49.0	127	3.26	20.0	34.0	29.1	4.21	59.7
Rhyolite (n=21)											
mean	15.0	6.8	37.0	40.3	83.2	3.3	2.9	10.5	8.0	2.2	61.1
median	12.2	7.1	33.8	39.2	65.2	3.2	1.4	7.0	6.3	1.8	60.5
min	5.00	3.60	16.0	28.3	42.8	1.00	0.50	2.00	<2	0.83	58.0
max	77.2	10.1	79.0	54.0	228	14.5	24.0	35.0	23.0	11.1	70.1
Glass separates (trachydacitic) (n=5)											
mean	8.9	4.7	17.2	26.5	123.4	3.4	3.1	6.8	12.9	1.9	59.4
median	8.7	4.5	16.6	25.1	93.7	3.3	2.6	7.4	13.5	1.9	59.1
min	7.45	4.22	15.3	25.0	66.7	2.11	0.96	3.85	7.97	1.77	58.2
max	11.2	5.60	21.5	30.5	273	5.64	7.29	8.17	15.6	2.00	61.2
Glass separates (rhyolitic) (n=1)											
	21.1	11.0	35.7	38.0	62.2	1.26	1.48	3.69	3.00	1.92	58.2
All rocks (n=40)											
mean	12.4	5.5	28.8	33.3	92.9	5.3	5.7	12.0	16.5	2.1	59.2
median	9.8	5.3	24.4	31.6	81.4	3.3	3.1	7.6	13.5	1.9	59.7
min	2.06	1.26	6.00	18.0	42.8	1.00	0.57	2.00	<2	0.44	52.9
max	77.2	11.0	79.0	54.0	273	68.0	27.0	35.0	143	11.1	70.1
Glass separates (rhyolitic) (n=13) (Nicolli et al. 2010)											
mean	6	15	n.a.	n.a.	59	/	/	19	8	0.4	58.4
median	6	10.6	n.a.	n.a.	55	/	/	14	8	0.6	57.6
min	<5	4.3	n.a.	n.a.	36	<20	<20	<10	<5		
max	8	27.7	n.a.	n.a.	107	273	<20	74	17		

Median As concentration in all rock samples is $9.8 \mu\text{g g}^{-1}$ with highest values in rhyolites (median $12.2 \mu\text{g g}^{-1}$, one outlier with $77.2 \mu\text{g g}^{-1}$, the second highest value – $21.1 \mu\text{g g}^{-1}$ As – was detected in the rhyolitic glass separate). Uranium median concentration is $5.3 \mu\text{g g}^{-1}$ ($1.26\text{--}11.0 \mu\text{g g}^{-1}$) for all rocks. Like for As, the highest median value ($7.1 \mu\text{g g}^{-1}$) is found in rhyolites, the highest single value in the rhyolitic glass. Compared to the rhyolitic glass separates analyzed by Nicolli et al. (2010), the highly differentiated rocks in the present study show significantly higher As concentrations while U contents are slightly lower, resulting in a typical As/U ratio of around 2 in San Luis Potosí volcanic rocks, compared to around 0.5 in the Argentinian glasses (cf. Tab. 5.2). The CIA values ranging from 53–70 (median ~ 60) document different grades of chemical rock alteration. Fresh rhyolites yield a CIA of 49, dacites between 46 and 50, while highly altered rocks approach 100 (i.e. pure kaolinite CIA), this development is caused by successive loss of geochemically less stable oxides and thus, a relative enrichment of Al_2O_3 (Dawood et al. 2004).

Figure 5.6 illustrates the distribution and interrelation of U and As in the different volcanic rocks sample groups.

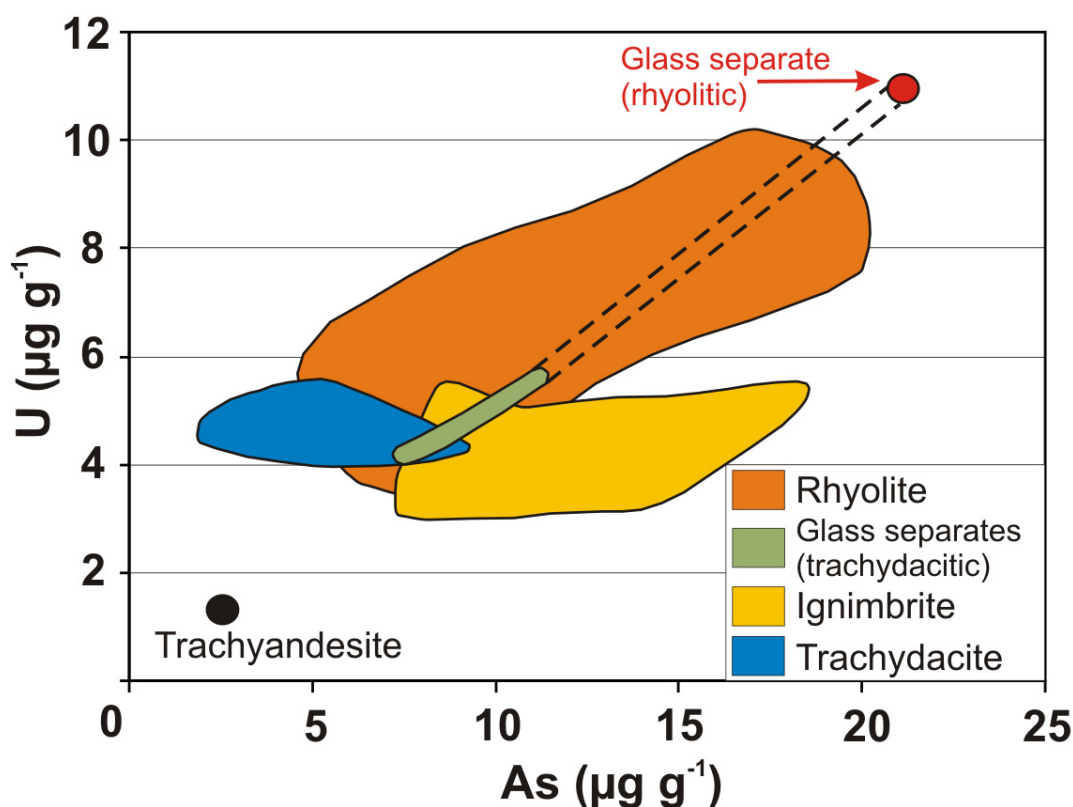


Fig. 5.6: As vs. U scatter plot for the volcanic rocks.

The rock samples cluster between two end members of low (trachyandesite) and high (rhyolitic glass) As and U concentrations. Rhyolite whole rock samples display a rather weak positive correlation between U and As ($R^2=0.38$). More distinct, the trachydacitic glass yields $R^2=0.98$ between As and U, even though with lower absolute concentrations. The rhyolitic glass sample is situated in direct extension of this trendline, indicating general common occurrence of the trace elements in the volcanic rocks' glassy matrix with enrichment towards more acid rocks (Fig. 5.6). These findings support the incompatible character of U and As during magmatic differentiation and their accumulation in the latest cooling products. Rhyolites and especially their glassy components may consequently be considered a potential primary source of the studied trace elements in the investigation area.

“Double correlation” scatter plots (i.e. correlation coefficient for As with other parameters vs. correlation coefficient for U with the same parameters) were developed for evaluating the dimension of geochemical similarity in occurrence and behaviour of As and U towards other major and trace elements in a given environment (Fig. 5.7).

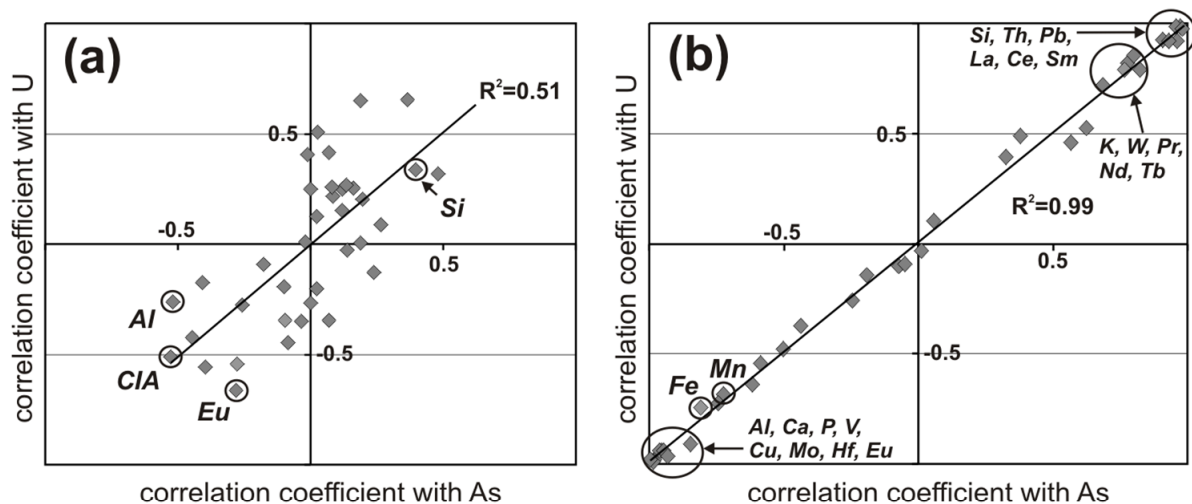


Fig. 5.7: „Double correlation“ plots for (a) rhyolite samples and (b) trachydacitic glass separates.

In the rhyolite sample group (Fig. 5.7a), U and As exhibit a similar geochemical behaviour, not only towards each other (cf. Fig. 5.6) but also towards most other chemical parameters as indicated by $R^2(R(\text{As}/\text{parameter}) \text{ vs. } R(\text{U}/\text{parameter}))=0.51$. Common positive correlation with Si, together with the negative trends towards Al, supports occurrence in the glassy matrix and not in silicate host minerals, especially feldspars. This finding is supported by Mahood and Hildreth (1983) who found partition coefficients significantly smaller than unity for $U_{\text{sanidine/rhyolitic glass}}$, and enhanced by the negative behaviour towards Eu which is incorporated as Eu^{2+} in feldspars during magmatic differentiation (e.g. Weill and Drake 1973) and thus withdrawn from the depleted melt (see also chapter 5.3.4).

A striking outcome of the plot is the common negative correlation of U and As with the CIA, i.e. the concentrations of both trace elements in the rocks decrease with increasing alteration intensity. They are mobilized together (CIA does not show any trend against the As/U ratio) from the volcanic rocks during weathering. Additional noteworthy features of CIA behaviour include a negative trend with Si ($R^2=0.29$) which is remarkably similar to $R^2_{CIA/U}=0.26$ and $R^2_{CIA/As}=0.28$ and suggests “congruent” mobilization of the three elements from the volcanic rocks. Further negative correlations of CIA with K ($R^2=0.61$), most probably due to the breakdown of feldspars, as well as with Cr, V and W indicate also these elements’ loss during weathering. Positive interrelations with CIA displaying relative refractory enrichment of elements during rock alteration are observed for Al ($R^2=0.48$, retained in clay minerals resulting from feldspar transformation which, nevertheless, do not represent effective secondary trace element sinks (Zielinski 1982)), Hf ($R^2=0.27$, most probably in refractory zircon) and Zn ($R^2=0.36$, likely to be retained in secondary Fe phases). Indifferent to slightly negative behaviour towards CIA is observable for REE (exception: Eu) indicating rather limited mobilization potentials.

Evaluating the separated trachydacitic glass samples in the same way (Fig. 5.7b), an even more significant geochemical similarity of U and As becomes obvious, expressed by $R^2=0.99$ in the dual correlation plot. The rhyolitic glass sample was not implemented in the calculations. It substantially supports and increases the geochemical trends but would exaggerate the correlation coefficient values in this data cohort due to significantly higher As and U concentrations, compared to the trachydacitic glass (cf. Fig. 5.6). The aforementioned relations in rhyolites towards Si, Al and Eu are clearly approved and enhanced, suggesting that the glassy matrix as the main host is largely responsible for As and U signatures in whole rock volcanics. A common occurrence with other incompatible elements (Th, W, REE except Eu) is observable while distinct negative correlations with Ca, P and Hf indicate that U and As are unlikely to be hosted within accessory mineral phases like apatite and zircon, both of which represent potential hosts in general (e.g. Zielinski 1981, Mahood and Hildreth 1983, Lee et al. 2009). Moreover, common negative behaviour towards Fe and Mn argues against primary (e.g. biotite) or secondary (e.g. hematite, Fe/Mn oxyhydroxides) phases of these elements to be significant hosts. While it is long since known that acid volcanic glasses represent sinks and potential sources of U (e.g. Rosholt and Noble 1969, Zielinski et al. 1977; exploration-related U research was triggered substantially in the 1960s and 70s), it was only recently shown for the first time by Borisova et al. (2010) that As is present in silicate glasses as As(III)-hydroxide species (similar to its preferential forms in aqueous solutions) and that concentrations can exceed $400 \mu\text{g g}^{-1}$ (study of Peruvian rhyolites). Zielinski (1981) found that U removal from volcanic glass mainly happens via glass-network dissolution, especially under high T and alkaline pH conditions of the dissolving solution, and that U and Si are mobilized in approximately equal proportions. Those findings are in good agreement with this study, considering the behaviour of U and Si discussed above and the observation of glass dissolu-

tion structures in the studied rocks (cf. Fig. 5.3b). For the investigation area, we can even extend these statements to As in view of the geochemical similarity to U and the U-analogue behaviour towards Si and CIA.

To conclude, U and As are dispersely distributed in the amorphous volcanic glass representing their primary source, subsequently remobilized together during rock alteration (with glass dissolution as dominant mobilization mechanism) and eventually inserted into sedimentary environments.

5.3.2 Basin filling sediments

Geochemical results of basin filling sediments analysis, classified according to the sample groups defined in chapter 5.2, are presented in Tab. 5.3, together with loess sediment data from the Salí River Basin/Argentina taken from Nicolli et al. (2010).

Tab. 5.3: Statistics on trace element concentrations and As/U ratios for the sampled basin filling sediments, and simple enrichment factors (EF) vs. volcanic rocks (median sediment divided by median volcanic rock composition). Additionally, loess basin sediment data from the Salí River Basin/Argentina (Nicolli et al. 2010) are implemented for comparison.

	As $\mu\text{g g}^{-1}$	U $\mu\text{g g}^{-1}$	Th $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	Cr $\mu\text{g g}^{-1}$	Ni $\mu\text{g g}^{-1}$	Cu $\mu\text{g g}^{-1}$	V $\mu\text{g g}^{-1}$	As/U -
Group I (clastic sediments) (n=18)										
mean	11.7	4.2	16.9	24.0	85.7	17.7	8.8	9.7	30.0	2.9
median	11.7	4.3	17.2	21.5	87.0	18.0	7.0	10.0	34.0	2.7
min	5.70	2.70	13.2	14.0	49.0	11.0	3.00	5.00	6.00	1.33
max	19.2	5.90	21.4	47.0	137	31.0	20.0	18.0	51.0	4.96
EF	1.19	0.81	0.70	0.68	1.07	5.45	2.28	1.32	2.52	1.41
Group IIa (caliche sediments) (n=7)										
mean	13.1	4.9	9.7	11.7	61.2	18.0	9.0	7.3	24.7	2.5
median	10.2	3.2	9.1	12.0	66.0	10.0	10.0	7.0	27.0	2.7
min	5.50	2.70	6.30	5.00	21.0	<2	5.00	3.00	13.0	1.22
max	37.4	14.0	15.8	20.0	99.0	59.0	19.0	13.0	36.0	4.89
EF	1.04	0.60	0.37	0.38	0.81	3.03	3.26	0.93	2.00	1.41
Group IIb ("pseudo-caliche" sediments) (n=5)										
mean	7.4	4.6	18.0	13.4	86.0	8.4	5.4	3.4	18.2	2.0
median	8.5	4.3	16.1	11.0	80.0	8.0	2.0	2.0	9.0	2.2
min	4.60	1.70	9.70	8.00	58.0	<2	2.00	1.00	<2	0.66
max	10.4	7.00	27.3	25.0	113	21.0	17.0	11.0	38.0	5.12
EF	0.87	0.81	0.66	0.35	0.98	2.42	0.65	0.26	0.67	1.16
All basin filling sediments (n=30)										
mean	11.3	4.4	15.4	19.5	80.2	13.4	8.6	7.9	27.0	2.8
median	10.4	4.3	15.7	20.0	79.0	13.0	7.0	9.0	28.5	2.6
min	4.60	1.70	6.30	5.00	21.0	<2	2.00	1.00	<2	0.66
max	37.4	14.0	27.3	47.0	137	59.0	20.0	18.0	51.0	5.12
EF	1.06	0.80	0.64	0.63	0.97	3.93	2.28	1.19	2.11	1.35
Basin sediments (loess) (n=18) (Nicolli et al. 2010)										
mean	10	4.9	n.a.	n.a.	78	46	/	21	84	2.1
median	10	3.88	n.a.	n.a.	81	45	/	20	85	2.6
min	7.00	3.60	n.a.	n.a.	<30	29	<20	13	53	
max	14.0	12.4	n.a.	n.a.	125	58	37	26	99	

Median As concentration in all basin fill sediment samples is $10.4 \mu\text{g g}^{-1}$ with highest median values in the clastic sediments ($11.7 \mu\text{g g}^{-1}$). However, the single highest value was detected in the most Ca-rich caliche sample ($37.4 \mu\text{g g}^{-1}$ As, 21.6 wt.% Ca). Uranium median concentration for all sediments is $4.3 \mu\text{g g}^{-1}$ ($1.7\text{--}14.0 \mu\text{g g}^{-1}$) with, like for As, the peak single value in the same caliche sample while the minimum U content was observed in the “pseudo-caliche” group. Arsenic and U concentrations (and their ratios) in the Argentinian sediments are similarly high. Nevertheless, the latter yield significantly elevated values for Cr and V. In the Villa de Reyes Graben, As exhibits a slight enrichment (especially in the clastic sediment group) together with Cu, Ni, V and Cr, while U is slightly depleted (same for Th and Pb), compared to the volcanic source rocks characterized in chapter 5.3.1. Consequently, the median As/U ratio is higher in the sediments, indicating growing differences in geochemical behaviour between As and U. Figure 5.8 shows the As-U scatter plot for the basin filling sediments.

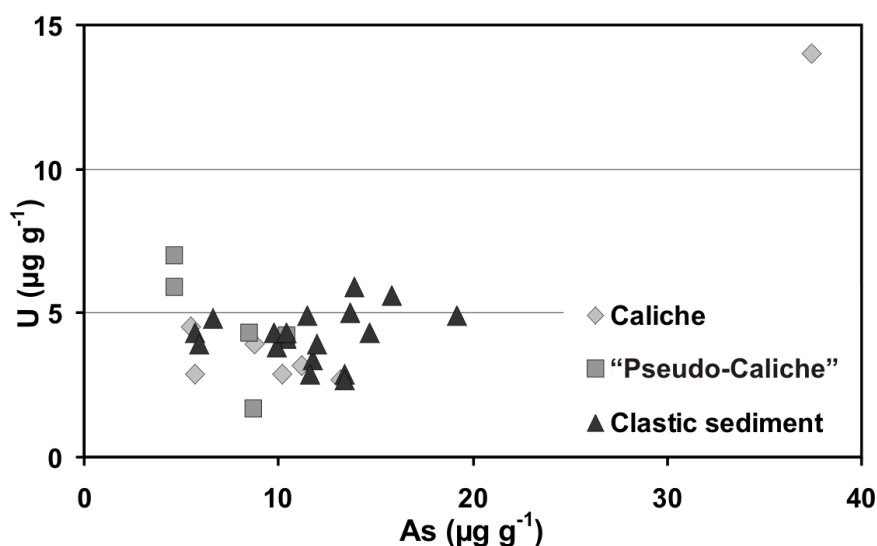


Fig. 5.8: As vs. U scatter plot for basin filling sediments.

The observation of highest concentrations of both As and U in the most Ca-rich caliche sample and lower values in the other members of the caliche (Ca: 3.84–14.7 wt.%) and the “pseudo-caliche” (Ca: 0.19–1.06 wt.%) groups (Fig. 5.8) leads to the assumption that trace element loss from these sediments occurs during decarbonatization, i.e. that U and As might be preferentially hosted in the relatively soluble carbonate fraction, especially when considering that calcite is able to incorporate both trace elements (Sturchio et al. 1998, McCall et al. 2001, Di Benedetto et al. 2006). Nevertheless, in view of lacking trends towards Ca and partly quite high U concentrations in the “pseudo-caliche” group, further clarification is needed. To assess this question and the general mineralogical fractionation of both

trace elements, the applied sequential extraction procedure (SEP, Tab. 5.1) contains a step targeting the carbonate fraction in the sediments.

Figure 5.9 illustrates the results of the SEP with an approach to evaluate potential preferences in leaching either As or U. Samples subjected to the SEP include the aforementioned high-Ca caliche containing highest trace element concentrations, a second caliche sample with lower Ca (7.84 wt.%), one unconsolidated whitish “pseudo-caliche” (Ca: 0.32 wt.%) and a reddish fine sand sample representing the clastic basin fill sediments.

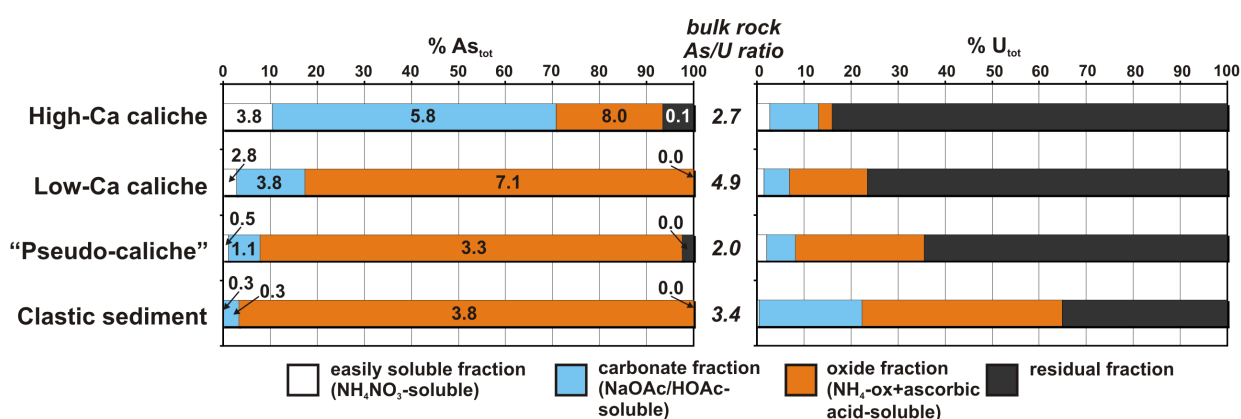


Fig. 5.9: Sequential extraction procedure (SEP) results for As (left side) and U (right side) and bulk rock As/U ratios of the studied samples. Figures in the left diagram represent As/U ratio factors (i.e. the As/U ratio in the different extracted fractions divided by the bulk rock As/U ratio, whereby factors >1 indicate preferential As leaching, <1 preferential U leaching and =1 congruent As and U leaching in the respective extraction steps).

A significant proportion of NH₄NO₃-soluble As was observed in the high-Ca caliche only (~10 % As_{tot} corresponding to 3.9 µg g⁻¹ As), other samples yielded <3 % for both U and As. The carbonate fraction of As decreases with decreasing Ca in the sample (i.e. with increasing decarbonatization) from 60 % As_{tot} (i.e. 22.5 µg g⁻¹, largest As fraction) in the high-Ca caliche to 7 % in the “pseudo-caliche”. This suggests that indeed, As is lost from the sediments during calcite dissolution. This trend is less distinct for U with a NaOAc/HOAc-soluble portion of 10 % U_{tot} in fresh caliche and 5-6 % in the more altered samples. As/U ratio factors between NaOAc/HOAc-leachate and bulk rock suggest clearly preferential As over U leaching in high- and low-Ca caliche and virtual congruent mobilization from the “pseudo-caliche”. Mobilization potential for As in this rather easily soluble fraction is clearly higher than for U, an equilibration seems to be reached upon completion of the decarbonatization process. In contrast, U leaching in this step is favoured over As from the clastic sediment sample (22 % U_{tot}; 3 % As_{tot}). Preferential As over U mobilization is obvious in all samples in the NH₄-oxalate-soluble trace element fraction, most prominently in the high-Ca caliche (ratio factor 8.0). In the other samples, this fraction is the most important for As, accounting for 86 % (low-Ca caliche) to 97 % (clastic sediment) of As_{tot}.

A shift in the mineralogical As fractionation from carbonates to Fe oxides during decarbonatization is obvious, supported by a significant negative trend between Ca and Fe in the caliche sample group indicating Ca loss and Fe relative enrichment. Considering the As concentration difference between fresh and altered caliches, however, the oxides are not able to effectively retain As mobilized from carbonates which consequently will be lost from the sediments to solution. In the applied SEP, the residual fraction is negligible, virtually bulk As was dissolved from the samples.

Similar to As, the U fraction bound to oxides is more important than the carbonate fraction (except for the high-Ca caliche, see above), it represents the dominant U portion in the classic sediment (43 % U_{tot}). Expressed by a ratio factor of 0.3, preferential U over As mobilization occurs most noticeably in the relatively easily soluble steps 1 and 2 for the clastic sediment. Compared to As, total U leachability in this SEP is significantly lower, ranging from 16 % U_{tot} in fresh caliche to 65 % U_{tot} in the clastic sediment which results in large residual fractions. Thus, an important part of the U appears to be effectively retained, especially in the caliche sediments. Sphene, known as uraniferous accessory mineral (Zielinski 1981), might offer an explanation for this phenomenon, as concluded from a positive trend between U and Ti in the caliche group. Another possible explanation, derived from the observation that in contrast to the clastic material, playa sediments contain at least measurable concentrations of sulfide-S ($350 \mu\text{g g}^{-1}$ on average, maximum value: $1000 \mu\text{g g}^{-1}$ in the high-Ca caliche sample), may be U accommodation in reduced accessory mineral phases like pyrite (Descostes et al. 2010) or uraninite (Leach et al. 1980). The U portion associated with the applied SEP's residual fraction would then at least partly be remobilizable in the course of meteoric oxidative alteration of the sediments.

Leach et al. (1980) studied the geochemical U exploration potential of playas, examining playa sediments from the U.S. Basin and Range Province, an area with very similar climatic and geological conditions as the Mexican example in this work. They concluded that evaporation processes in the playa lakes lead to U enrichment in the carbonaceous sediments (up to $58 \mu\text{g g}^{-1}$, median: $3.9 \mu\text{g g}^{-1}$, cf. Tab. 5.3) even with low U inflow water, but vulnerability to alteration and remobilization substantially limits the U exploration potential. Large residual U fractions in sediments (after treatment with 1 M HCl; up to 95 % U_{tot}) is another similarity between the studies (which is not further discussed by Leach et al. 1980). Those results are supported by the data in this study, the genetic model can thus be transferred to the playas in San Luis Potosí and extended to As enrichment therein.

In summary, a heterogeneous dissolution behaviour with a preference for As mobilization from the studied basin fill sediments is observable, compared to the rather homogeneous common mobilization of both trace elements via glass dissolution from volcanic rocks as discussed in the previous chapter.

5.3.3 Groundwater

Selected trace element results for the groundwater samples are presented in Tab. 5.4 and compared to the studies of Nicolli et al. (2010) and Rango et al. (2010).

Tab. 5.4: Statistics on trace element concentration and As/U ratio for the groundwater samples in this study, and comparison with WHO guideline or recommended values. Additionally, groundwater data from the Salí River Basin/Argentina (Nicolli et al. 2010) and the Central Main Ethiopian Rift Valley/Ethiopia (Rango et al. 2010) are implemented for comparison (n.a. – not analyzed).

	As μg L ⁻¹	U μg L ⁻¹	Th μg L ⁻¹	Pb μg L ⁻¹	Zn μg L ⁻¹	Cr μg L ⁻¹	Ni μg L ⁻¹	Cu μg L ⁻¹	V μg L ⁻¹	Se μg L ⁻¹	Sb μg L ⁻¹	Mo μg L ⁻¹	Al μg L ⁻¹	Fe μg L ⁻¹	Mn μg L ⁻¹	SiO ₂ mg L ⁻¹	As/U -
WHO (2008) guideline or recommended values																	
	10	15	-	10	-	50	20	2000	-	10	20	70	200	-	400	-	
Groundwater Villa de Reyes Graben/Mexico (deep aquifer, T=30-40(-70)°C, n=61, this study)																	
mean	11.4	7.6	0.004	0.9	20.7	1.5	0.6	3.0	4.4	1.7	0.2	1.7	25.1	71.6	1.9	80.7	5.9
med.	10.6	4.7	0.003	0.7	12.6	0.9	0.3	2.2	4.2	1.2	0.2	1.7	17.0	20.0	0.9	76.3	2.5
max	25.8	138	0.03	5.2	250	5.3	2.9	12.9	22.4	8.7	1.37	4.1	92	2470	29.8	117	87.2
min	1.86	0.1	0.001	0.16	2.9	0.25	0.15	0.5	0.8	0.4	0.04	0.2	5	5	0.2	18.6	0.1
% dataset exceeding guideline value																	
	54	5		0		0	0	0		0	0	0	0		0		
Groundwater Salí River Basin/Argentina (deep artesian aquifer, T=21-45°C, n=17, Nicolli et al. 2010)																	
mean	36.4	1.8	n.a.	n.a.	n.a.	178	n.a.	n.a.	77.5	2.1	0.11	10.1	8.7	170	16.1	41.4	20.4
med.	26.5	1.3	n.a.	n.a.	n.a.	178	n.a.	n.a.	63.8	2.1	0.09	5.5	7	183	8.3	35.2	20.5
max	76.9	6.19	n.a.	n.a.	n.a.	218	n.a.	n.a.	162	3.6	0.29	29.9	22	365	90.6	74.3	
min	16.2	0.10	n.a.	n.a.	n.a.	110	n.a.	n.a.	44.8	0.2	0.03	0.4	2	40	0.5	21	
% dataset exceeding guideline value																	
	100	0				100				0	0	0	0		0		
Groundwater Central Main Ethiopian Rift Valley/Ethiopia (T=22-36°C, n=23, Rango et al. 2010)																	
mean	21.3	9.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	31.3	n.a.	n.a.	38.5	112	107	34.1	n.a.	29.0
med.	2.5	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5.6	n.a.	n.a.	5.5	77	72	2.6	n.a.	2.9
max	157	49.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	148	n.a.	n.a.	446	382	483	268	n.a.	354
min	<DL	<DL	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<DL	n.a.	n.a.	1.01	<DL	<DL	<DL	n.a.	0.1
% dataset exceeding guideline value																	
	35	17										13	23		0		

More than half of the characterized groundwaters exhibit As concentrations in exceedance of the WHO guideline value (median As: 10.6 μg L⁻¹) which demonstrates the extent of the As-related water quality problem in the study area. Only 5 % of the U data exceed the actual WHO recommended guideline value of 15 μg L⁻¹. Nevertheless, in view of a maximum value of 138 μg L⁻¹ and nearly half of the samples being above 5 μg L⁻¹ (for comparison: a national survey in the U.S.A. found a mean U groundwater concentration of 1.86 μg L⁻¹, Longtin 1988), the study area's groundwater U can be characterized as elevated. As/U ratios are variable at a median value of 2.5. Low concentrations of Fe and

Mn support the widely oxidizing character of the groundwater, albeit one Fe outlier ($\sim 2.5 \text{ mg L}^{-1}$, but no elevated As or U) indicates the localized presence of reducing conditions.

Arsenic and U exhibit a general positive trend in groundwater samples (Fig. 5.10) which is in agreement with Nicolli et al. (2010) and Rango et al. (2010). Nevertheless, outliers from this trend with elevated As or U, respectively, are observable. In Fig. 5.10, the greyish zone is defined by the average As/U ratio in volcanic rock samples $+2$ standard deviations (lower boundary) and -2 standard deviations (upper boundary) to approach a confidence area in which dissolution from volcanic rocks may be made responsible for the As/U signature in groundwater. Two-thirds of the samples plot within this field, $\sim 25\%$ show more elevated As concentrations, 8% exhibit disproportionally high U. This distribution is responsible for the displacement of median groundwater As/U ratio towards the “As side” displaying As sources in addition to volcanic rocks. These are likely to be found in the basin filling sediments that were shown to have a higher As than U mobilization potential (see previous chapter), especially the playa caliches. Arsenic loss from Fe oxides in carbonate or clastic sediments may also contribute to this shift of the As/U ratio. Uranium-dominated trace element input lowering groundwater As/U may be expected in early stages of mainly clastic sediment alteration, as concluded from SEP results. Supporting the assumed processes, outlier groundwater samples mainly stem from the basin fill sediments and, to a lower degree, from the contact zone between sediments and fractured volcanic rocks (Fig. 5.10).

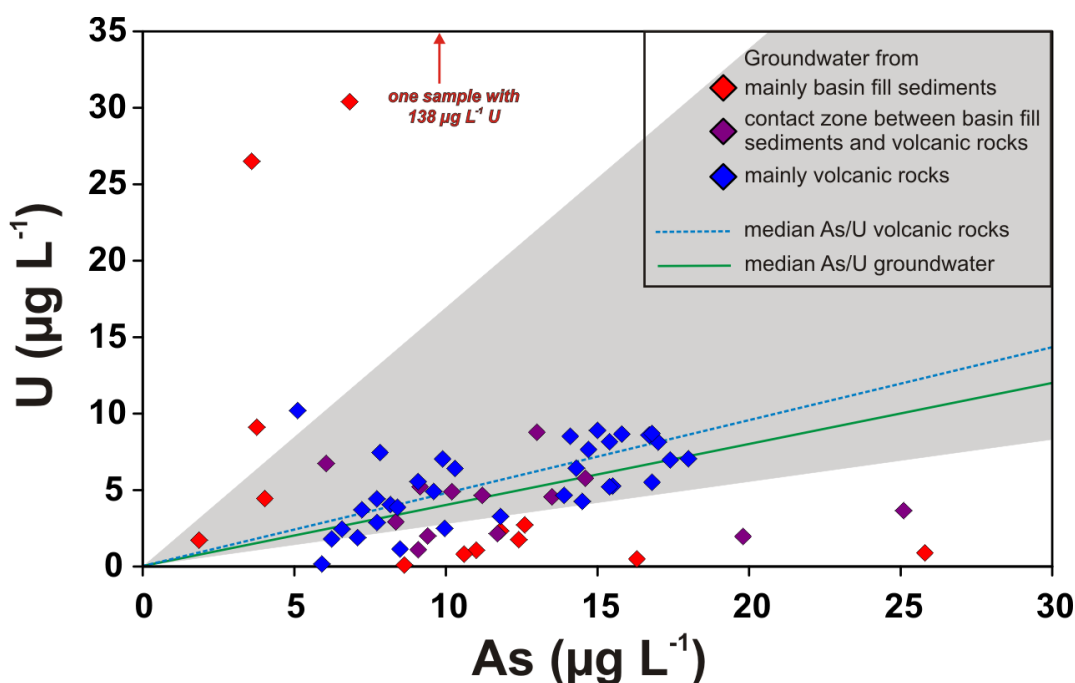


Fig. 5.10: As vs. U scatter plot for groundwater, the grey zone indicates an area defined by median volcanic rock As/U ratio $+2$ standard deviations (lower line) and -2 standard deviations (upper line).

To follow up the development of As and U hydrogeochemical behaviour after mobilization from their common primary source, “double correlation” diagrams were produced, as earlier presented for volcanic rocks (Fig. 5.7), for clastic basin filling sediments (Fig. 5.11a) and groundwater (Fig. 5.11b).

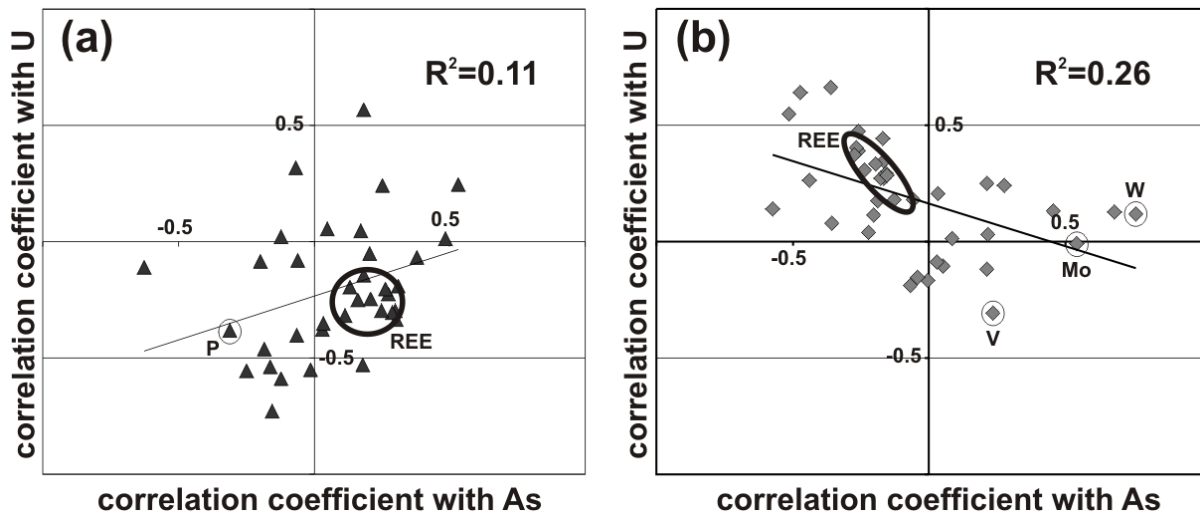


Fig. 5.11: „Double correlation“ plots (i.e. correlation coefficient for As with other parameters vs. correlation coefficient for U with the same parameters) for (a) clastic basin filling sediments and (b) groundwater samples.

Compared to the findings for volcanic rocks and especially the glass separates, the positive trend between U and As behaviour towards other elements is significantly less distinct for the clastic basin fill sediments (Fig. 5.11a). Moreover, the trendline shows a considerable offset from the center of the diagram. Both observations argue for a less similar geochemical behaviour of the trace elements and thus a beginning split-up of As and U in the sedimentary environment. Negative trends towards P suggest that also in the sediments, accessory apatite is unlikely to host significant amounts of the trace elements.

A similarly diffuse but negative trend is exhibited by the groundwater “double correlation” plot (Fig. 5.11b). Although As and U occur together in the water (as discussed before, cf. Fig. 5.10), their chemical speciation is known to differ in solutions, dependent on their unequal affinity towards complexing reagents. While under the hydrochemical conditions prevailing in the studied aquifer (chapter 5.1.2), U is most likely transported as carbonate complexes, As will preferably be present as oxyanion species. The former assumption is supported by rare earth elements’ (REE) positive relation towards U (and negative towards As) – REE tend to form carbonate complexes in the given milieu as well (Luo and Byrne 2004). The latter statement is underlined by rather positive As trends towards other mobile oxyanion forming elements like Mo, W or V.

In consequence, the very similar geochemical behaviour of As and U in volcanic primary host rocks is successively decoupled after crossing the interface between magmatic and sedimentary environment, although the primary source's hydrogeochemical fingerprint is still clearly visible in absolute trace element concentrations.

5.3.4 Rare earth elements analysis

REE plots were produced for the compartments volcanic rocks (Fig. 5.12a), basin fill sediments (Fig. 5.12b) and groundwater (Fig. 5.12c) as another approach to study the interrelations between the different potential As and U reservoirs in the study area. Additionally, the intensity of the observed Eu anomaly was plotted against U concentrations in volcanic rocks (Fig. 5.12d).

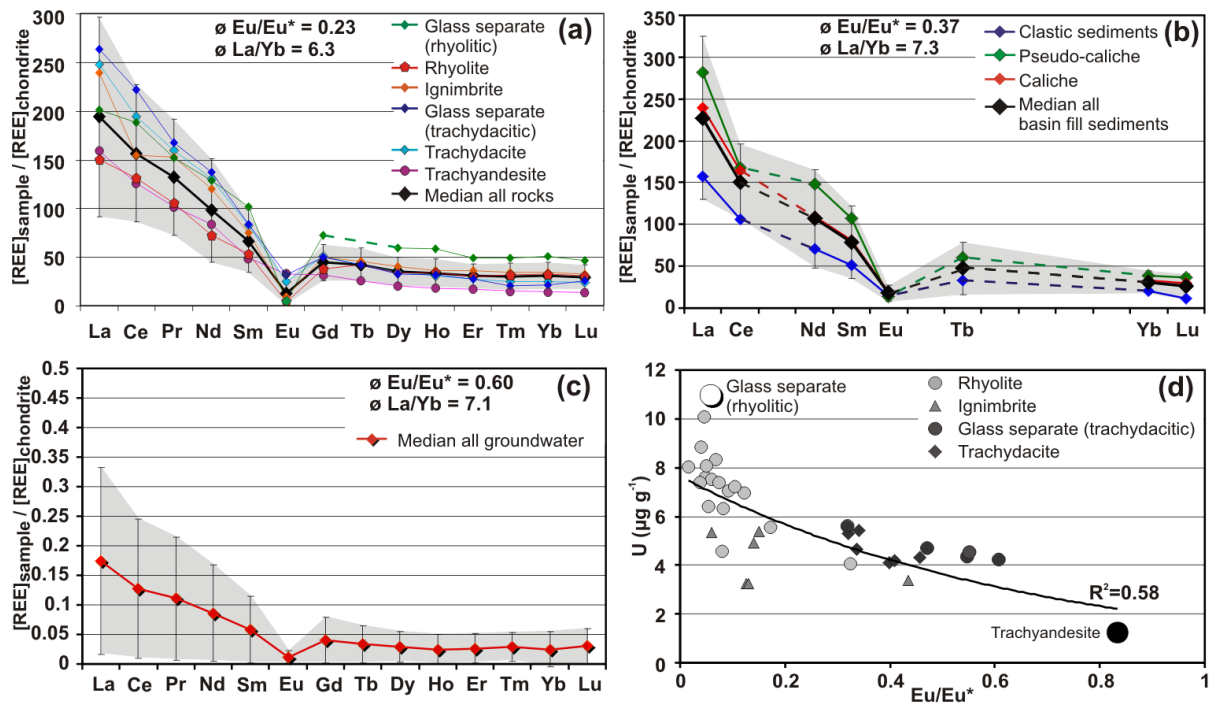


Fig. 5.12: Rare earth element (REE) plots normalized to C1 chondrite data (after Evensen et al. 1978) and some REE proxies for (a) volcanic rocks, (b) basin filling sediments and (c) groundwater, grey zones indicating standard deviation from median compartment values; (d) plot of U vs. intensity of Eu anomaly (Eu/Eu^*) for volcanic rocks.

Several characteristic features are observable in the chondrite-normalized REE pattern of the volcanic rocks (Fig. 5.12a): light rare earth elements (LREE) are enriched compared to the heavy ones (HREE), expressed by an average La/Yb ratio of 6.3. A distinct negative Eu anomaly is developed in all volcanic units except for the trachyandesite.

Both basin filling sediments (Fig. 5.12b) and groundwater (Fig. 5.12c) share the most striking features of the volcanic rocks' REE pattern – LREE > HREE with similar La/Yb ratios and a clear, even though less steep, negative Eu anomaly (Eu/Eu* may be overestimated for the sediments as Gd data is not available and the parameter was calculated on the basis of Sm and Tb). These patterns must have been inherited from the source rocks as in systems <200°C, especially oxidizing ones, Eu anomalies cannot be generated (Bau and Möller 1992). Consequently, hydrogeochemistry of sediments and groundwater in the studied basin is dominated by supply from, and interaction with, the acid volcanic rocks.

There is a significant negative correlation ($R^2=0.58$) between U concentrations and depths of the Eu anomaly (Eu/Eu*) for the volcanic rocks (Fig. 5.12d) with end members being trachyandesite and rhyolitic glass, clearly expressing once more that most differentiated rocks have the highest potential for U enrichment. The same trend is observable, though less distinct ($R^2=0.34$), for As. In highly evolved acid magmas, feldspar fractionation removed large amounts of Eu^{2+} , leaving the remaining melt Eu-depleted but enriched in incompatible elements like U and As. Highest accumulation levels are then reached in most differentiated magmas and especially their latest cooling products, represented in this study by the rhyolitic glass.

5.3.5 Comparison with recent studies in similar environments

In the studies from Argentina (Nicolli et al. 2010) and Ethiopia (Rango et al. 2010), median U concentrations are lower than in the Villa de Reyes Graben, quantitatively clearly below the WHO guideline in the Argentinian case (at least in the deep aquifer best comparable to the studied Mexican aquifer); highly variable contents partly in excess of the limitation (Tab. 5.4) were found in Ethiopia. In contrast, As is above $10 \mu\text{g L}^{-1}$ in 100 % of the groundwater samples from the Salí River Basin studied by Nicolli et al. (2010), resulting in high As/U ratios of more than 20 on average. In the Ethiopian study, As concentrations are extremely heterogeneous. Nevertheless, the median As/U ratio is in the same range as in this study. Besides fluoride, being a water quality problem in all three study areas discussed here, elevated Cr concentrations (100 % of the samples above the WHO guideline value of $50 \mu\text{g L}^{-1}$) are obvious in Salí River Basin groundwaters studied by Nicolli et al. (2010), while low concentrations prevail in San Luis Potosí. This observation is in accordance with much higher Cr contents in basin loess sediments in the Argentinian case study (cf. Tab. 5.3), potentially representing a Cr source. Apart from As and U, Rango et al. (2010) measured Mo and Al concentrations partly exceeding WHO recommendations in groundwaters from the Central Main Ethiopian Rift Valley (Tab. 5.4). The following paragraph attempts to explain some of the observed hydrogeochemical differences be-

tween the deep artesian aquifer in the Salí River Basin/Argentina and the deep aquifer in the Villa de Reyes Graben/Mexico.

Compared to the studied Mexican aquifer, the Argentinian deep groundwaters contain significantly higher concentrations of dissolved Fe and Mn, both being elevated by ~factor 9 (Tab. 5.4). Apart from the aforementioned much more abundant Cr (factor 200!), also V shows concentrations elevated by ~factor 15, while SiO₂ contents are substantially higher in the Mexican case. Together with the distribution of As and U and the geochemical data from both study areas, these observations lead to the following interpretation of the differing hydrogeochemical signatures: inheritance of As/U ratios in groundwaters from rocks as well as high dissolved SiO₂ and low Fe and Mn argue for volcanic glass dissolution as dominant trace element mobilization mechanism in the Mexican case, compared to desorption from metal hydr(oxides) in basin filling sediments. Nevertheless, this water-sediment-interaction acts as modifier of the superior hydrogeochemical fingerprint derived from water-rock-interaction. Vice versa, As abundance in the Argentinian deep groundwater is clearly favoured over U (ratios >20) while rhyolitic glasses separated from basin sediments show As/U ratios <1. Direct inheritance of groundwater As/U signatures from volcanic rocks is therefore unlikely. On the other hand, bulk loess basin sediments clearly exhibit As/U>1 (Tabs. 5.2-4), documenting preferential secondary accumulation of As over U, most likely in metal (hydr)oxides. Together with higher Fe and Mn and lower SiO₂ in groundwater, these findings argue for trace element (and here mainly As) desorption from secondary metal (hydr)oxides under alkaline conditions to be the dominating mobility control and thus support the genetic model of Nicolli et al. (2010). Additional evidence is provided by comparison of oxyanion forming elements (besides As): high Cr and V contents are found in loess sediments and groundwater (and not in the rocks), a distribution not observed in the present study. These hydrochemically similar elements are likely to share source and mobilization mechanism with As. In the shallower aquifers in both areas, growing influence of evaporation effects lead to further enrichment of trace elements which, as mentioned before, is not discussed here. Elevated fluoride concentrations in groundwater, being comparably high in both regions, may contribute to enhanced As release from the primary sources by anion exchange processes (Casentini et al. 2010).

Differences in trace element mobilization modes (glass dissolution vs. desorption from metal (hydr)oxides) described here may partly be explained by the configuration of the aquifers themselves: the deep aquifer in the Villa de Reyes Graben/Mexico includes the uppermost part of the fractured volcanic rocks with the glassy matrix accounting for 80-85 vol.% of the whole rocks in addition to the volcanic glass shards present in the basin filling sediments. Access to rhyolitic glass in the Quaternary deep aquifer of the Salí River Basin/Argentina is limited to its proportion in the sediments (25-50 %, Nicolli et al. 2010). Furthermore, differences in T and pH between the two aquifers may contribute to the observed diversities: median groundwater pH in the Argentinian case is 8.1 (7.5 in the aquifer

studied here), while groundwater T is higher in the Mexican case (30-40(-70)° C compared to a median of 23.6° C in the Salí River Basin). More alkaline pH contributes significantly to enhanced desorption of As from metal (hydr)oxides (e.g. Smedley and Kinniburgh 2002) while the removal rate of trace elements and Si during volcanic glass dissolution is more sensitive to temperature than to solution pH (Zielinski 1981).

5.4 Conclusions

Partly exceeding WHO guideline values for drinking water, elevated concentrations of U and As were identified in deep groundwater of the volcano-sedimentary Villa de Reyes Graben around the city of San Luis Potosí in semiarid north-central Mexico. Hydrogeochemical characterization of the trace element reservoirs volcanic rocks – basin filling sediments – groundwater allowed for the derivation of the As and U sources and sinks structure. Chemical signatures of sediments and groundwater are largely dominated by interaction with acid volcanic glass representing the primary trace element source in the study area. Congruent dissolution of the glass, which is shown to be successively enriched in incompatible trace elements during magmatic differentiation, is the principal mechanism of As and U release into groundwater, modified by additional input from basin fill sediments. The latter exhibit preferential As over U mobilization potential during meteoric decarbonatization of playa lake sediments and desorption from Fe-(hydr)oxide coated clastic material. The hydrochemical fingerprint of volcanic glass dissolution is thus slightly shifted towards the As side.

The common fate of U and As during magmatic processes and the successive dissociation in hydrogeochemical behaviour when crossing the interface between magmatic and sedimentary environments are illustrated in this study. The trace element situation in the investigation area shows similarities with known high-As regions under comparable geological and climatic conditions. However, also important differences in the evolution of present day As and U distribution were figured out. Therefore, this study contributes to the understanding of natural trace element dynamics in semiarid volcano-sedimentary regions where groundwater often represents the only drinking water resource whose anthropogenically as well as geogenically influenced quality is a major concern to a large and continuously growing population worldwide.

Part 6: Common discussion

The final chapter of this work will comparatively recapitulate findings from the five study areas and shortly assess the core theses formulated in the common introduction. Subsequently, a geodynamic model explaining geogenic As and U distribution in Germany as a whole is developed and discussed.

Regional significance and comparative overview

Important outcomes of the five single studies conducted in the course of the present work are summarized in Tab. 6.1 and Fig. 6.1 whereby the background geological/hydrogeological situation, concentrations and distributions of As and U, accumulation and remobilization mechanisms as well as actual and potential impact on groundwater quality are assessed.

Unravelling the geogenic As and (partly) U dynamics in each studied area contributes massively to the awareness and comprehension of, and eventually the responses to, potential groundwater contaminants on a regional scale:

Part 1 first succeeded in explaining the occurrence and development of recently discovered elevated U concentrations in Franconian groundwater. It furthermore extends the comprehension of high groundwater As and facilitates the understanding of common occurrence of both trace elements in the region.

Part 2 documented formerly unpublished significant As accumulations in iron ores widespread along the margins of the Upper Rhine Graben. Though actually obviously an inactive source for groundwater As around the sampled quarry, the study calls attention to this lithology in terms of its potential source function under different hydrochemical conditions.

Parts 3 and 4 identified reduced sediments containing high-As pyrite as potential sources for As release to groundwater. In the western Münsterland Cretaceous Basin as well as the central Lower Rhine Embayment, these sediments represent important aquifers. Groundwater extraction has to account for stabilization of the redox milieu to prevent As mobilization through triggered pyrite oxidation. The effect of a paleo redox event on As redistribution in different areas was not formerly assessed.

Part 5 discovered elevated groundwater U in San Luis Potosí/central Mexico and succeeded in unravelling its common occurrence with As, and the evolution of both elements' signatures from magmatic differentiation to output into groundwater via dissolution of felsic volcanic glass representing the incompatible trace elements' source.

next page:

Tab. 6.1: Comparative overview of the studied areas (n.a. – not analyzed).

Part No	1	2	3	4	5
Geology and hydrogeology					
Region	Franconia	Upper Rhine Graben	Münsterland	Lower Rhine Embayment	San Luis Potosi/ Mexico
Sediment provenance	Moldanubian	Rhenohercynian	Rhenohercynian	Rhenohercynian	Paleogene volcanics
Sediment age	Triassic (Norian)	Jurassic (Aalenian/Bajocian)	Cretaceous (Santonian)	Paleogene (Chattian)	Post-Paleogene
Sediment type	Alluvial sandstones with apatitic high-U „active arkoses“	Carbonate-bound ooidic Fe ores and ambient clastic and carbonatic rocks	Lower part: reduced fine sands, near-surface: oxidized sands with hydroxidic concretions	Lower part: reduced fine sands, near-surface: oxidized sands with hydroxidic concretions	Volcano-sedimentary, clastic and carbonatic, products of mainly rhyolite erosion
Depositional facies	Terrestrial (semiarid, partly sabhka/playa)	Shallow marine	Shallow marine	Shallow marine	Terrestrial (semiarid, partly sabhka/playa)
Aquifer type	Porous/fractured	Karstic(?)/fractured	Porous	Porous	Porous/fractured
Aquifer importance for regional water supply	High	Low	Very high	High	Very high
Solid samples As (n)	47	32	38	36	40 (rocks) + 30 (basin filling)
As mean/median (range) in whole rock, $\mu\text{g g}^{-1}$, all samples	16/11 (1.8-170)	77/75 (10.3-223)	14/7.5 (0.8-73.1)	68/13 (3.2-1860)	Volc. rocks: 12/10 (2.1-77.2) Sediments: 11/10 (4.6-37.4)
Dominant host phase	Hematite	Goethite	Pyrite (reduced part) Goethite (oxidized part)	Pyrite (reduced part) Goethite (oxidized part)	Volcanic glass
Solid samples U (n)	47	32	38	36	40 (rocks) + 30 (basin filling)
U mean/median (range) in whole rock, $\mu\text{g g}^{-1}$, all samples	25/2.3 (<0.5-260)	1.8/2.0 (<0.5-3.2)	1.3/0.7 (<0.5-7.5)	2.4/2.4 (<0.5-7.2)	Volc. rocks: 5.5/5.3 (1.3-11.0) Sediments: 4.4/4.3 (1.7-14.0)
Dominant host phase	Francolite	n.a.	Siderite (?)	n.a.	Volcanic glass
Groundwater As and U situation					
Known As >10 $\mu\text{g L}^{-1}$	Yes	No	No	No (neighbouring similar aquifer: yes)	Yes
Known U >10 $\mu\text{g L}^{-1}$	Yes	No	No	No	Yes
Current source classification	Active (As, U)	Inactive	Inactive	Inactive	Active (As, U)
Estimated release risk	High (ongoing francolite weathering)	Low (As desorption/reduction unlikely)	Medium (As, triggered pyrite oxidation possible)	Medium (As, triggered pyrite oxidation known)	High (ongoing volcanic glass dissolution)
Trace element accumulation and redistribution					
Process	Precipitation from groundwater	As sorption to Fe (hydr)oxide ooids	As pyritization; Fe-U precipitates at siderite surfaces (?)	As pyritization	Magmatic differentiation
Timing	Early diagenetic	Syn depositional	Syn depositional	Syn depositional	Syngenetic
Redistribution to	n.a.	n.a.	Fe hydroxides during paleo redox event; Fe hydroxides during subrecent pedogenesis	Fe hydroxides during paleo redox event	Basin sediments (calcite, Fe (hydr)oxides)
Redistribution timing	n.a.	n.a.	Since Neogene	Neogene	Since volcanic activity

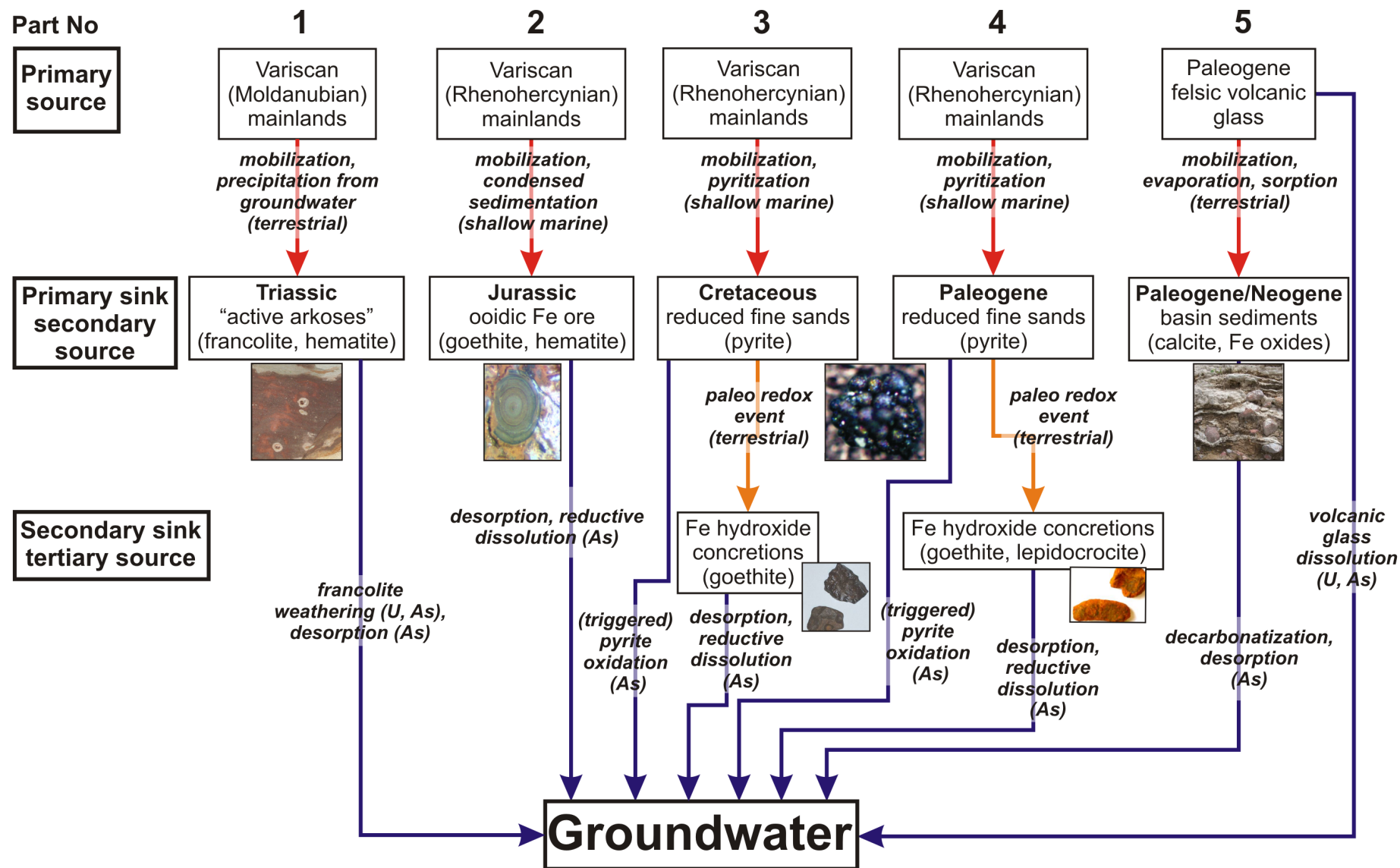


Fig. 6.1: Graphical overview of As and U sources and sinks structures including mobilization and immobilization processes in the studied areas.

Core theses reflection

The core theses formulated in the common introduction to this work will be reassessed in the following.

1. Terrestrial uraniferous phosphates (“active arkoses”) represent As and U sinks and contribute to elevated concentrations in groundwater (Part 1).

→ Phosphates were characterized as weathering-susceptible carbonate fluorapatites (francolites) with high U contents. While the U distribution in northern Bavarian groundwater is controlled by these deposits, As bound on both hematite and francolite in the arkose matrix at least contributes to the groundwater As problem.

2. Shallow marine environments fostering ooidic Fe ore formation provide conditions for syngenetic As accumulation (Part 2).

→ The studied depositional conditions proved suitable for As enrichment in mainly goethitic Fe ooids during condensed sedimentation. Thereby, As accumulation is preferred over other trace elements.

3. Postdepositional paleo redox events cause extremely heterogeneous As and other trace element distribution in shallow marine sediments, leading to partly massively enriched secondary concretions (Parts 3 and 4).

→ Both studies proved that this is indeed the case. Mainly pyrite-controlled rather homogeneous As distribution in the original deeper sediment facies changes under formation of highly reactive redox transition zones and distinct paleo redox boundaries into extremely heterogeneous Fe hydroxide-controlled distribution in near-surface sediments.

4. Large-scale redox events alter comparable lithologies and redistribute trace elements hosted therein in the same way, independent of sediment age (Parts 3 and 4).

→ Santonian and Chattian shallow marine sediments exhibit very similar responses to the late Tertiary oxidative redox event, including rock fabric and mineralogical changes, trace element (esp. As) redistribution and remobilization potentials. The developed genetic and geochemical patterns are obviously of general validity for the studied geo-environment.

5. Both U and As are incompatible elements in magmatic differentiation and therefore enriched in felsic lithologies (Part 5).

→ This is strongly supported by the findings from the Mexican case study. Absolute concentrations, inter-elemental behaviour and geochemical proxies argue for successively increasing U and As abundance towards more differentiated magmatic lithologies.

6. The observation of common geogenic As and U occurrence despite oppositional redox and transport behaviour in groundwater of a given area is indicative for a common source (Parts 1 and 5).

→ Dissolution of volcanic glass was identified as the main common release mechanism of U and As in the volcano-sedimentary Mexican basin. It represents input from a common source into groundwater, supported by geochemical signatures in all studied compartments. For the Franconian case, see first core thesis in this chapter.

7. Secondary hydrogeochemical processes in affected aquifers are responsible for As and U separation upon input into groundwater (Parts 1 and 5).

→ While As and U both occur in groundwater of certain sedimentary basins, it became obvious that in most samples, only one of the trace elements showed high concentrations. This is explainable by separation due to redox heterogeneity in the aquifer (esp. Part 1), or by additional preferential input from secondary sources (esp. Part 5).

8. In an actuogeological approach, characterization of recent trace element dynamics in a given geological-climatic environment can help understand As and U accumulation and remobilization processes in comparable paleo milieus (Parts 1 and 5).

→ This approach proved to be promising though not directly applicable in this work. It is most likely that evaporative U/As enrichment observed in subrecent playa caliches (Part 1) is also the responsible process for elevated contents in carbonaceous paleo deposits of the same facies in Triassic Franconia (“calcretes”, part 5). The latter were, however, not studied here. Characterized “phoscretres” are diagenetic successors of “calcretes” and illustrate a possible future alteration of the latter.

9. High-As/U primary sources are a prerequisite for elevated concentrations in sediments/groundwater of a given area (Parts 1 to 5).

→ This is not necessarily the case. Given a source material of sufficient volume and suitable hydrogeochemical conditions, moderate absolute concentrations can account for elevated U/As presence. Volcanic glass (Part 5) is such an example. Francolite (Part 1) requires high U concentrations to produce the elevated groundwater signal as the deposits are of small volume, compared to the total aquifer. Depositional conditions are responsible for As accumulation in Fe ooids (Part 2) and pyrite (Parts 3 and 4), statements on primary source concentrations are not possible. Evaluating the redistribution of homogeneous As contents to Fe hydroxide concretions (Parts 3 and 4) is scale-dependent: while bulk rock concentrations are in moderate $\mu\text{g g}^{-1}$ ranges, host phase-(pyrite-)As is ~ 0.2 wt.%. Generally, hydrogeochemical conditions suitable for trace element mobilization are considered equally important to absolute concentrations (cf. Part 2 – Fe ores as high-As sediments without actual release due to unsuitable hydrochemical milieu).

- 10.** Trace element accumulation processes and reservoirs can be of different orders such that spatio-temporal structure models of sources and sinks can be developed for a given area (Parts 1 to 6).

→ Structure models of As and U reservoirs and transfer processes between them were successfully developed for all study areas with up to three orders of trace element sources/sinks (cf. graphical summary, Fig. 6.1). Evaluation of all relevant processes and compartments, and their spatio-temporal order, is considered necessary to fully illustrate trace element dynamics of a given study area.

- 11.** The structure of As and U sources and sinks in the different geo-environments characterized in this work can help unravel trace element dynamics in similar milieus worldwide (Parts 1 to 6).

→ The choice of study areas representing a variety of geological backgrounds and histories of development make approaches and obtained results transferable to other regions. Sandstone-hosted uraniferous phosphates (Part 1), shallow marine ooidic Fe ores (Part 2), reduced glauconitic/pyritic marine sandy sediments (Parts 3 and 4) and felsic volcano-sedimentary basins (Part 5) are widespread geological environments worldwide and often share genetic and geochemical characteristics. Since detailed studies on geogenic As and U dynamics and their potential impact are scarce in most of these geo-milieus, the methodological and data processing approaches and derived interpretations in the present work can serve as a basis for assessing these topics in comparable areas. This is especially supported by striking similarities between the studies in Cretaceous and Paleogene sediments (Parts 3 and 4) exhibiting close analogies not only in geological situation and development but also in As distribution and behaviour in spite of a time span of ~50 Ma between sediment deposition in both areas.

- 12.** Geological evolution, expressed by geochemical proxies, can explain trace element distribution on different temporal and spatial scales, and help forecast potential problem areas (Parts 1 to 6).

→ In this work, a large variety of (hydro)geochemical signals was successfully used to characterize trace element occurrence and behaviour in space and time as well as paleo and recent geo-milieu conditions. Thereby, considered scales in the single study areas ranged from microscopic (e.g., development within a single Fe ooid grain, Part 2) to basin size (e.g., As/U distribution in the Franconian Keuper basin, Part 1). In methodological combination with characterization of solid phase mineralogical composition and trace element fractionation, this proved to be a successful approach for the given tasks. Trace element abundance was shown to directly reflect supraregional and intra-basinal geological evolution. A model to explain geogenic U and As distribution on a nationwide scale allowing for the prediction of further potential problem areas in Germany is presented in the following chapter.

- 13.** There is an ultimate large-scale control mechanism of U and As distribution in sedimentary environments which may still be traceable in basins where internal processes can account for redistribution and the present-day situation (Part 6).

→ The distribution of areas with elevated As and U in Germany is large-scale widely determined by Variscan and Quaternary geology. Geochemical sediment provenance controls elevated As (felsic provenance) and U (highly felsic provenance) supply to sedimentary environments, whereby the different Variscan sections are decisive. Thus, magmatic geochemistry based on incompatibility of U and As is the ultimate control of trace element supply to sedimentary systems where subsequent intra-basinal processes of trace element accumulation, redistribution and eventually remobilization to groundwater take place and create the present-day situation. This model is developed and discussed in the following chapter.

Geodynamic model for natural As and U distribution in Germany

Besides the major importance of the obtained results on a regional scale and global transferability based on comparable conditions between single areas, more may be learned from general geochemical comparison of all study areas and their distribution in space and time. Therefore, the impact of sediment provenance and the spatio-temporal development of Europe on geogenic As and U distribution are evaluated in the following. Geochemical proxies will be assessed to characterize the studied sediments' provenance and combine the results with the As and U accumulation processes derived in the present work (cf. Tab. 6.1 and Fig. 6.1). Figure 6.2 illustrates a ternary plot of La-Th-Sc to deduce source rock geochemistry and tectonic setting.

All studied sediments plot in a rather dense cloud near the La corner of the diagram. Regarding the distal position of the samples from standard amphibolite, basalt and andesite (characterized by higher contents of compatible Sc) and the proximity to granite (higher degree of incompatible La and Th), a generally rather felsic provenance is obvious for all sediments (Fig. 6.2). Also in comparison to NASC, the North American Shale Composite (representative of upper crustal sediments; e.g., Gromet et al. 1984), samples nearly quantitatively plot in the more felsic range and are in this respect rather comparable to typical cratonic sandstone plotting within the data aggregation.

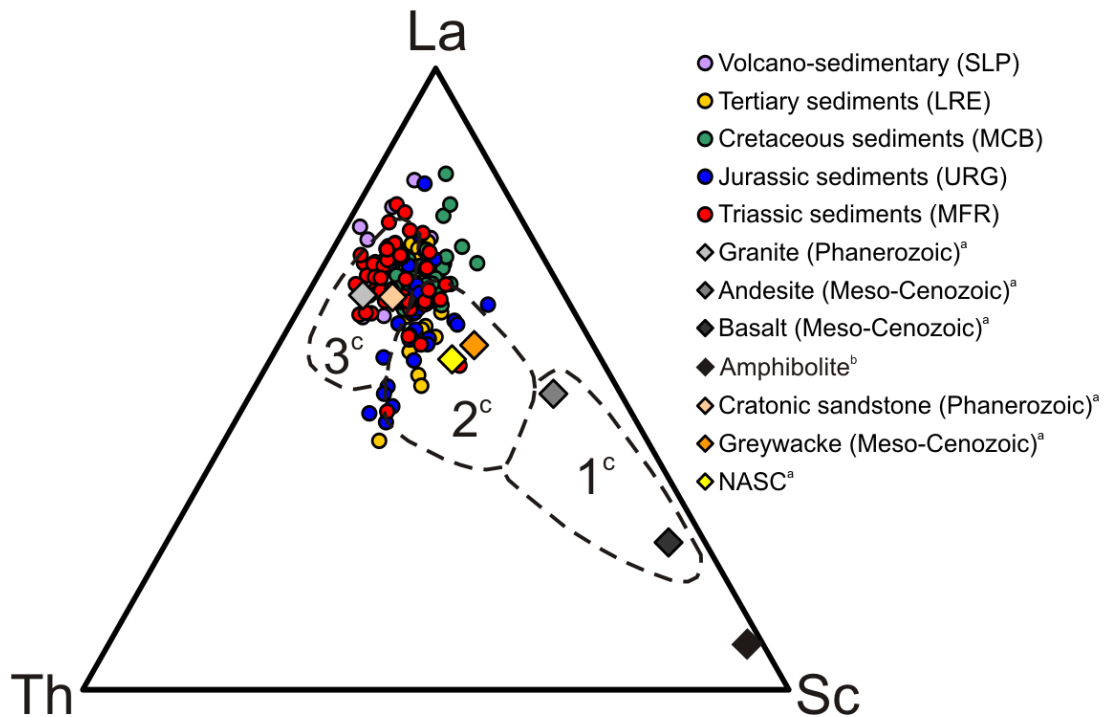


Fig. 6.2: La-Th-Sc plot of all sediment samples, whereby SLP: San Luis Potosí, LRE: Lower Rhine Embayment, MCB: Münsterland Cretaceous Basin, URG: Upper Rhine Graben, MFR: Middle Franconia; NASC: North American Shale Composite. For comparison, plots of typical lithologies were implemented after ^aCondie (1993) and ^bCullers (1994). Furthermore, fields in the diagram after ^cBhatia and Crook (1986) indicate provenance rock tectonic setting with 1: oceanic island arc, 2: continental island arc, 3: active or passive continental margin.

Concerning tectonic setting of the provenance sensu Bhatia and Crook (1986), most samples indicate derivation from continental margins with an overlap to the field of continental island arcs (Fig. 6.2), thus reflecting the tectonic configuration of Variscan central Europe as will be discussed later on. Sediment origin from oceanic island arcs can be excluded which was expectable regarding the choice of study areas.

To better differentiate between the single study areas with regard to geochemical provenance, a binary plot of incompatible La vs. compatible Sc is presented in Fig. 6.3.

The observation of general rather felsic provenance, also in comparison to average upper crustal sediment (NASC), is clearly supported by the binary plot (Fig. 6.3). In spite of partly considerable scattering (R^2 of the five data subsets: 0.11-0.72, cf. Fig. 6.3), differences between the single study areas become evident. Triassic sediments from Middle Franconia (La/Sc ratio derived from trendline equation: 6.09) and volcano-sedimentary basin filling from San Luis Potosí (5.88) exhibit clearly more felsic provenance than marine sediments of Jurassic (3.13), Paleogene (4.21) and Cretaceous (4.71) age.

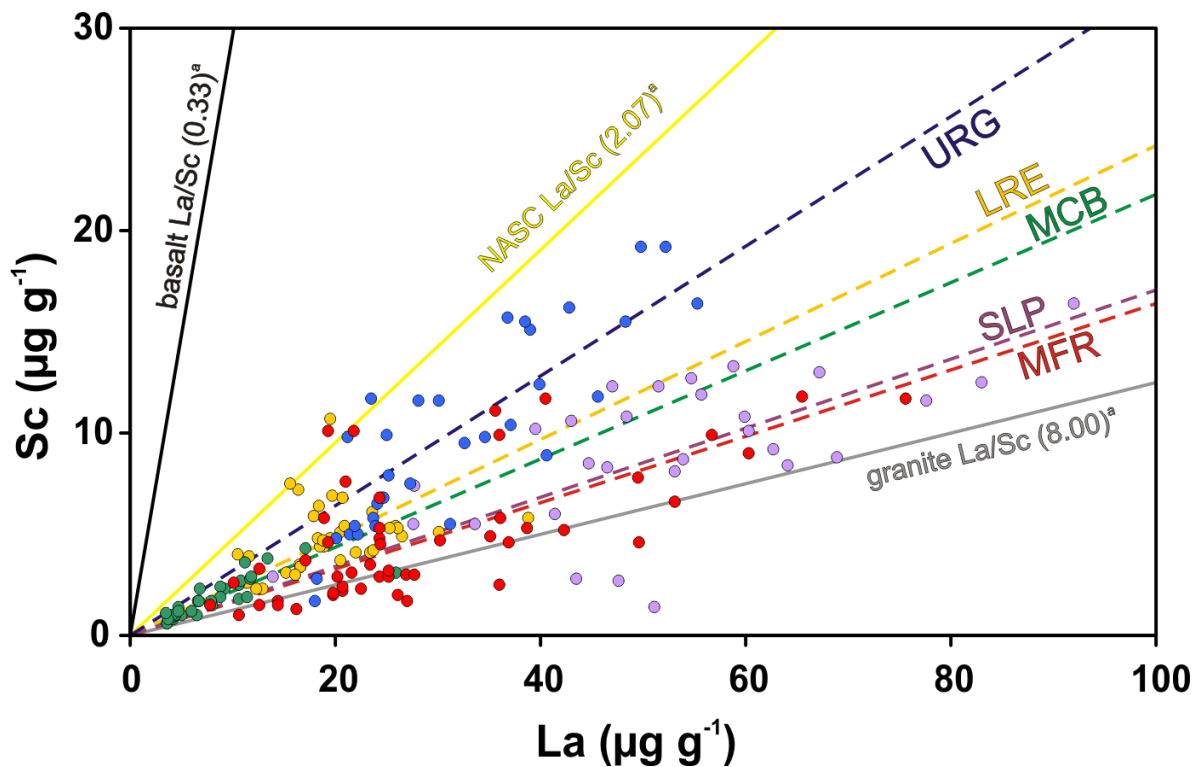


Fig. 6.3: La vs. Sc scatter plot and trendlines for sediment samples from the five study areas, abbreviations: see caption of Fig. 6.2. Basalt, NASC and granite standard ratios after ^aCondie (1993).

Consequently, the areas with high U potential in terms of accumulation in rocks/sediments and elevated concentrations in groundwater (cf. Tab. 6.1) originate from more felsic sources than sediments hosting “only” As.

The following is hypothesized:

- a) Sedimentary environments potentially fostering As enrichment require above-average felsic provenance to assure sufficient supply of the incompatible trace element.
- b) Sedimentary environments potentially fostering U enrichment require highly felsic provenance to assure sufficient supply of the (more?) incompatible trace element, i.e. highly felsic origin is a prerequisite for sedimentary systems to create both, high As *and* U. Of course, conditions of redeposition, climate, hydrochemistry and microbiology (let alone anthropogenic activity) control potential final groundwater concentrations.
- c) Classical geochemical proxies like the one presented here may serve as pre-diagnostic tools to characterize geochemical provenance (and thus, primary trace element sources) of sedimentary areas potentially affected by As and/or U.

In an effort to combine this approach and the previously discussed trace element accumulation processes, plots of La vs. U and La vs. As are presented as Fig. 6.4 and Fig. 6.5, respectively.

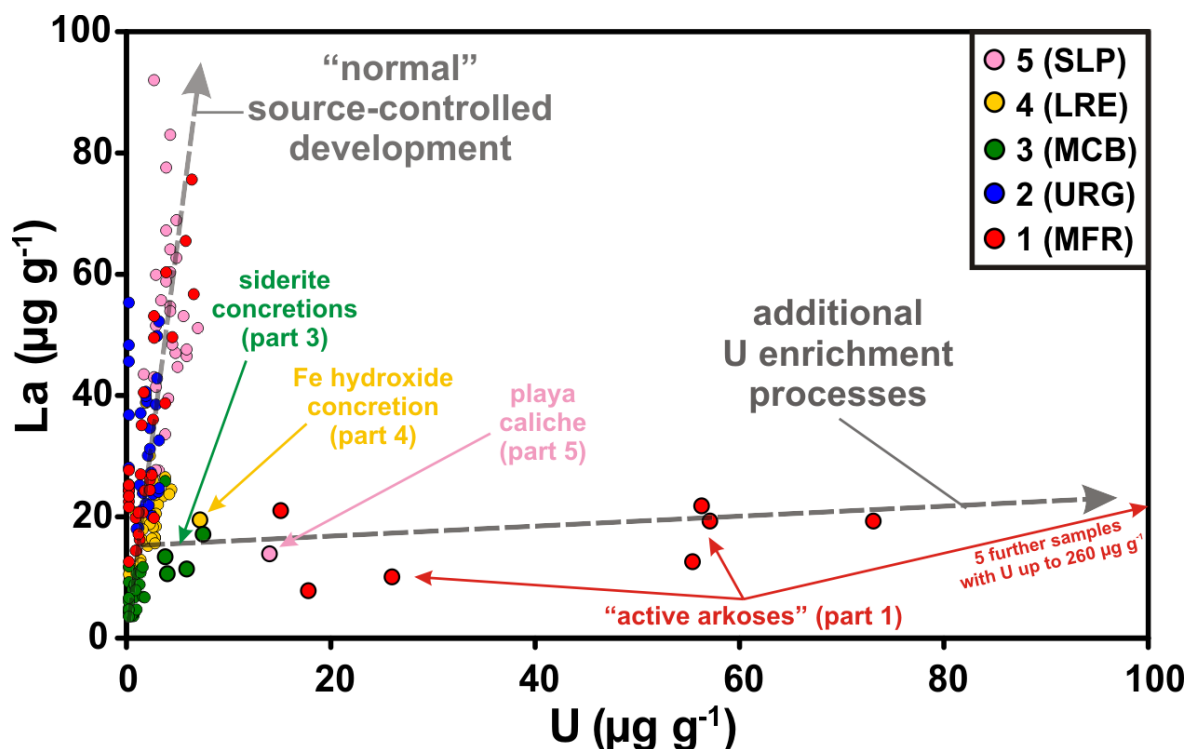


Fig. 6.4: U vs. La scatter plot for all studied sediments, abbreviations: see caption of Fig. 6.2, and U accumulation processes referring to the respective parts of the present work.

The majority of samples in Fig. 6.4 exhibit a development along a positively trending line (R^2 in the scatter plot for all samples without additional U enrichment processes, cf. Fig. 6.4, is 0.43) interpreted to represent “normal” source (i.e. provenance)-controlled behaviour. Here, common successive increase of both incompatible trace elements is obvious. Offsets from this “background” development, i.e. excess U, reflect additional sedimentary enrichment processes in the different areas. Slight accumulation was found in siderite concretions within Cretaceous fine sands (cf. part 3 of this work). Uranium sorption to the highest-Fe hydroxidic concretion in oxidized sands of the Lower Rhine Embayment (cf. part 4, this sample contains the single highest As concentration ($1860 \mu\text{g g}^{-1}$) of the present work) was not able to accumulate more than $7.2 \mu\text{g g}^{-1}$ U. This finding supports the hypothesis that a more felsic provenance is needed for sufficient U supply – U availability was just too low in the Paleogene sediments such that not even this concretionary best option for accumulation could be taken advantage of. Evaporative concentration accounts for elevated U contents in relic playa lake caliches (cf. part 5 of this work). Apatite precipitation from U-bearing groundwater on former playa carbonates resulted in high U contents in “active arkoses” (cf. part 1 of this work).

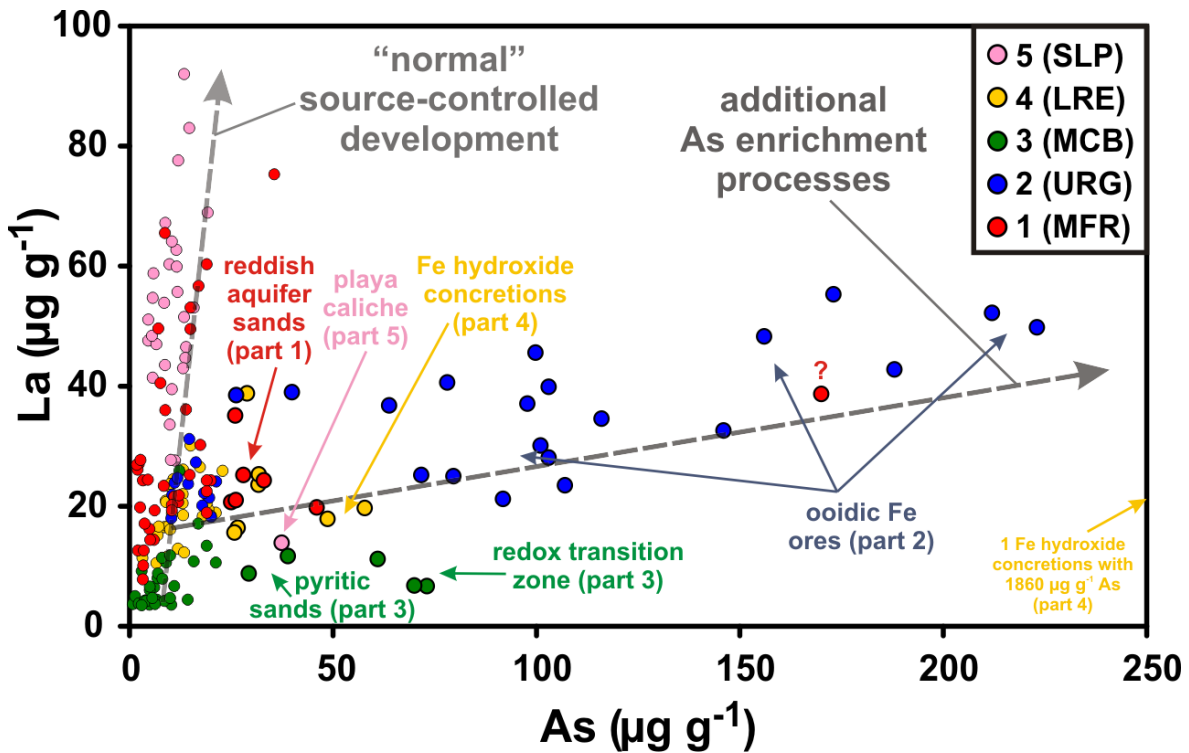


Fig. 6.5: As vs. La scatter plot for all studied sediments, abbreviations: see caption of Fig. 6.2, and As accumulation processes referring to the respective parts of the present work.

Similar observations can be made in the As vs. La plot (Fig. 6.5) – a provenance-driven “background” development is overlain by different additional As enrichment processes occurring in the studied sediment basins as indicated in Fig. 6.5 and described in the respective parts of this work: sorption to Fe hydroxide coatings of silicate aquifer material (part 1), accumulation in ooidic Fe ores during condensed sedimentation (part 2), fixation in pyrite and subsequent redistribution to redox transition zones and Fe hydroxide concretions (parts 3 and 4), enrichment by evaporation in playa caliches (part 5). The Jurassic ooidic Fe ores (cf. part 2) with high As enrichment only yield U concentrations of $1.5 \mu\text{g g}^{-1}$ on average although depositional environment and potential host phases seem suitable for higher accumulation. Again, U availability in the sediment provenance is suggested to be the limiting factor for this phenomenon. Compared to the U-La plot (Fig. 6.4, $R^2=0.43$), the trend of “normal” source-controlled development between As and La for all samples without additional As enrichment processes (Fig. 6.5) is less distinct yielding $R^2=0.07$. Obviously, the signature of the more incompatible U regarding geochemical provenance proxies is clearer which was already observed in part 5 of the present work (cf. chapter 5.3.4). Moreover, additional redistribution processes after sediment deposition (like paleo redox events) seem to preferentially fractionate As, thereby altering primary geochemical signals.

To pursue these observations and possibly further support the formulated hypotheses, the stratigraphical and spatial distribution of the study areas in Germany will be assessed in the following and set in

relation to their sediment provenance areas. Figure 6.6 offers an overview of the study areas' stratigraphical situation and the plate tectonic framework.

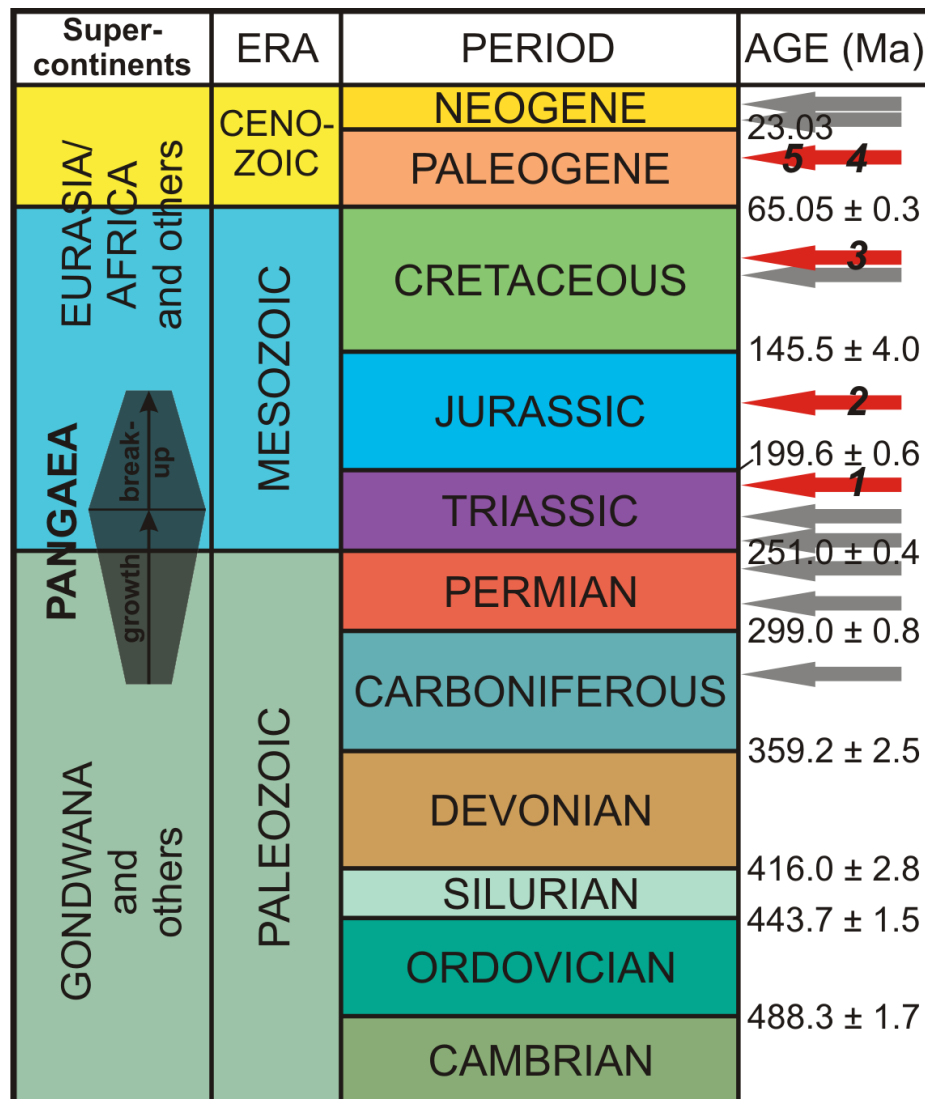


Fig. 6.6: Stratigraphical distribution of study areas (red arrows, number: part of the present work) and studied occurrences of sedimentary As in Germany from literature (grey arrows, cf. Fig. 1), absolute ages (right side) after ICS (2009). Additionally, major crustal development (supercontinents, left side) after Bahlburg and Breitzkreuz (1998) is indicated.

The stratigraphical distribution of studied elevated sedimentary As in Germany reflects affected units ranging from Carboniferous to Neogene in age. A clustering of cases in Permo-Triassic is conspicuous which includes Germany's most significant As (and U) problem area in Middle Franconia (cf. part 1 of this work). Sediments from these periods often represent cratonic sandstones (cf. Fig. 6.2) derived from weathering of the then young Variscan massifs. Surveys of groundwater U conducted so far identified the Triassic as "hot spot" age for affected aquifers (Birke et al. 2010, Kurth 2010, HLUG 2008, LGL and LfU 2007; cf. Common introduction of this work). Likewise, an overview of As in German

groundwater (Heinrichs and Udluft 1996) reports elevated concentrations mainly in Permo-Triassic aquifers. During that time, the formation climax of the supercontinent Pangaea as a result of the collision between Laurasia and Gondwana was reached (Bahlburg and Breitzkreuz 1998, Fig. 6.6). This process was accompanied by the Variscan Orogeny representing a mountain-building event, relics of which are found today as e.g., the Rhenish Massif, the Black Forest or the Bohemian Massif in Germany and neighbouring countries. Denudation of the orogen and transport of resulting material to sediment basins started in Upper Carboniferous. Concluding from Fig. 6.6, only stratigraphies younger than that appear to be affected by elevated As. Moreover, the upper limit of a stratigraphical “window” of sedimentary As occurrences seems to be defined by the end of the Neogene age. Possible explanations for that must be sought in the spatio-temporal geological development of Germany. Figure 6.7 illustrates the spatial distribution of studied sedimentary As (cf. Fig. 1 for explanations) as well as Variscan terrains and thick Quaternary overburden.

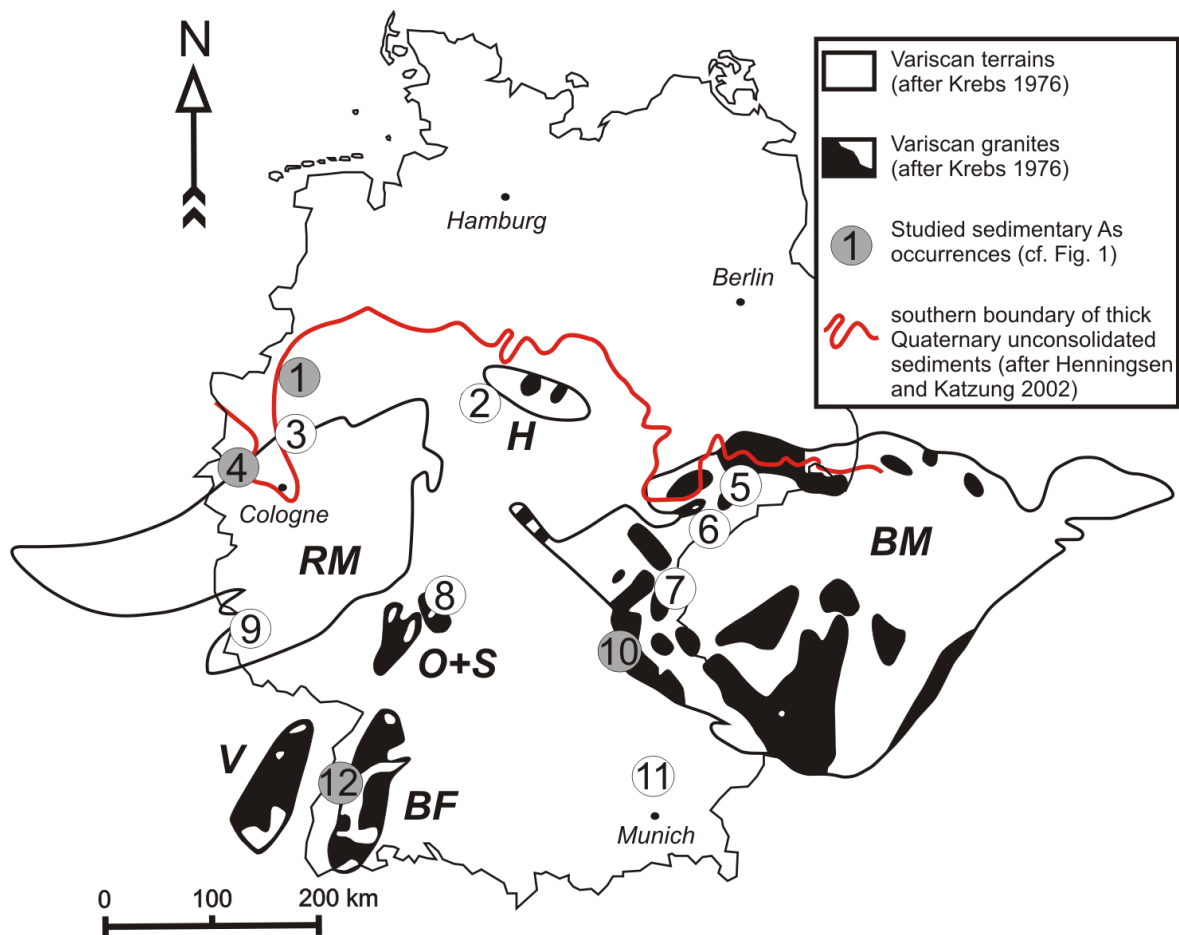


Fig. 6.7: Distribution of studied sedimentary As occurrences (cf. Fig. 1), Variscan terrains and granite intrusions therein (after Krebs 1976) and southern boundary of thick Quaternary cover sediments (after Henningsen and Katzung 2002). From north to south: H: Harz Mountains, RM: Rhenish Massif, BM: Bohemian Massif, O+S: Odenwald and Spessart, BF: Black Forest, V: Vosges.

It is evident from Fig. 6.7 that all known cases of elevated sedimentary As in Germany are located south of the thick unconsolidated Quaternary cover governing geology and landscape of northern Germany. These mostly Pleistocene glacial and periglacial deposits with main provenance areas in northern and northeastern Europe (Henningsen and Katzung 2002) obviously did not bring a significant As potential along (nor are occurrences of elevated sediment U published so far). Not only would these observations explain the northern boundary of As study areas (Fig. 6.7) but also raise expectations concerning better shallow groundwater quality with respect to As and U in northern Germany. Indeed, Kunkel et al. (2004) characterized natural groundwater quality in Germany and found in an evaluation of a large As dataset ($n=1661$) from sand and gravel aquifers of the North German Plain (widely identical with the area north of the red line indicated in Fig. 6.7) 90th percentile values of 3.3–3.5 $\mu\text{g L}^{-1}$ As with hardly any single values above 10 $\mu\text{g L}^{-1}$ in different aquifer depth intervals of up to 50 m below ground surface. Supporting this in their earlier survey, Heinrichs and Udluft (1996) do not report on geogenic groundwater concentrations in exceedance of 10 $\mu\text{g L}^{-1}$ As from this area.

The organisation foodwatch collected and published drinking water U data from federal state authorities (foodwatch 2009). In the dataset, they found that concentrations in the northern and central German federal states Brandenburg, Berlin, Bremen, Hamburg, Schleswig-Holstein, Lower Saxony, North Rhine-Westphalia and Saarland are quantitatively below 10 $\mu\text{g L}^{-1}$ U (2 out of 427 samples in Mecklenburg-Western Pomerania were above that content) while southern states generally exhibit more abundant violations of the proposed limit (cf. e.g. part 1 of this work).

A second observation from Fig. 6.7 is the close spatial relation of most conducted sedimentary As studies to Variscan terrains in Germany supporting a relation between Variscan geology and trace element distribution as was already suspected from stratigraphy (Fig. 6.6). Differences between sedimentary occurrence of As and U in the single studied areas of this work can be derived from the distribution of Variscan granites and support the hypotheses on degree of provenance felsicity formulated earlier: the study in Franconia (cf. part 1 of this work, No. 10 in Fig. 6.7) is the only one (in Germany) to show significantly elevated U in sediments (Fig. 6.4) while Jurassic, Cretaceous and Paleogene (parts 2–4) are widely restricted to As. The Franconian sediments derive from weathering of the Bohemian Massif which belongs to the Moldanubian section of the European Variscides (like main parts of Black Forest and Vosges) representing the most metamorphic part with abundant felsic intrusions (Krebs 1976, Bahlburg and Breitzkreuz 1998) while Cretaceous and Paleogene sediments (parts 3 and 4) originate from the Rhenohercynian Variscan section with low degree of metamorphism and widely absent granitic intrusions (Fig. 6.7). At first glance, it seems surprising that the Jurassic sediments (part 2), being located in direct vicinity to the Moldanubian granite-rich Black Forest and Vosges (Fig. 6.7) do neither show highly felsic provenance (Fig. 6.3) nor elevated U potential (Fig. 6.4). Nevertheless, the Moldanubian crystalline terrains did not serve as sediment provenance but were submerged during the Middle Jurassic (Ziegler 1990), sediment (and Fe/As, but no U) input was ac-

complished from the Rhenish Massif (Sauer and Simon 1975) and thus, from the Rhenohercynian – a provenance of lower felsicity.

To crosscheck this hypothesis, a short review of another basin that actually received its sedimentary filling from weathering of the Black Forest was conducted. Within the range of this Moldanubian terrain, only few rather small sedimentary basins filled with Upper Carboniferous to Permian material fulfill this condition, the biggest of which is the one around Baden-Baden in the northern Black Forest (Henningsen and Katzung 2002). Stefanian (Upper Carboniferous) partly C_{org} -rich arkoses and sandstones in that area, underlain by granite and derived from erosion of the proximal granitic young Variscan mountains, host several sedimentary uranium anomalies prospected in the past, the most significant of which is the deposit Müllenbach (Kneuper et al. 1977). The mineralization is of the roll-front type, main U carriers are uraninite and coffinite, bulk U_3O_8 contents of several wt.% are known. Arsenic is present in concentrations of up to $3000 \mu g g^{-1}$, mainly as arsenopyrite. Kneuper et al. (1977) also found a positive correlation between As and U in the sediments. The authors genetically suggest common U and As precipitation from groundwater with trace elements primarily mobilized from Black Forest granites. This development is thus very similar to the one described for “active arkoses” in part 1 of the present work. Also Permian sediments in that basin partly show common enrichment of both U and As (Plinninger and Thuro 1999). Hydrothermal U mineralizations within granites are known from the southern Black Forest, e.g., near Menzenschwand. This site is the type locality of several secondary U-As minerals, the most recent of which – Nielsbohrite $[(KUO_2)_3(AsO_4)(OH)_4 \cdot H_2O]$ – was described by Walenta et al. (2009). These studies clearly underline Black Forest granites’ high source potential for both U and As. The receiving sediment basins in the area are probably too small (in comparison to e.g., the Franconian Keuper Basin) to account for significant postdepositional redistribution processes and prominent groundwater As and U problems. Nevertheless, elevated U concentrations in Black Forest mineral waters are known (Birke et al. 2010). Moreover, the thermal springs of Baden-Baden, recharged by meteoric waters circulating in the regional granites (Bender 1995, cited in Rüde 1996), show high As concentrations of $200 \mu g L^{-1}$ on average (Rüde 1996); U presence is documented by U-bearing amorphous thermal Mn hydroxides and opaline sinters (Kirchheimer 1959, cited in Rüde 1996). In consequence, this short overview of a second Moldanubian massif fully supports the model of Variscan control over geogenic As and U distribution in Germany developed in the present work.

One exception among the existing studies of sedimentary As in Germany probably without Variscan influence should be mentioned: Bayer (1997) states that partly high As concentrations (up to $1900 \mu g g^{-1}$) in Fe-rich sections of the Bavarian molasse basin, esp. Badenean sands (No. 11 in Fig. 6.7), originate, like the sediments themselves, from weathering of the Alpine Mountains; As is believed to primarily derive from mineralized zones in the eastern Alps. Uranium concentrations are low in the Fe concretions, Bayer (1997) detected $<1 \mu g g^{-1}$ U in all his samples. According to the genetic model

developed in the present work, this data argues for a primary trace element source of moderately high felsicity not able to supply sufficient U for enrichment in sediments. This source indeed is likely to be found in the eastern Alps which, in contrast to the central and western parts of the orogen, do not host significant granitic intrusions (Gwinner 1971). Nevertheless, several occasions of elevated U are known in groundwater and sediments from the range of the Miocene molasse basin (e.g. LGL and LfU 2007, cf. part 1 of this work). An explanation for that can be given by another paleogeographical observation: after deposition of the Badenian sands, sediment provenance changed for the eastern and northern parts of the basin. During the subsequent Sarmatian and Pannonian, clastic material and groundwater supply were partly accomplished from the Bohemian Massif (Unger 1989) – a provenance of high felsicity with proven ability to produce U enrichment in associated sediment basins (cf. part 1 of this work).

The conclusions drawn above may partly be transferable to other countries and even orogenies. In a survey of U occurrences in British groundwater, Smedley et al. (2006) found highest concentrations in sandstones derived from weathering of the Caledonian orogen (e.g. Old Red Sandstone) and speculate on U sorbed to abundant Fe (hydr)oxides as direct source for elevated contents (although no solid phases were studied). The primary source is likely to be the Caledonides which exhibit, akin to the German Moldanubian Variscides, numerous granite intrusions (e.g. Brown and Locke 1979).

To conclude, the distribution of As and U problem areas in Germany (regarding presence in sediments as well as in groundwater in the central and southern part and absence in the north) is large-scale widely determined by Variscan and Quaternary geology. Geochemical sediment provenance controls elevated As (moderately felsic provenance) and U (highly felsic provenance) supply to sedimentary environments, whereby the different Variscan sections are decisive. Thus, originally magmatic prerequisites based on incompatible behaviour of U and As in magmatic differentiation (as studied in Mexico, part 5 of this work) have to be provided to sedimentary systems in order to enable subsequent trace element accumulation processes as characterized for different geological environments in Germany (parts 1 to 4 of this work).

The present work contributes to a deeper understanding of the interplay between geological history (magmatic and sedimentary), geochemistry, mineralogy, hydrogeology and hydrochemistry with respect to potentially hazardous geogenic trace elements, focussing on the still little understood situation in Germany. Increased comprehension of occurrence and behaviour of not only anthropogenic but also natural contaminants will be necessary in the future in view of growing awareness regarding health impacts along with more stringent drinking water limitations, and continuously more severe population pressure on water resources.

Summary

Both being geogenically occurring trace elements with potentially adverse effects on human health, As and U received considerably different scientific and public attention in the past decades. Proven As toxicity and the identification of large problem areas worldwide lead to extensive research and meanwhile established drinking water standards (WHO: $10 \mu\text{g L}^{-1}$, Germany: $10 \mu\text{g L}^{-1}$) whereby lively discussion on As occurrence, biogeochemical behaviour and effects is still ongoing.

Uranium, on the other hand, was only recently recognized by its toxicity besides its radioactivity, information on environmental dynamics and health effects is limited. Nevertheless, Germany decided on a fixed drinking water limitation of $10 \mu\text{g L}^{-1}$ U lately, WHO “provisional guideline value” is $15 \mu\text{g L}^{-1}$.

Little information is available on the development of geogenic As enrichments in German sediments and their potential impact on groundwater quality, and even less on U, let alone a systematic overview of the country's As and U occurrences. This work aims at characterizing geogenic As and U accumulation processes in aquifers actually or potentially affected by elevated concentrations of these trace elements, and their timings in geological history. Selected study areas provide different geological and stratigraphical backgrounds. The identification of geogenic sources of As and U, and derivation of respective structures of their environmental reservoirs in the different study areas were goals of this work. Remobilization mechanisms potentially resulting in trace element release to groundwater were assessed.

Short summaries of the five single studies conducted in Germany and Mexico, and the common discussion about them, are given in the following. A graphical summary of As and U sources and sinks structures including mobilization and immobilization processes in the studied areas can be found in Fig. 6.1 (page 134).

Part I – Triassic/Franconia

Drinking water supply in Franconia/Northern Bavaria is dependent on groundwater extraction from terrestrial Upper Triassic sandstones. Elevated concentrations of geogenic U (up to $42 \mu\text{g L}^{-1}$) and As (up to $150 \mu\text{g L}^{-1}$) in excess of the German drinking water limitations have been identified in this groundwater, making the region Germany's most significant U and As problem area. Uncertainty concerning the sources and processes gave rise to the present study which focuses on the detailed characterization of aquifer material in terms of geochemical (INAA/ICP-OES) and mineralogical (XRD with Rietveld analysis) composition, trace elements distribution on a microscale (LA-ICP-MS) and their mineralogical fractionation and mobilization behaviour (sequential extraction). Results were set in relation to spatial and hydrochemical patterns of groundwater composition, physico-chemical conditions, the distribution of the affected aquifer itself as well as information on the paleoenvironment during deposition. It was shown that uraniferous inclusions within the aquifer sandstones, so-

called “active arkoses”, represent the most likely source for U and As in the study area. They contain up to 50 wt.% carbonate fluorapatite (francolite) hosting U concentrations of up to $1071 \mu\text{g g}^{-1}$. Arsenic in these rocks (up to $77 \mu\text{g g}^{-1}$) also occurs in francolite which forms the sediment matrix together with hematite and clay minerals, albeit a higher proportion appears to reside in the Fe oxide. Trace element accumulation occurred syndiagenetically by mineral precipitation from paleo-groundwater. The analyzed francolite was shown to exhibit biologically, structurally and radiation-enhanced solubility and indeed, loss of both U and As during alteration and weathering was documented. Altogether, hydrochemical, geochemical, mineralogical and paleogeographical evidence as well as spatial trends and mobilization behaviour, argue strongly for “active arkoses” being a major source of groundwater As and especially U. The trace elements are subsequently separated by the redox-heterogeneity of the aquifer. Together with uraniferous dolomitic inclusions north of the study area, “active arkoses” are likely to control the geogenic U problem in northern Bavarian groundwater, and contribute significantly to the observed elevated groundwater As.

Part 2 – Jurassic/Upper Rhine Graben

Shallow marine iron ores of Middle Jurassic (“Dogger”) age were sampled from a prominent sedimentary profile in the Upper Rhine Graben, southwestern Germany, to examine Fe and As accumulation processes. Samples were analyzed for bulk rock geochemistry (INAA/ICP-OES), quantitative mineralogy (XRD with Rietveld analysis), element distribution on a microscale (electron microprobe) and As fractionation (sequential extraction). Bulk Jurassic ores contain up to 32.2 wt.% Fe and $223 \mu\text{g g}^{-1}$ As (average content: $123 \mu\text{g g}^{-1}$), but a mean U concentration of only $1.8 \mu\text{g g}^{-1}$. Arsenic is hosted in mainly goethite ooids (up to $\sim 1 \text{ mg g}^{-1}$) which slowly formed in times of condensed sedimentation, while the calcite matrix of the ore exhibits low As. Enrichment occurred syndepositionally, its scale was assessed calculating Enrichment and Contamination Factors. These indicate that accumulation of As in Fe ores was significant (up to factor 12.7) and favoured over other potential contaminants – As enrichment potential is ~ 3 times higher than that of Cu, Pb, Zn, Ni, Co and Cr; Mn rather resides in the calcitic cement. Conditions for As accumulation varied during deposition which is visible on a macro- (outcrop) as well as on a microscale (single Fe ooid). Ooidic Fe ores with comparable composition and genesis are widespread in Central Europe and elsewhere, making the applied methods and obtained findings concerning As occurrence therein transferable to other regions.

Part 3 – Cretaceous/Münsterland Cretaceous Basin

Shallow marine fine sands of Santonian (Upper Cretaceous) age in the western Münsterland Cretaceous Basin exhibit a distinct sediment colour and geochemical boundary in several decametres below ground surface, witnessing an oxidative paleo redox process under terrestrial conditions during the late Tertiary 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 redis-

tributional consequences of the redox event. Bulk rock geochemistry (INAA/ICP-OES), mineralogical composition (XRD, Rietveld analysis) and As fractionation (SEP) were assessed. Arsenic was shown to reside in pyrite in the reduced section with a bulk rock maximum concentration of $39 \mu\text{g g}^{-1}$, calculated mean $\text{As}_{\text{pyrite}}$ is $\sim 0.2 \text{ wt.}\%$. Siderite concretions occurring in the fine sands do not function as As sinks, however, they tend towards collecting U (mean U is $4.0 \mu\text{g g}^{-1}$, compared to $0.8 \mu\text{g g}^{-1}$ in the ambient sands). In the zone of redox transition, reduced and oxidized phases coexist, elevated As concentrations up to $73 \mu\text{g g}^{-1}$ with high proportions of reactive As (up to $18 \mu\text{g g}^{-1}$ $\text{NH}_4\text{H}_2\text{PO}_4$ -soluble) were identified. Behaviour of As changes from relatively homogeneous Fe sulfide-control in the unaltered sediments to very heterogeneous Fe hydroxide-control above the paleo redox boundary. Uranium occurrence is inconspicuous in redox transition and oxidized facies. Early stages of hydroxidic Fe/As accumulations resulting from mobilization from the reduced sediments are interpreted as precursors of high-As goethite concretions, widespread in the near-surface oxidized section of the sediments. The structural model of As sources and sinks in the western Münsterland set up in an earlier study is thus approved.

Part 4 – Paleogene/Lower Rhine Embayment

Widespread Paleogene (Oligocene) marine sandy sediments from the Lower Rhine Embayment, North Rhine-Westphalia, exhibit features of a paleo redox event: primary reduced Fe phases (glauconite, pyrite, siderite) are observable in boreholes as widely unaltered facies, near-surface sediments show hydroxidic Fe mineralogy and significant major and trace element redistribution caused by Neogene terrestrial weathering in the area. In these respects, considerable similarities to the postdepositional redox history of Cretaceous sediments from the Münsterland Cretaceous Basin (part 3 of this work) become obvious. Both reduced and oxidized facies were sampled from boreholes and outcrops, respectively, to characterize geochemistry (INAA/ICP-OES) and mineralogy (XRD, Rietveld analysis) in unaltered layers and the effect of the paleo redox event in the oxidized sediments, especially regarding As and Fe dynamics. Mineralogical fractionation and remobilization potential in both redox facies were compared applying sequential extraction. Pyrite was identified as the main As carrier in the reduced layers where a relatively homogeneous As distribution ($\bar{12.3} \mu\text{g g}^{-1}$) is observable, the maximum concentration ($21.2 \mu\text{g g}^{-1}$) is reached at the paleo redox boundary. In contrast, the near-surface oxidized facies exhibits an extremely heterogeneous element redistribution culminating in Fe hydroxide (goethite and lepidocrocite) concretions with up to $1860 \mu\text{g g}^{-1}$ As and thus, a secondary accumulation process. Cumulative Contamination Factors indicate clearly preferential As enrichment over heavy metals in concretions which, nevertheless, only contribute $\sim 12 \%$ of total reactive As in the sediments. Uranium is rather homogeneously distributed in both redox facies ($\bar{2.5} \mu\text{g g}^{-1}$ in reduced, $\bar{2.3} \mu\text{g g}^{-1}$ in oxidized layers) and obviously little affected by the paleo redox event in terms of concretionary redistribution regarding a maximum content of $7.2 \mu\text{g g}^{-1}$ in the most Fe- and As-rich hydroxide concretion.

Part 5 – Paleogene-Neogene/San Luis Potosí, Mexico

Uranium and As in deep groundwater of the volcano-sedimentary Villa de Reyes Graben around the city of San Luis Potosí in semiarid north-central Mexico ($\bar{U}$: $7.6 \mu\text{g L}^{-1}$, up to $138 \mu\text{g L}^{-1}$; $\bar{\text{As}}$: $11.4 \mu\text{g L}^{-1}$, up to $25.8 \mu\text{g L}^{-1}$) were shown to partly exceed WHO guidelines and thus to endanger the quality of the by far most important drinking water source in the area. To unravel the mechanisms for their enrichment in groundwater (whose trace element composition was characterized by ICP-MS), the potential trace element sources volcanic rocks (XRF/ICP-MS) and basin filling sediments (INAA/ICP-OES, sequential extraction) were characterized in terms of geochemistry and mobilization potential. The As/U hydrogeochemical signatures, their behaviour during rock alteration and evidence from other major and trace elements, e.g. REE, strongly argue for dissolution of acid volcanic glass to be the dominating process of U and As release into groundwater. Its hydrogeochemical fingerprint is modified by additional mobilization of especially As from the sedimentary basin filling, representing an intermediate trace element reservoir, in the course of playa lake sediment decarbonatization and desorption from Fe-(hydr)oxide coated clastic material. Common behaviour of both incompatible elements during magmatic differentiation and growing drift-apart in sedimentary systems are discussed. Comparison with recent studies in similar environments yielded a common ground in primary trace element source identification but significant differences in the evolution of present day As and U distribution. The study area's geological and climatic similarity to numerous volcano-sedimentary basins make the findings transferable to other semiarid regions facing challenges of geogenically impacted drinking water quality.

Part 6 – Common discussion

It was shown for the study areas in Franconia (part 1) and San Luis Potosí (part 5) that groundwater As and U concentrations partly exceed international drinking water standards (see above) leading to potential health threats for exposed populations. Water suppliers have to respond to this actual endangerment. Concluding from the hydrochemical milieu, rock characteristics and extraction results obtained in part 2, the risk of As release from Jurassic Fe ores to groundwater of the Upper Rhine Graben is considered to be rather insignificant. In contrast, loss of As to oxidizing solutions in redox transition and reduced sediments is likely to occur in areas affected by paleo redox events like the Lower Rhine Embayment and the Münsterland Cretaceous Basin (parts 3 and 4). Although no violation of As drinking water standards is actually documented from the studied aquifers, attention during groundwater extraction is demanded, especially as depth of the paleo redox boundary below ground surface is shown to vary considerably even at short distance. In spite of higher bulk As contents in the shallow oxidic rocks, the mainly pyrite-hosted As pool within the reduced deeper parts of the sediment basins was shown to have a higher potential for remobilization and creation of elevated As concentrations in groundwater. Uranium release potential was not studied in detail for parts 2-4 of the present work but is estimated to be rather limited in view of low concentrations in aquifer materials.

Besides the major importance of the obtained results for the respective regions, and transferability of findings based on the choice of study areas representing a variety of geological backgrounds and developments comparable to numerous regions worldwide, geochemical comparison of all study areas (a total of 223 solid samples were considered in the present work) and their spatio-temporal distribution offers additional explanations for the geogenic situation of As and U in Germany. While Pleistocene geological development can explain their absence in sediments as well as in related groundwater in northern Germany, their presence and distribution in the central and southern parts are widely controlled by provenance geochemistry. Only highly felsic origin (Moldanubian Variscides) enables creation of elevated U in the systems while somewhat lower degrees of provenance felsicity (Rhenohercynian Variscides) appear to be sufficient for As presence, subsequent intrabasinal redistribution and mobilization processes contribute to the present-day situation. Therefore, the ultimate control of these incompatible trace elements is magmatic, even in old sedimentary systems, and still clearly traceable in nowadays large-scale geogenic As and U distribution in Germany and elsewhere.

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Natural arsenic and uranium accumulation and remobilization in different geological environments

Dissertation summary

Objectives

Despite the fact that both As and U represent geogenically occurring trace elements with potentially adverse effects on human health, little information is available on the development of natural As enrichments in German sediments and their potential impact on groundwater quality, and even less on U, let alone a systematic overview of the country's natural occurrences of these trace elements. The latter is one main goal of this work. It aims at characterizing geogenic accumulation processes in aquifers actually or potentially affected by elevated concentrations of As and/or U, and their timings in geological history. The five selected study areas provide different geological and stratigraphical backgrounds. Identification of geogenic sources of As and U, and derivation of respective structures of their environmental reservoirs in the different study areas as well as remobilization mechanisms potentially resulting in trace element release to groundwater were assessed.

Part 1 – Triassic: Sources and hydrogeochemical mechanisms behind the geogenic uranium and arsenic problems in Franconian groundwater

Drinking water supply in Franconia/Northern Bavaria is dependent on groundwater extraction from terrestrial Upper Triassic sandstones. Elevated concentrations of geogenic U and As in excess of the German drinking water limitations have been identified in this groundwater, making the region Germany's most significant U and As problem area. Detailed characterization of aquifer material in terms of geochemical and mineralogical composition, trace elements distribution on a microscale and their mineralogical fractionation and mobilization behaviour in relation to spatial and hydrochemical patterns of groundwater composition, physico-chemical conditions, the distribution of the affected aquifer itself and information on the paleoenvironment, showed that uraniferous francolite/hematite inclusions within the aquifer sandstones, so-called "active arkoses", represent the most likely source for U and As in the study area. Trace element accumulation occurred syndiagenetically by mineral precipitation from paleo-groundwater. Francolite exhibits biologically, structurally and radiation-enhanced solubility; loss of both U and As during alteration and weathering was documented. The trace elements are subsequently separated by the redox-heterogeneity of the aquifer.

Part 2 – Jurassic: Evolution, scale and impact of arsenic accumulations in ooidic iron ores from southwestern Germany

Shallow marine Fe ores of Middle Jurassic age were sampled from a prominent sedimentary profile in the Upper Rhine Graben to examine Fe and As accumulation processes. Bulk ores exhibit significant

As which is hosted in mainly goethite ooids slowly formed in times of condensed sedimentation. Enrichment occurred syndepositionally, its scale was assessed calculating Enrichment and Contamination Factors indicating that As accumulation was favoured over other potential contaminants – As enrichment potential is ~3 times higher than that of Cu, Pb, Zn, Ni, Co and Cr. Conditions for As accumulation varied during deposition which is visible on a macro- (outcrop) as well as on a micro-scale (single Fe ooid). Despite high As contents, the risk of release to groundwater of the region is considered to be rather insignificant.

Part 3 – Cretaceous: Arsenic in paleo redox events, case I – Münsterland Cretaceous Basin

An oxidative paleo redox process under terrestrial conditions during the late Tertiary affected shallow marine sands of Santonian age in the western Münsterland Cretaceous Basin resulting in a distinct sediment colour and geochemical boundary in several decametres below ground surface. 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. Arsenic was shown to reside in pyrite in the reduced section. In the zone of redox transition, reduced and oxidized phases coexist, elevated As concentrations with high proportions of reactive As were identified. Behaviour of As changes from relatively homogenous Fe sulfide-control in the unaltered sediments to very heterogeneous Fe hydroxide-control above the paleo redox boundary. Early stages of hydroxidic Fe/As accumulations resulting from mobilization from the reduced sediments are interpreted as precursors of high-As goethite concretions, widespread in the near-surface oxidized section of the sediments.

Part 4 – Paleogene: Arsenic in paleo redox events, case II – Lower Rhine Embayment

Widespread Oligocene marine sandy sediments from the Lower Rhine Embayment exhibit features of a paleo redox event: primary reduced Fe phases (glauconite, pyrite, siderite) are observable in boreholes as widely unaltered facies, near-surface sediments show hydroxidic Fe mineralogy and significant major and trace element redistribution caused by Neogene terrestrial weathering in the area. Striking similarities to the postdepositional redox history of Cretaceous sediments from the Münsterland Cretaceous Basin (part 3 of this work) became obvious. Pyrite was identified as the main As carrier in the reduced layers where a relatively homogenous As distribution is observable, maximum concentrations are reached at the paleo redox boundary. In contrast, the near-surface oxidized facies exhibits an extremely heterogeneous element redistribution culminating in Fe hydroxide concretions with massive As enrichment and thus, documenting a secondary accumulation process. Cumulative Contamination Factors indicate clearly preferential As enrichment over heavy metals in concretions. Uranium is rather homogeneously distributed in both redox facies and obviously little affected by the paleo redox event in terms of concretionary redistribution. In spite of higher bulk As in the oxidic rocks, the reduced deeper part of the sediments is the more probable candidate for creating elevated As

concentrations in groundwater, especially if the present redox milieu is anthropogenically disturbed by groundwater extraction or input of oxidants like nitrate.

Part 5 – Paleogene-Neogene: Arsenic and uranium signatures and evolution in a volcano-sedimentary basin in central Mexico

Uranium and As in deep groundwater of the volcano-sedimentary Villa de Reyes Graben around the city of San Luis Potosí in semiarid north-central Mexico were shown to partly exceed WHO guidelines and thus to endanger the quality of the by far most important drinking water source in the area. The As/U hydrogeochemical signatures, their behaviour during rock alteration and evidence from other major and trace elements, e.g. REE, strongly argue for dissolution of acid volcanic glass to be the dominating process of U and As release to groundwater. Its hydrogeochemical fingerprint is modified by additional mobilization of especially As from the sedimentary basin filling, representing an intermediate trace element reservoir, in the course of playa lake sediment decarbonatization and desorption from Fe-(hydr)oxide coated clastic material. Common behaviour of both incompatible elements during magmatic differentiation and growing drift-apart in sedimentary systems are discussed. Comparison with recent studies in similar environments yielded a common ground in primary trace element source identification but differences in the evolution of present day As and U distribution.

Part 6 – Common discussion and geodynamic model for natural As and U distribution in Germany

Besides the major importance of the obtained results for the respective regions, and transferability of findings based on the choice of study areas representing a variety of geological backgrounds and developments comparable to numerous regions worldwide, geochemical comparison of all study areas (a total of 223 solid samples were considered in the present work) and their spatio-temporal distribution offers additional explanations for the geogenic situation of As and U in Germany. While Pleistocene geological development can explain their absence in sediments as well as in related groundwater in northern Germany, their presence and distribution in the central and southern parts are widely controlled by provenance geochemistry. Only highly felsic origin (Moldanubian Variscides) enables creation of elevated U in the systems while somewhat lower degrees of provenance felsicity (Rhenohercynian Variscides) appear to be sufficient for As presence. Subsequent intrabasinal redistribution and mobilization processes contribute to the present-day situation. Therefore, the ultimate control of these incompatible trace elements is magmatic, even in old sedimentary systems, and still clearly traceable in nowadays large-scale geogenic As and U distribution in Germany and probably elsewhere.

Natürliche Arsen- und Uran-Anreicherung und -Remobilisierung unter verschiedenen geologischen Bedingungen

Kurzfassung der Dissertation

Ziele

Trotz der Tatsache, dass As und U natürlich vorkommende Spurenelemente mit Gesundheitsgefährdungspotential sind, ist über ihre Anreicherungsprozesse in Sedimentgesteinen in Deutschland und möglichen Austrag daraus ins Grundwasser wenig bekannt. Ein systematischer nationaler Überblick zu den geogenen Vorkommen dieser Spurenelemente fehlte bisher und ist ein Hauptziel der vorliegenden Arbeit. Anreicherungsprozesse in aktuell oder potentiell von erhöhten U- und/oder As-Gehalten im Grundwasser betroffenen Aquiferen sowie das geologische Timing dieser Akkumulation wurden charakterisiert. Die fünf in dieser Arbeit untersuchten Gebiete bieten verschiedene stratigraphische und geologische Hintergründe, vor denen die Struktur geogener As- und U-Quellen und -Senken, sowie Immobilisierungs- und Remobilisierungsprozesse zwischen den Reservoirs erarbeitet wurden.

Teil 1 – Trias: Quellen und hydrogeochemische Prozesse hinter der geogenen Uran- und Arsen-Problematik im Grundwasser Frankens

Die Trinkwasserversorgung Mittelfrankens ist abhängig von der Förderung aus terrestrischen Keuper-Sandstein-Aquiferen. In diesem Grundwasser wurden grenzwertüberschreitende Gehalte an geogenem U und As festgestellt, die die Region zum diesbezüglich bedeutendsten Problemgebiet in Deutschland machen. Die an verschiedenem Aquifermaterial (Burgsandstein) analysierte geochemische und mineralogische Zusammensetzung, Spurenelementverteilung, -fraktionierung und -mobilisierungspotential im Zusammenhang mit Grundwasserchemie, physiko-chemischen Bedingungen, der Ausdehnung des Aquifers selbst sowie Informationen zu den Paläoumweltbedingungen zeigen, dass uranführende Francolit/Hämatit-Einschlüsse im Grundwasserleiter, sog. „Aktivarkosen“, die wahrscheinlichste Quelle für U und As im Untersuchungsgebiet darstellen. Die Spurenelementanreicherung geschah syndiagenetisch durch Präzipitation aus dem Paläo-Grundwasser. Der untersuchte Francolit zeigt strukturell und strahlungsbedingt erhöhte Lösungsanfälligkeit; U- und As-Verlust durch Alteration und Verwitterung konnten nachgewiesen werden. Nach Eintritt in das Grundwasser werden die Spurenelemente durch die Redox-Heterogenität im Aquifer getrennt.

Teil 2 – Jura: Entwicklung, Ausmaß und Auswirkungen von Arsen-Anreicherungen in ooidischen Eisenerzen Südwestdeutschlands

Flachmarine Dogger-Eisenerze wurden in einem prominenten sedimentären Profil im Oberrheingraben beprobt, um Fe- und As-Anreicherungsprozesse zu untersuchen. Die Erze zeigen signifikante As-Gehalte, die an während Phasen kondensierter Sedimentation gebildeten Goethit-Ooiden gebunden sind. Die Anreicherung geschah syndementär, ihre Ausmaße wurden durch die Berechnung von An-

reicherungs- und Kontaminationsfaktoren erfasst, die eine bevorzugte As-Akkumulation gegenüber anderen potentiellen Kontaminanten dokumentiert. Das Anreicherungspotential von As ist etwa dreimal höher als das von Cu, Pb, Zn, Ni, Co und Cr. Anreicherungsbedingungen variierten während der Ablagerung in makroskopischem (Aufschluss) und mikroskopischem (Einzelooid) Maßstab. Trotz der hohen As-Gehalte in den Eisenerzen wird das Risiko für einen Grundwassereintrag aus diesen Gesteinen als unbedeutend angesehen.

Teil 3 – Kreide: Arsen in Paläo-Redoxprozessen, Fallstudie I – Münsterländer Kreidebecken

Ein im späten Tertiär unter festländischen Bedingungen abgelaufener Paläo-Redoxprozess alterierte marine Sande des Santoniums im westlichen Münsterländer Kreidebecken und führte zu deutlichen farblichen und geochemischen Grenzen im Sediment in einigen Zehnermetern Teufe. Gesteinsproben wurden aus Bohrungen in unterschiedlicher Entfernung zur Paläoküste gewonnen und umfassen sowohl reduzierte als auch oxidierte Fazies, um das Vorkommen von As und Fe in nicht alterierten Sedimenten sowie die Umverteilung durch das Redoxereignis zu untersuchen. Im reduzierten Liegenden ist As an Pyrit gebunden, im Redox-Übergangsbereich koexistieren reduzierte und oxidierte Phasen. Hier wurden die höchsten As-Gehalte mit einem hohen Anteil an reaktivem As festgestellt. Die Verteilung von As wechselt von homogen Sulfid-kontrolliert im Liegenden zu extrem heterogen Fe-Hydroxid-kontrolliert oberhalb der Paläo-Redoxgrenze. Frühe Formen hydroxidischer Fe/As-Anreicherungen, die aus der Mobilisierung aus den reduzierten Sedimenten abzuleiten sind, werden als Vorstufen As-reicher Goethit-Konkretionen interpretiert, welche in den oberflächennahen oxidierten Sedimenten weit verbreitet sind.

Teil 4 – Paläogen: Arsen in Paläo-Redoxprozessen, Fallstudie II – Niederrheinische Bucht

In der Niederrheinischen Bucht weit verbreitete marine Sedimente des Oligozäns zeigen ebenfalls Merkmale eines Paläo-Redoxprozesses: reduzierte Fe-Phasen (Glaukonit, Pyrit, Siderit) belegen in Bohrkernen die primäre Fazies, oberflächennahe Sedimente werden von Fe-Hydroxiden und deutlicher Umverteilung von Haupt- und Spurenelementen durch die neogene festländische Verwitterung in der Region geprägt. Deutliche Ähnlichkeiten zu den Sedimenten des Münsterländer Kreidebeckens (Teil 3 dieser Arbeit) sind somit zu beobachten. Pyrit stellt den Haupt-Arsenträger in den reduzierten Schichten dar, eine relativ homogene Verteilung mit Maximalgehalten um die Paläo-Redoxgrenze ist festzustellen. Demgegenüber dokumentiert die oberflächennahe oxidierte Fazies eine extrem heterogene Elementumverteilung, die in hoch As-angereicherten Fe-Hydroxid-Konkretionen gipfelt und somit einen sekundären Akkumulationsprozess bezeugt. Kontaminationsfaktoren ergeben bevorzugte As-Anreicherung gegenüber Schwermetallen in diesen Konkretionen. Uran ist in beiden Redoxfazies relativ homogen verteilt und scheinbar kaum von der oxidativen Umverteilung betroffen. Trotz höherer As-Gehalte in den oxidierten Gesteinen zeigen die liegenden reduzierten Schichten ein höheres As-Remobilisierungspotential. Austräge in das Grundwasser sind vor allem bei durch anthropogene Akti-

vität gestörten Redoxbedingungen (Absenkung der Grundwasseroberfläche oder Eintrag von Oxidationsmitteln wie Nitrat) zu erwarten.

Teil 5 – Paläogen-Neogen: Signaturen und Entwicklung von Arsen und Uran in einem vulkano-sedimentären Becken in Zentral-Mexiko

In tiefen Grundwässern des vulkano-sedimentären Villa de Reyes-Grabens um die Stadt San Luis Potosí im semiariden nördlich-zentralen Mexiko wurden U und As-Konzentrationen oberhalb der WHO-Richtlinien festgestellt, was zu einer Gefährdung der mit Abstand wichtigsten Trinkwasserquelle der Region führt. Hydrogeochemische As/U Signaturen, das Verhalten dieser Spurenelemente im Zuge von Gesteinsalteration und Hinweise aus anderen Haupt- und Spurenelementen, z.B. Seltenen Erden, weisen deutlich auf die Lösung felsischer Vulkangläser als Haupteintragsprozess für U und As ins Grundwasser hin. Dieser hydrogeochemische Fingerabdruck wird durch den Eintrag (besonders von As) aus intermediären Reservoirs, den Beckensedimenten, v.a. durch Dekarbonatisierung von Playa-Sedimenten und Desorption von Fe-Hydroxiden in klastischem Material, modifiziert. Die Diskussion umfasst das gemeinsame Verhalten der beiden inkompatiblen Spurenelemente während der magmatischen Differentiation und anschließende Auftrennung in sedimentären Systemen. Vergleiche mit aktuellen Studien in ähnlichen Gebieten erbrachten Gemeinsamkeiten hinsichtlich der Primärquelle von As und U, jedoch deutliche Unterschiede in der Entwicklung der heutigen Verteilung dieser Elemente.

Teil 6 – Gesamtdiskussion und geodynamisches Modell der Verbreitung von natürlichem As und U in Deutschland

Die erzielten Ergebnisse sind von großer regionaler Bedeutung, und durch die Auswahl der geologisch diversen Arbeitsgebiete wird eine Übertragbarkeit auf zahlreiche andere Areale weltweit ermöglicht. Darüber hinaus können durch geochemischen Vergleich der hier untersuchten Gebiete (insgesamt wurden 223 Feststoffproben bearbeitet) und ihre raum-zeitliche Verteilung zusätzliche Erklärungsansätze für die geogene As- und U-Verteilung in Deutschland abgeleitet werden. Während die geologische Entwicklung im Pleistozän für die weitgehende Abwesenheit von U und As in Sedimenten und Grundwässern Norddeutschlands verantwortlich ist, wird ihre Verteilung in den zentralen und südlichen Landesteilen durch die Geochemie der Sediment-Provenanz gesteuert. Lediglich hoch felsische Ursprungsgebiete (Moldanubikum) ermöglichen die Erzeugung von erhöhten U-Gehalten in sedimentären Systemen während weniger felsische Provenanz (Rhenoharzynikum) für die Anwesenheit von As auszureichen scheint. Anschließende beckeninterne Umverteilungs- und Remobilisierungsprozesse tragen zum heutigen Verteilungsmuster bei. Daraus folgt, auch für alte sedimentäre Systeme, eine letztlich magmatische Kontrolle der großmaßstäblichen Verteilung von As und U in Deutschland.