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Geogenic arsenic and uranium in Germany: Large-scale distribution control in sediments and groundwater

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ABSTRACT

Arsenic (As) and uranium (U) are naturally occurring trace elements with potentially adverse effects on human health. This work revisits nine case studies on As/U accumulation and remobilization mechanisms in aquifers with different geological and stratigraphical backgrounds to develop a systematic overview of Germany's geogenic inventory of these trace elements. It uses geochemical proxies for a total of 270 solid samples to explain their spatio-temporal distribution: while Pleistocene geological development can explain their extensive absence in sediments and related groundwater in northern Germany, their abundance and distribution in the central and southern parts are widely controlled by sediment provenance geochemistry. Only highly felsic origin (Moldanubian Variscides) enables creation of elevated U in the systems while lower degrees of provenance felsicity (Rhenohercynian Variscides) appear to be sufficient for As presence. Postdepositional (hydro)geological and anthropogenically triggered intra-basinal processes of trace element accumulation, redistribution and eventually remobilization to groundwater 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.

1. Introduction

1.1. 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 (1.5–2 μg g^{-1}; Matschullat, 1999; Taylor, 1964: 1.8 μg 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).

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 uranyl hydroxo or calcium uranyl carbonato complexes (e.g. Katsoyiannis et al., 2007; Stewart et al., 2010). 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; Banning et al., 2012; Banning and Rüde, 2015).

Taylor (1964) cites the average uranium (U) abundance in the continental crust as 2.7 μg g^{-1}. Thereby, generally higher concentrations are detected in felsic rocks (granite average: 4.8 μg g^{-1} U) compared to mafic lithologies (basalt average: 0.6 μg g^{-1} U). Uranium has a strongly incompatible behavior in silicate magmatic differentiation because of its large ion radius and high valence. It is preferentially fractionated into high-temperature metaluminous melts during partial melting and crystal fractionation (Cuney, 2010), and therefore often accumulates in

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granitic and pegmatitic lithologies. Also As is considered one of the incompatible elements which do not fit easily into the lattices of rock-forming minerals precipitating from melt (Webster and Nordstrom, 2003).

1.2. 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 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 1990s, mostly down to 10 μg 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), the Rioverde Basin (Planer-Friedrich et al., 2001) and the Villa de Reyes Graben around San Luis Potosí (Banning et al., 2012). 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).

While the toxicity of As is well documented and drinking water limitations are established and reconsidered for several decades (actually 10 μg 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; Bjørklund et al., 2017). 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. ~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 30 μg L^{-1}, German legislation decided on a fixed limitation of 10 μg L^{-1}, valid since 2011. Compared to As, the number of identified geogenic groundwater U problem areas worldwide is low but growing. 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 WHO guideline. These authors also give a short overview of case studies from other affected states and countries. 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 μg L^{-1} U. In the north-west Indian state of Punjab, high U concentrations in groundwater have relatively recently been observed over a wide geographical area. Several studies (Patnaik et al., 2015; Kumar et al., 2016; Bajwa et al., 2017; Lapworth et al., 2017) point to potential risks for the exposed population. Unverified hypotheses on the origin of groundwater U include fly ash from coal combustion or input from agricultural fertilisation. However, most authors consider geogenic processes more likely, primarily the weathering of the Siwaliks, i.e. Himalayan foothills (e.g., Patnaik et al., 2015). Also high As groundwaters are known from the region (e.g., Kumar and Singh, 2020).

1.3. Known cases of elevated As and U contents in German sediments and groundwater

While the mechanism of large-scale As accumulation in delta sediments of Southeast Asia (e.g. Acharyya et al., 2000; Stanger, 2005) or in (semi)arid Latin America (e.g. Bundschuh et al., 2004; Nicolli et al., 2010) are subject to extensive research and discussions, relatively little was known about the origin and development of geogenic As accumulations in Germany. These have been studied 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). Fig. 1 illustrates a survey of conducted studies on elevated As occurrences in sedimentary rocks and partly groundwater, whereby no claim to completeness is made. It does neither include high As observed in thermal waters 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 As-related studies shown in Fig. 1 will be shortly summarized in the following.

Banning et al. (2009) detected partly high As contents up to 140 μg g^{-1} in secondary Fe concretions in oxidized Upper Cretaceous (Santonian) sediments from the Münsterland Cretaceous Basin (area 2 in Fig. 1) and identified them as the source for significant As contents in soils of the region. A postdepositional paleo redox event during the late Tertiary caused extremely heterogeneous As and other trace element distribution in shallow marine sediments, leading to partly massively enriched secondary concretions. 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 (Banning et al., 2013a). The same mechanism applied to Tertiary marine sediments in the Lower Rhine Embayment (area 5; Banning and Rüde, 2010): 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: large-scale redox events alter comparable lithologies and redistribute trace elements hosted therein in the same way, independent of sediment age.

Concentrations of As in groundwater from southern Lower Saxony (area 3) above the drinking water standard were attributed to output from Lower Triassic ("Buntsandstein") clastic sediments (up to 693 μg g^{-1} As) by Goldberg et al. (1995). Mertens (2000) found an average of 108 μg g^{-1} As in Upper Cretaceous (Cenomanian) glauconitic sands in the Ruhr Area (area 4) whereby output from the rocks to groundwater was not observed. In a Pliocene aquifer from the Lower Rhine Embayment (area 5), Cremer et al. (2003) detected up to 130 μg L^{-1} As in groundwater, attributable to mobilization via pyrite oxidation, probably triggered by anthropogenic NO_3^- input.

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 μg g^{-1} As in Mississippian (Lower Carboniferous) bituminous coals from Saxony (area 7). 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 μg g^{-1}. For comparison: the Clarke value for bituminous coal is 9.0 ± 0.8 μg 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 μg g^{-1} in Lower Permian ("Rotliegend") basin sediments in Saxony (area 8) and correlated elevated values to groundwater As anomalies. In Miocene lignite from northeastern Bavaria (area 9), Dill and Wehner (1999) detected 89 μg g^{-1} As on average (Clarke value for lignite: 7.4 ± 1.4 μg g^{-1}, Yudovich and Ketris, 2005). In single wells in the Spessart (northwestern

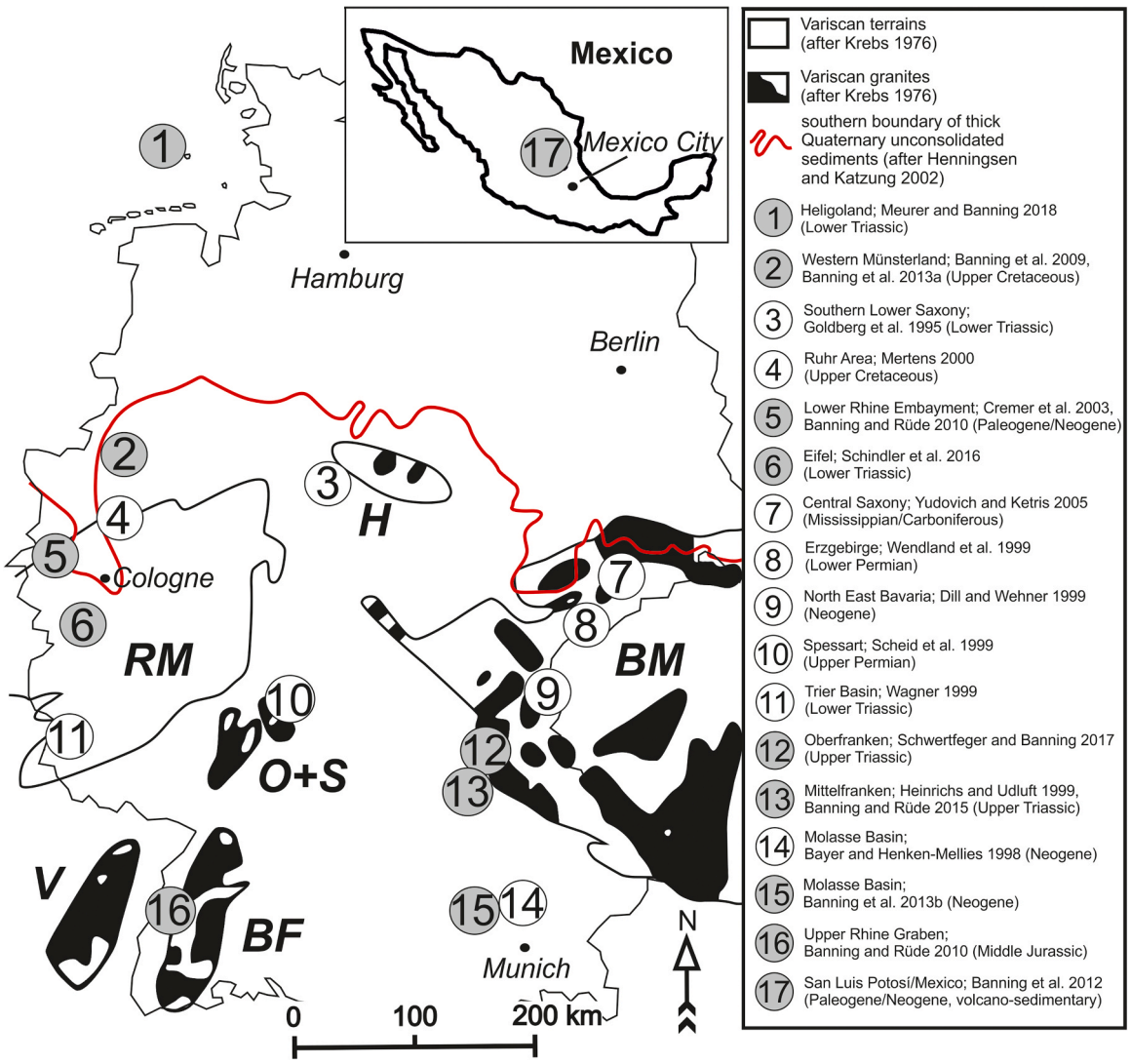


Fig. 1. Distribution of case studies on geogenic As and U in sedimentary rocks and groundwater in Germany (and one study in Mexico; numbering ascending from north to south; studies considered in this work marked as filled grey circles), Variscan terrains and granite intrusions therein (after Krebs, 1976) and southern boundary of thick Quaternary cover sediments (after Henningsen and Katzung, 2002). Variscan terrains from north to south: H: Harz Mountains, RM: Rhenish Massif, BM: Bohemian Massif, O+S: Odenwald and Spessart, BF: Black Forest, V: Vosges.

Bavaria, area 10), 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 (area 11) were shown to partly have high As concentrations of up to 880 μg g^{-1} (Wagner, 1999). Heinrichs and Udluft (1999) found that the distribution of extensively elevated As concentrations in Middle Franconian (northern Bavaria, area 13) groundwater (up to 150 μg 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. In southern Bavaria, Middle Miocene terrestrial sands ("Obere Süßwassermolasse", area 14) contain Fe hydroxide concretions with up to 1900 μg g^{-1} As that can locally lead to elevated groundwater concentrations when reducing conditions occur (Bayer and Henken-Mellies, 1998). Accumulation processes of As in Middle Jurassic ("Dogger") sedimentary Fe ores in the Upper Rhine Graben/Baden-Württemberg (area 16) were described by Banning and Rüde (2010): shallow marine environments fostering ooidic Fe ore formation provide conditions for syngenetic As accumulation. 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.

Studies on sedimentary aquifer U and associated concentrations in groundwater derived from water–rock interaction in Germany were scarce until about ten years ago. 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 attracted more attention due to the new drinking water limitation. Birke et al. (2010) found a median of 0.17 μg L^{-1} U in 908 German bottled water samples (maximum: 16 μg L^{-1}). They statistically found that Triassic sandstone and crystalline basement aquifers (mainly Black Forest) represent the main hosts for elevated groundwater U. Hessian environmental authorities detected concentrations above 10 μg L^{-1} U in 2.7% of 965 analyzed wells with a maximum concentration of 86 μg L^{-1}, elevated values were ascribed to geogenic input from Triassic rocks or Holocene peat deposits (HLUG, 2008). For the SW German federal state of Baden-Württemberg, Liesch et al. (2015) found groundwater U concentrations controlled by geology with highest mean values associated to Upper Triassic aquifers. Uraniferous Upper Triassic sediments are also known from northern Bavaria and referred to as "active arkoses" (Abele et al., 1962). These

syndiagenetic carbonate fluorapatite inclusions in the Keuper aquifer sandstones contain up to 1070 μg g^{-1} U and were found to show structurally (CO_3^{2-} substitution in the crystal structure) and radiatively (α-recoil damage from U decay) enhanced mineral solubility. Extraction experiments indicated U release to groundwater during weathering: apatite alteration was identified as the responsible mechanism for widespread groundwater U concentrations in the region (16% of wells >10 μg L^{-1}) (area 13, Banning and Rüde, 2015). Further north, the Keuper aquifer system hosts dolomitic inclusions instead of phosphates. Mineralogical and extraction data revealed that also this facies has a significant potential to release U to groundwater (area 12, Steffanowski and Banning, 2017); the two uraniferous facies control the geogenic U groundwater problem in northern Bavaria. The subsurface of the "Mechernich Triassic triangle" in the far west of Germany consists of Buntsandstein sediments. Groundwater in this Lower Triassic aquifer contains up to 56 μg L^{-1} U, with 7% of all samples in the study dataset exceeding the German guideline value (area 6, Schindler et al., 2016). Further studies describe anthropogenic mobilisation of geogenic subsurface U pools by agricultural activity in Mecklenburg-West Pomerania/NE Germany (Van Berk and Fu, 2017) and southern Bavaria (area 15, Banning et al., 2013b), drinking water treatment in North Rhine-Westphalia (Banning et al., 2017) or managed aquifer recharge on the island of Heligoland (area 1, Meurer and Banning, 2019). The latter is basically a Buntsandstein rock in the North Sea, uplifted by salt tectonics. In the otherwise widely homogeneous red sandstones, Cu- and U-bearing cavity fillings and "fish eyes" – round reduction spots, partly with a black U-rich centre – can be found. They represent the source of geogenic U mainly bound in the carbonate fraction. On Heligoland, brackish water with partly elevated U concentrations is treated via reverse osmosis for use as drinking water. Rain water is irrigated to recharge the aquifer, an artificial accumulation of Buntsandstein debris. The fresh water dissolves part of the geogenic U pool in the sandstones, leading to U groundwater peaks during low tide.

This work revisits and extends nine earlier regional studies which unravelled geogenic As and/or U accumulation processes in aquifers with different geological and stratigraphical background, and their timings in geological history. These aquifers were hydrogeochemically, mineralogically and genetically characterized, they are actually or potentially affected by naturally elevated groundwater concentrations of As and/or U. 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 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 this study. Geochemical proxies derived from so far unpublished trace element data will be assessed to characterize the studied sediments' provenance, combine the results with the earlier As/U-focused studies, and derive a geodynamic explanation for large-scale natural As and U distribution in Germany.

2. Materials and methods

A total of 270 sediment samples from nine study areas (eight studies in Germany, one in Mexico, Fig. 1) were considered in the present study, an overview is given in Table 1. Samples were taken from outcrops and boreholes, details about sediment sampling, geological and hydrogeological conditions, as well as regional As and/or U occurrence can be found in the papers cited in Figs. 1 and 2.

All samples were ground to powder grain size and analysed for bulk rock trace element geochemistry using Instrumental Neutron Activation Analysis (INAA). A sample aliquot of 1 g was encapsulated in a polyethylene vial and irradiated along with flux wires at a thermal neutron flux of 7 × 1012 n cm^{-2} s^{-1}. ^{24}Na was allowed to decay for 7 days. Subsequently, the samples were counted on a high purity Ge detector with resolution of better than 1.7 KeV for the 1332 keV ^{60}Co photopeak.

Table 1
Overview of investigation areas and samples used in this study (in stratigraphical order, cf. Fig. 1 for location of investigation areas).

Area no.	n	Stratigraphy	Main lithology; As/U host phases
15	46	Neogene/ Quaternary	Miocene alluvial sands, Quaternary fluvial gravels; Lignite, Fe hydroxides
5	36	Paleogene/ Neogene	little consolidated marine sands, lower reduced and upper oxidized facies; pyrite, Fe hydroxide concretions
17	30	Paleogene/ Neogene	terrestrial volcano-sedimentary basin filling (little consolidated sands, playa lake sediments); carbonates, Fe hydroxides
2	38	Upper Cretaceous	little consolidated marine sands, lower reduced and upper oxidized facies; pyrite, Fe hydroxide concretions, siderite concretions
16	32	Middle Jurassic	shallow marine limestone, mudstone, sandstone, ooidic Fe ores; Fe (hydr)oxides
12	14	Upper Triassic	terrestrial sandstone; uraniferous dolomite inclusions
13	47	Upper Triassic	terrestrial sandstone; uraniferous apatite inclusions, Fe oxides
1	18	Lower Triassic	red terrestrial sandstone; carbonate cavity fillings, U-rich black reduction spots
6	9	Lower Triassic	red terrestrial sandstone; Fe hydroxides

These analyses were performed by ISO 17025:2017-accredited Activation Laboratories Ltd., Ancaster, Ontario/Canada. For the trace element data presented here, analytical detection limits were 0.5 μg g^{-1} for La, U and As; 0.2 μg g^{-1} for Th and 0.1 μg g^{-1} for Sc. For quality control, flux wires and control standards were used to compare decay-corrected activities to a calibration developed from certified international reference materials: DMMAS 108, 108-B, 111 or 119. One standard was run for every 11 samples. Replicates and blanks were analysed to check accuracy and precision of the data.

3. Results and discussion

3.1. Regional significance and comparative overview

Important outcomes from five of the nine regional studies evaluated in the course of the present work are visualized in Fig. 2 whereby As and U sources and sinks structures including mobilization and immobilization processes in the studied areas are assessed. Studies 13, 16, 2 and 5 mentioned in Fig. 2 were conducted in different parts of Germany (Fig. 1, Chapter 1.3). Study 17 (Banning et al., 2012) discovered elevated groundwater As and U concentrations in the Villa de Reyes Graben, San Luis Potosí/central Mexico and succeeded in unravelling their common occurrence as well as the evolution of both elements' geochemical signatures. Absolute concentrations, inter-elemental behaviour and geochemical proxies supported the aforementioned view that both U and As are incompatible elements in magmatic differentiation and therefore accumulated in felsic lithologies. 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 (e.g., normalized REE patterns) in volcanic rocks, basin fill sediments and groundwater (Banning et al., 2012). While As and U can both occur in groundwater of 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, or by additional preferential input from secondary sedimentary sources (in this case preferential As over U input due to desorption from Fe (hydr)oxides and decarbonatization from caliche deposits).

Fig. 2 indicates that trace element accumulation processes and reservoirs can be of different orders such that spatio-temporal structure models of sources and sinks, and transfer processes between them, can

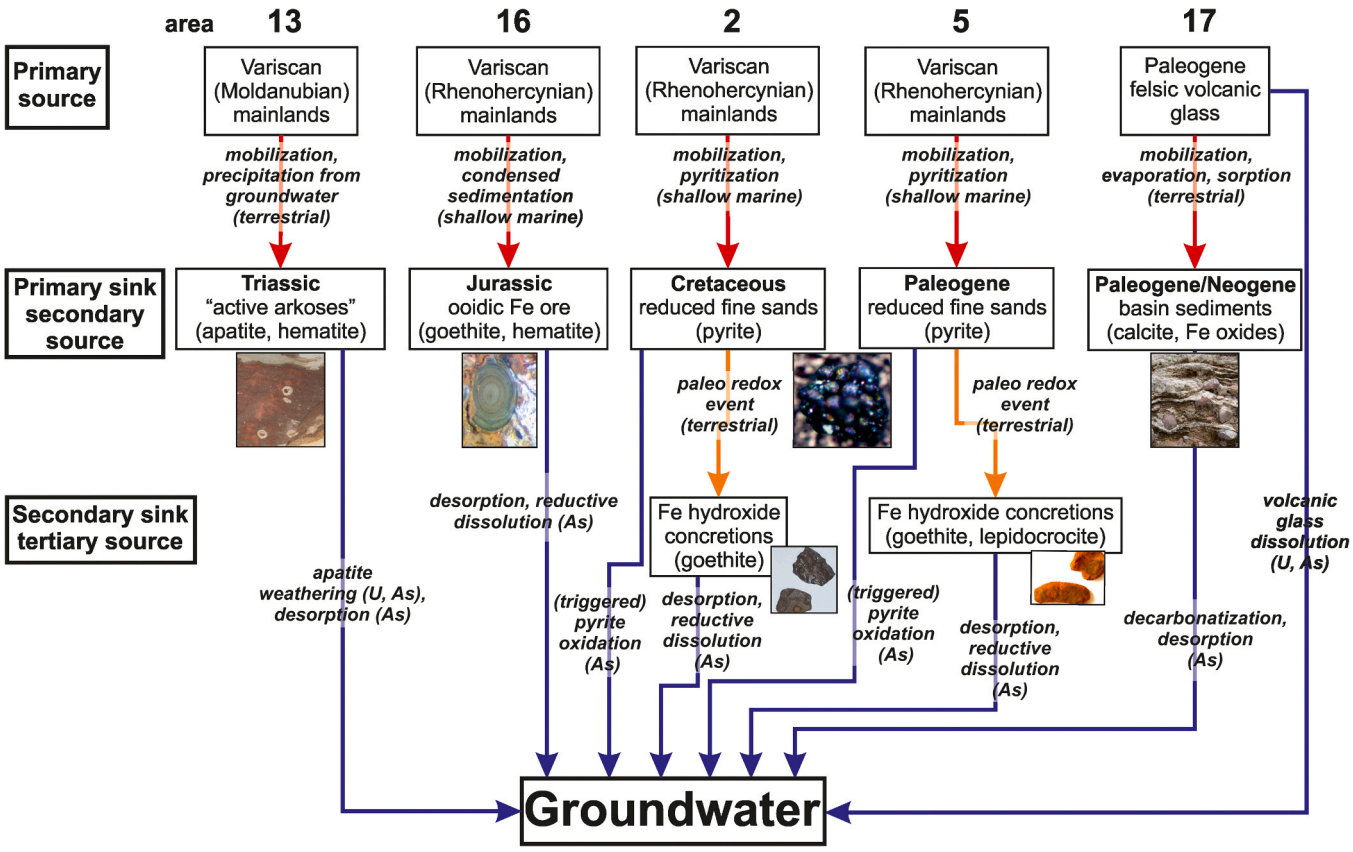


Fig. 2. Graphical overview of As and U sources and sinks structures including mobilization and immobilization processes in some of the studied areas. Area 13: Banning and Rüde (2015), area 16: Banning and Rüde (2010), area 2: Banning et al. (2013a), area 5: Banning and Rüde (2010), area 17: Banning et al. (2012).

be developed for a given area. The choice of study areas representing a variety of geological backgrounds and evolution make approaches and obtained results transferable to other regions. Sandstone-hosted uraniferous phosphates (area 13), shallow marine ooidic Fe ores (area 16), reduced glauconitic/pyritic marine sandy sediments (areas 2 and 5) and felsic volcano-sedimentary basins (area 17) are widespread geological environments worldwide and often share genetic and geochemical characteristics. This is especially supported by striking similarities between the studies in Cretaceous and Paleogene sediments (areas 2 and 5) 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.

3.2. Geodynamic model for large-scale 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 are assessed to characterize the studied sediments' provenance and combine the results with the As and U accumulation processes derived in earlier studies. Fig. 3 illustrates a ternary plot of La-Th-Sc to deduce source rock geochemistry and tectonic setting of the studied sediments.

Most 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

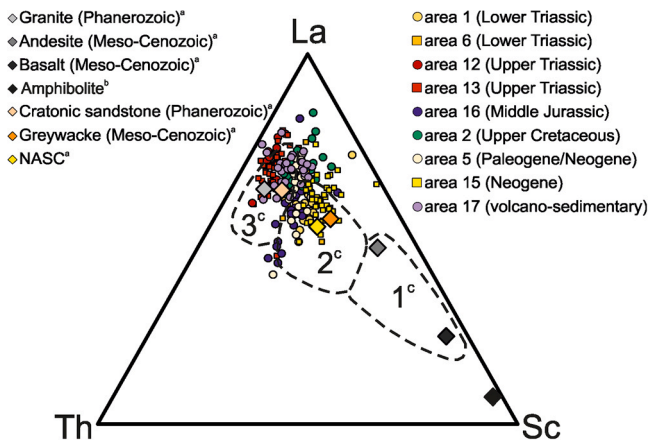


Fig. 3. La-Th-Sc plot of all studied sediment samples (cf. Fig. 1 for study area allocation). For comparison, plots of typical lithologies were implemented after [a]Condie (1993) and [b]Cullers (1994). Furthermore, fields in the diagram after [c]Bhatia and Crook (1986) indicate provenance rock tectonic setting with 1: oceanic island arc, 2: continental island arc, 3: active or passive continental margin. NASC: North American Shale Composite.

for all sediments (Fig. 3). Also in comparison to NASC, the North American Shale Composite (representative of upper crustal sediments; e.g., Gromet et al. 1984), the majority of samples plot in the more felsic range and are in this respect rather comparable to typical cratonic sandstone plotting within the data aggregation.

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. 3), 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. 4.

The observation of geochemical proxies indicating rather felsic provenance, also in comparison to average upper crustal sediment (NASC), is supported by the binary plot (Fig. 4). In spite of partly considerable scattering (R^2 of the nine data subsets: 0.11–0.72), differences between the single study areas become evident. Upper Triassic sediments from areas 12 (La/Sc ratio derived from trendline equation: 8.73) and 13 (6.09) as well as volcano-sedimentary basin filling from San Luis Potosí (area 17, 5.88) exhibit clearly more felsic provenance than marine sediments of Jurassic (area 16), Paleogene (area 5), Cretaceous (area 2) and Lower Triassic (areas 1 and 6) age. Neogene sediments from the southern German Molasse basin (area 15) document average La/Sc ratios very close to the NASC signature.

Consequently, areas with high U potential in terms of accumulation in rocks/sediments and elevated concentrations in groundwater originate from more felsic sources than sediments hosting "only" As.

The following is hypothesized:

(a) Sedimentary environments potentially fostering As enrichment require above-average (i.e., above NASC) 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 those 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 As/U accumulation processes, plots of La vs. U and La vs. As are presented as Figs. 5 and 6, respectively.

The majority of samples in Fig. 5 exhibit a development along a positively trending line 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

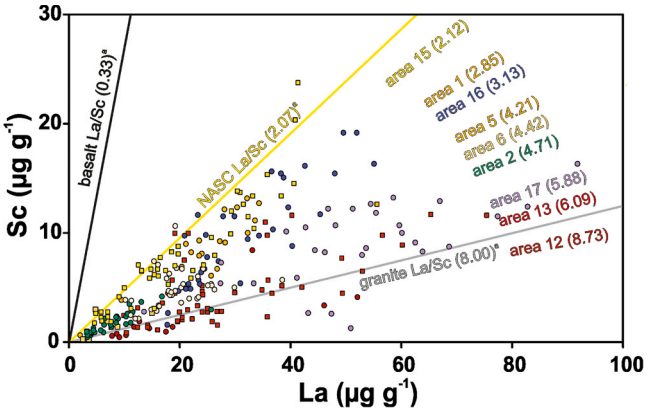


Fig. 4. La vs. Sc scatter plot and average La/Sc ratios for sediment samples from the nine study areas, cf. Fig. 1 for study area allocation. Basalt, NASC and granite standard ratios after [a]Condie (1993).

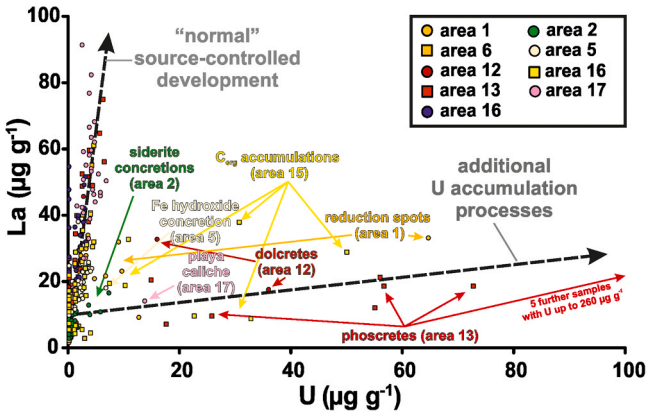


Fig. 5. U vs. La scatter plot for all studied sediments (cf. Fig. 1 for study area allocation), and secondary U accumulation mechanisms in sediment basins (cf. Fig. 2 and Chapter 1.3).

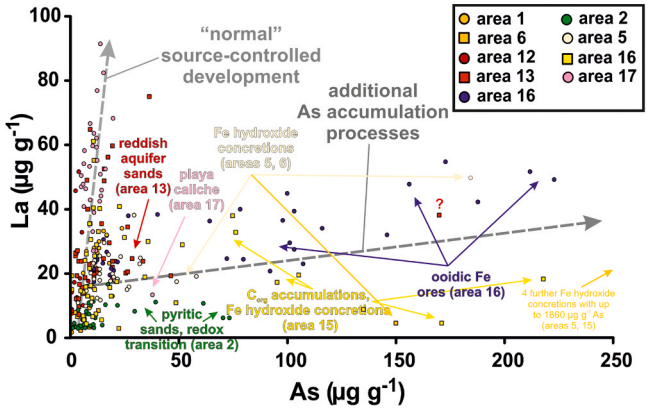


Fig. 6. As vs. La scatter plot for all studied sediments (cf. Fig. 1 for study area allocation), and secondary As accumulation mechanisms in sediment basins (cf. Fig. 2 and Chapter 1.3).

enrichment processes in the different areas. Slight accumulation was found in siderite concretions within Cretaceous fine sands (area 2). Uranium sorption to the purest Fe hydroxide concretion in oxidized sands of the Lower Rhine Embayment (area 5, this sample has the singular highest As content (1860 µg g^{-1}) of all study area) was not able to accumulate more than 7.2 µg 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 (area 17). Apatite precipitation from U-bearing groundwater on former playa carbonates resulted in high U contents in phoscretes (area 13), also the more proximal original dolcretes (area 12) show some U accumulation. Very localized reducing conditions lead to punctual U hot spots in Lower Triassic sandstone on Heligoland (area 1), this phenomenon is also known from e.g., Switzerland (Hofmann, 1990; Burkhalter, 1995). Uranium accumulation in Neogene sediments (area 15) is almost exclusively observed in post-sedimentary, i.e., Holocene, C_{org}-rich deposits like peat which successively concentrated U from groundwater.

Similar observations can be made in the As vs. La plot (Fig. 6) – a provenance-driven "background" development is overlain by different additional As concentration processes occurring in the studied sediment basins: sorption to Fe hydroxide coatings of silicate aquifer material (areas 6 and 13), accumulation in ooidic Fe ores during condensed sedimentation (area 16), fixation in pyrite and subsequent redistribution

to redox transition zones and Fe hydroxide concretions (areas 2 and 5), enrichment by evaporation in playa caliches (area 17), concentration by sorption to organic material and in Fe(III) concretions (area 15). Jurassic ooidic Fe ores (area 16) with high As values only yield U contents of 1.5 µg 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. 5), the trend of "normal" source-controlled development between As and La for all samples appears less distinct. Obviously, the signature of the more incompatible U regarding geochemical provenance proxies is clearer. 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 will be assessed in the following and set in relation to their sediment provenance areas. Fig. 7 offers an overview of the study areas' stratigraphical situation and the plate tectonic framework.

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 Northern Bavaria (areas 12, 13). Sediments from these periods often represent cratonic sandstones (cf. Fig. 3) 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. Chapter 1.3). 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 Breitkreuz, 1998; Fig. 7). 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 the Upper Carboniferous. Concluding from Fig. 7, 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 period. Possible explanations for that must be sought in the spatio-temporal geological development of Germany.

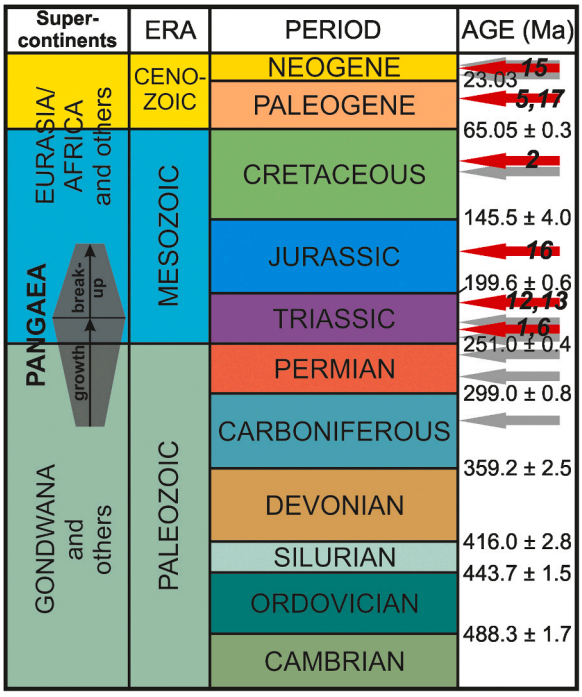


Fig. 7. Stratigraphical distribution of study areas (red arrows) and studied occurrences of sedimentary As in Germany from literature (grey arrows, cf. Fig. 1), absolute stratigraphical boundary ages (right side) after ICS (2009). Additionally, major crustal development (supercontinents, left side) after Bahlburg and Breitkreuz (1998) is indicated.

Fig. 1 illustrates the spatial distribution of studied sedimentary As as well as Variscan terrains and thick Quaternary overburden. It becomes evident 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 (except for the Triassic rock island Heligoland, area 1, which is not covered by Quaternary). 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 (or U) potential along. Not only would these observations explain the northern boundary of As study areas (Fig. 1) 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. 1) 90th percentile values of 3.3–3.5 µg L^{-1} As with hardly any single values above 10 µg 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 µg L^{-1} As from this area.

The organisation Foodwatch collected and published drinking water U data from German federal state authorities (Foodwatch, 2009). In the dataset, they found that concentrations in the northern and central federal states Brandenburg, Berlin, Bremen, Hamburg, Schleswig-Holstein, Lower Saxony, North Rhine-Westphalia and Saarland are quantitatively below 10 µg L^{-1} U (2 out of 427 samples in Mecklenburg-West Pomerania were above that limit) while southern federal states generally exhibit more abundant violations of the drinking water guideline.

Another observation from Fig. 1 is the close spatial relation of most conducted sedimentary As and U studies to Variscan terrains in Germany supporting a relation between Variscan geology and trace element distribution as was already suspected from stratigraphy (Fig. 7). Differences between sedimentary occurrence of As and U in the single studied areas in this work can be derived from the distribution of Variscan granites and support the hypotheses on degree of provenance felsicity formulated earlier: Upper Triassic sediments from northern Bavaria (areas 12, 13) 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 Breitkreuz, 1998) while Cretaceous and Paleogene sediments (areas 2, 5) originate from the Rhenohercynian Variscan section with low degree of metamorphism and widely absent granitic intrusions (Fig. 1). At first glance, it seems surprising that the Jurassic sediments (area 16), being located in direct vicinity to the Moldanubian granite-rich Black Forest and Vosges (Fig. 1) do neither show highly felsic provenance (Fig. 4) nor elevated U potential (Fig. 5). 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 accomplished 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 U 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 μg 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 here for Triassic phoscretes (area 13). 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, one of which – Nielsbohrite [(KUO2)3(AsO4)(OH)4*H2O] – 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 South German 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, show high As concentrations of 200 μg L^{-1} on average; U presence is documented by U-bearing amorphous thermal Mn hydroxides and opaline sinters (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 μg g^{-1}) in Fe-rich sections of the Bavarian molasse basin, esp. Badenean sands (area 14 in Fig. 1), 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 μg 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). An explanation for that can be given by another paleogeographical observation: after deposition of the Badenean 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.

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 groundwater U concentrations (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).

Limitations of this study include the partly unequal distribution of the number of samples from the different study areas, ranging from 9 to 47, associated with heterogeneous levels of significance in statistical considerations. Also, trace element rich sample types (concretions, inclusions, etc.) are likely to be overrepresented in the dataset and therefore do not resemble the composition of the whole aquifer/sediment system. Lastly, revisited studies were published within a decade (2010–2019), with partly differing people accomplishing sampling, sample preparation and sample analysis.

4. Conclusions

Geological evolution, expressed by geochemical proxies, can explain trace element distribution on different temporal and spatial scales, and help understand and forecast the occurrence of actual and potential groundwater quality problem areas. Trace element abundance was shown to directly reflect supraregional and intra-basinal geological evolution. 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.

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 on a global scale 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, especially under climate change conditions.

CRediT authorship contribution statement

Andre Banning is the single author of this manuscript.

Declaration of Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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