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1 **Geogenic arsenic and uranium in Germany: large-scale distribution control in sediments**
2 **and groundwater**

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13
14
15 **Abstract**

16
17 Arsenic (As) and uranium (U) are naturally occurring trace elements with potentially adverse effects
18 on human health. This work revisits nine case studies on As/U accumulation and remobilization
19 mechanisms in aquifers with different geological and stratigraphical backgrounds to develop a system-
20 atic overview of Germany's geogenic inventory of these trace elements. It uses geochemical proxies
21 for a total of 270 solid samples to explain their spatio-temporal distribution: while Pleistocene geolog-
22 ical development can explain their extensive absence in sediments and related groundwater in northern
23 Germany, their abundance and distribution in the central and southern parts are widely controlled by
24 sediment provenance geochemistry. Only highly felsic origin (Moldanubian Variscides) enables crea-
25 tion of elevated U in the systems while lower degrees of provenance felsicity (Rhenohercynian
26 Variscides) appear to be sufficient for As presence. Postdepositional (hydro)geological and anthropo-
27 genically triggered intra-basinal processes of trace element accumulation, redistribution and eventually
28 remobilization to groundwater contribute to the present-day situation. Therefore, the ultimate control of
29 these incompatible trace elements is magmatic, even in old sedimentary systems, and still clearly
30 traceable in nowadays large-scale geogenic As and U distribution in Germany and probably elsewhere.

31
32 **Keywords**

33 magmatic differentiation, geochemical proxies, sediment provenance, Variscides, accumula-
34 tion processes

38 **1 Introduction**

39 **1.1 Arsenic and uranium – a short geochemical overview**

40 Showing characteristics of both chalcophile and siderophile behaviour, arsenic (As) tends to be prefer-
41 ably hosted by sulphide minerals like pyrite or (hydr)oxidic Fe phases like goethite, both of which can
42 contain As up to several wt.% (Smedley and Kinniburgh 2002). In spite of its low average abundance
43 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
44 crust), As can accumulate in rocks to concentrations several orders of magnitude higher than these
45 values. The metalloid's fate in the environment is controlled by the prevailing physico-chemical condi-
46 tions and the presence of other ions. Redox milieu, pH and ionic competition are crucial parameters
47 governing As behaviour (adsorption, desorption, transport, redox transformation). Reducing condi-
48 tions can lead to As mobilization from oxides while oxidizing conditions may mobilize As bound to
49 sulphides. High groundwater pH constrains As adsorption to mineral surfaces and may therefore be
50 responsible for elevated concentrations in solution. Ions competing with As species for surface binding
51 sites, especially phosphate, can lead to the same result (e.g. Stollenwerk 2002, Smedley and Kinni-
52 burgh 2002, Pedersen et al. 2006).

53 The mobility of U in the environment is, akin to that of As, governed by the Eh-pH milieu and the
54 presence of adsorbers like Fe (hydr)oxides, clay minerals or organic matter (e.g. Doi et al. 1975,
55 Giblin et al. 1981, Merkel and Sperling 1998, Missana et al. 2003, Bots and Behrends 2008). Never-
56 theless, contrary to As, U is significantly more mobile in its oxidized form U(VI) which is reasoned by
57 its affinity to form stable uranyl hydroxo or calcium uranyl carbonate complexes (e.g. Katsoyiannis et
58 al. 2007, Stewart et al. 2010). In spite of their differing redox and transport properties, As and U fre-
59 quently occur together in (ground)water of affected areas (e.g. Brown et al. 2007, Kipp et al. 2009,
60 Nicolli et al. 2010, Banning et al. 2012, Banning and Rude 2015).

61 Taylor (1964) cites the average uranium (U) abundance in the continental crust as $2.7\ \mu\text{g g}^{-1}$. Thereby,
62 generally higher concentrations are detected in felsic rocks (granite average: $4.8\ \mu\text{g g}^{-1}$ U) compared to
63 mafic lithologies (basalt average: $0.6\ \mu\text{g g}^{-1}$ U). Uranium has a strongly incompatible behavior in sili-
64 cate magmatic differentiation because of its large ion radius and high valence. It is preferentially
65 fractionated into high-temperature metaluminous melts during partial melting and crystal fractionation
66 (Cuney 2010), and therefore often accumulates in granitic and pegmatitic lithologies. Also As is con-
67 sidered one of the incompatible elements which do not fit easily into the lattices of rock-forming
68 minerals precipitating from melt (Webster and Nordstrom 2003).

69 **1.2 Arsenic and uranium as contaminants – health aspects and affected areas**

70 The recognition of As toxicity and its initially underestimated impact on human health on a global
71 scale substantially increased the intensity of As research during the past decades, focussing on large
72 problem areas, especially in Southeast Asia (e.g. Berg et al. 2001, Ravenscroft et al. 2005, Zahid et al.

73 2009). Consequently, drinking water threshold values were broadly lowered in the 1990ies, mostly
74 down to $10 \mu\text{g L}^{-1}$. This confronted water suppliers with the problem of an increased need to process
75 raw water in order to match drinking water requirements. In recent years, it was also found that in the
76 large majority of cases, naturally occurring As is responsible for elevated groundwater concentrations.
77 Thereby, mobilization from As-enriched minerals is the dominating process (e.g. Lowers et al. 2007).
78 Besides the large tropical, mainly deltaic regions with As-exposed populations (e.g. Bangladesh, West
79 Bengal, Vietnam, Taiwan), (semi)arid As problem areas have been identified worldwide. Prominent
80 examples can be found in Chile (e.g. Oyarzun et al. 2004) and the western U.S.A. (e.g. Welch and
81 Lico 1998). Identified As problem areas in Mexico include the Zimapán Valley (Armienta et al. 2001),
82 the Rioverde Basin (Planer-Friedrich et al. 2001) and the Villa de Reyes Graben around San Luis Po-
83 tosí (Banning et al. 2012). Even endemic As poisoning was described in the Lagunera region (Del
84 Razo et al. 1990). An overview of elevated As occurrences in Mexico is given by Armienta and Segovia
85 (2008).

86 While the toxicity of As is well documented and drinking water limitations are established and recon-
87 sidered for several decades (actually $10 \mu\text{g L}^{-1}$, WHO 2006), U was neglected in this respect for a long
88 time. It was shown that the risk of U exposure primarily derives from its toxicity as a nephrotoxic
89 heavy metal (i.e., leading to kidney diseases), rather than from its radioactive character (Zamora et al.
90 1998, Orloff et al. 2004, Bjørklund et al. 2017). For adults in Germany, a total radiation exposure of
91 2.1 mSv a^{-1} was determined, whereby exposure via drinking water only contributes 0.009 mSv a^{-1} (BfS
92 2009), i.e. $\sim 0.4 \%$ of the annual radiation dosage. There is no general agreement on fixed limitations
93 for U concentrations in drinking water up to date, although drinking water is considered the most im-
94 portant source of U uptake. WHO announced a “provisional guideline value” of $30 \mu\text{g L}^{-1}$, German
95 legislation decided on a fixed limitation of $10 \mu\text{g L}^{-1}$, valid since 2011. Compared to As, the number of
96 identified geogenic groundwater U problem areas worldwide is low but growing. Nevertheless, it has
97 been recognized that high-U aquifers represent a phenomenon of global extent. Felsic magmatic aqui-
98 fers in Scandinavia are partly affected by elevated concentrations (Frengstad et al. 2000 and citations
99 therein). Sherman et al. (2007) found 29 % of the studied water samples from a sandstone aquifer in
100 Michigan in excess of the WHO guideline. These authors also give a short overview of case studies
101 from other affected states and countries. In the course of a national monitoring of domestic well water
102 in the U.S.A., Focazio et al. (2006) detected 4 % of all samples exceeding $30 \mu\text{g L}^{-1}$ U. In the north-
103 west Indian state of Punjab, high U concentrations in groundwater have relatively recently been ob-
104 served over a wide geographical area. Several studies (Patnaik et al. 2015; Kumar et al. 2016; Bajwa et
105 al. 2017; Lapworth et al. 2017) point to potential risks for the exposed population. Unverified hypoth-
106 eses on the origin of groundwater U include fly ash from coal combustion or input from agricultural
107 fertilisation. However, most authors consider geogenic processes more likely, primarily the weathering
108 of the Siwaliks, i.e. Himalayan foothills (e.g., Patnaik et al. 2015). Also high As groundwaters are
109 known from the region (e.g., Kumar and Singh 2020).

110 **1.3 Known cases of elevated As and U contents in German sediments and groundwater**

111 While the mechanism of large-scale As accumulation in delta sediments of Southeast Asia (e.g.
112 Acharyya et al. 2000, Stanger 2005) or in (semi)arid Latin America (e.g. Bundschuh et al. 2004,
113 Nicolli and Bundschuh 2010) are subject to extensive research and discussions, relatively little was
114 known about the origin and development of geogenic As accumulations in Germany. These have been
115 studied on a rather local to regional scale, although elevated As concentrations in groundwater have
116 been detected in many parts of the country, an overview is given by Heinrichs and Udluft (1996). Fig-
117 ure 1 illustrates a survey of conducted studies on elevated As occurrences in sedimentary rocks and
118 partly groundwater, whereby no claim to completeness is made. It does neither include high As ob-
119 served in thermal waters known from e.g., Baden-Baden (Rüde 1996), Aachen (Herch 1997) and
120 Wiesbaden (Rosenberg et al. 1999), nor anthropogenically induced As problems (e.g., from former
121 mining, past agricultural techniques or ammunition). The As-related studies shown in Fig. 1 will be
122 shortly summarized in the following.

123 Banning et al. (2009) detected partly high As contents up to $140 \mu\text{g g}^{-1}$ in secondary Fe concretions in
124 oxidized Upper Cretaceous (Santonian) sediments from the Münsterland Cretaceous Basin (area 2 in
125 Fig. 1) and identified them as the source for significant As contents in soils of the region. A postdepo-
126 sitional paleo redox event during the late Tertiary caused extremely heterogeneous As and other trace
127 element distribution in shallow marine sediments, leading to partly massively enriched secondary con-
128 cretions. Mainly pyrite-controlled, rather homogeneous As distribution in the original deeper sediment
129 facies changes under formation of highly reactive redox transition zones and distinct paleo redox
130 boundaries into extremely heterogeneous Fe hydroxide-controlled distribution in near-surface sedi-
131 ments (Banning et al. 2013a). The same mechanism applied to Tertiary marine sediments in the Lower
132 Rhine Embayment (area 5; Banning and Rüde 2010): Santonian and Chattian shallow marine sedi-
133 ments exhibit very similar responses to the late Tertiary oxidative redox event, including rock fabric
134 and mineralogical changes, trace element (esp. As) redistribution and remobilization potentials. The
135 developed genetic and geochemical patterns are obviously of general validity for the studied geo-
136 environment: large-scale redox events alter comparable lithologies and redistribute trace elements
137 hosted therein in the same way, independent of sediment age.

138 Concentrations of As in groundwater from southern Lower Saxony (area 3) above the drinking water
139 standard were attributed to output from Lower Triassic (“Buntsandstein”) clastic sediments (up to 693
140 $\mu\text{g g}^{-1}$ As) by Goldberg et al. (1995). Mertens (2000) found an average of $108 \mu\text{g g}^{-1}$ As in Upper Cre-
141 taceous (Cenomanian) glauconitic sands in the Ruhr Area (area 4) whereby output from the rocks to
142 groundwater was not observed. In a Pliocene aquifer from the Lower Rhine Embayment (area 5),
143 Cremer et al. (2003) detected up to $130 \mu\text{g L}^{-1}$ As in groundwater, attributable to mobilization via py-
144 rite oxidation, probably triggered by anthropogenic NO_3^- input.

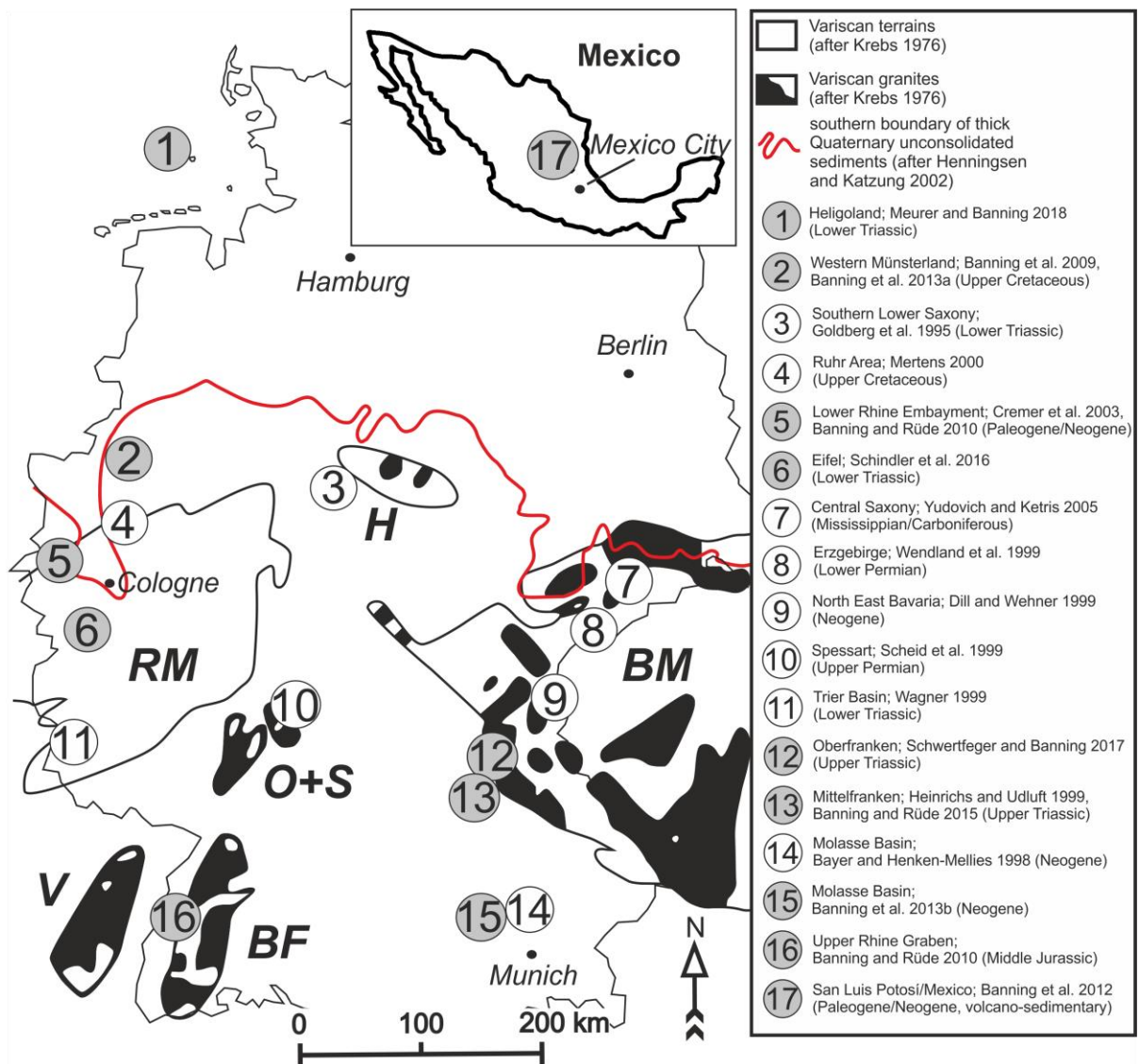


Fig. 1: Distribution of case studies on geogenic As and U in sedimentary rocks and groundwater in Germany (and one study in Mexico; numbering ascending from north to south; studies considered in this work marked as filled grey circles), Variscan terrains and granite intrusions therein (after Krebs 1976) 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.

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154 Arsenic contents are partly elevated in coal, an overview is given by Yudovich and Ketris (2005).
155 Therein, the authors mention contents of up to $400 \mu\text{g g}^{-1}$ As in Mississippian (Lower Carboniferous)
156 bituminous coals from Saxony (area 7). Interestingly, they found that Eastern German black coal is
157 significantly more enriched than the Western German Upper Carboniferous coal with average As con-
158 tents 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
159 host in coal is dominantly pyrite but also organic As can be of importance (Yudovich and Ketris
160 2005). Wendland et al. (1999) determined a mean As concentration of $55 \mu\text{g g}^{-1}$ in Lower Permian
161 (“Rotliegend”) basin sediments in Saxony (area 8) and correlated elevated values to groundwater As
162 anomalies. In Miocene lignite from northeastern Bavaria (area 9), Dill and Wehner (1999) detected

163 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 sin-
164 gle wells in the Spessart (northwestern Bavaria, area 10), a correlation between elevated groundwater
165 As and the distribution of Upper Permian (“Zechstein”) sediments was observed by Scheid et al.
166 (1999). Lower Triassic (“Buntsandstein”) sandstones containing plant fossils in the Trier Basin (area
167 11) were shown to partly have high As concentrations of up to $880 \mu\text{g g}^{-1}$ (Wagner 1999). Heinrichs
168 and Udluft (1999) found that the distribution of extensively elevated As concentrations in Middle
169 Franconian (northern Bavaria, area 13) groundwater (up to $150 \mu\text{g L}^{-1}$) is dependent on depositional
170 aquifer facies: only terrestrial sediments of the Upper Triassic (“Keuper”) seem to produce groundwa-
171 ter As in excess of the drinking water standard. In southern Bavaria, Middle Miocene terrestrial sands
172 (“Obere Süßwassermolasse”, area 14) contain Fe hydroxide concretions with up to $1900 \mu\text{g g}^{-1}$ As that
173 can locally lead to elevated groundwater concentrations when reducing conditions occur (Bayer and
174 Henken-Mellies 1998). Accumulation processes of As in Middle Jurassic (“Dogger”) sedimentary Fe
175 ores in the Upper Rhine Graben/Baden-Wuerttemberg (area 16) were described by Banning and Rüde
176 (2010): shallow marine environments fostering ooidic Fe ore formation provide conditions for syngen-
177 etic As accumulation. The studied depositional conditions proved suitable for As enrichment in
178 mainly goethitic Fe ooids during condensed sedimentation. Thereby, As accumulation is preferred
179 over other trace elements.

180 Studies on sedimentary aquifer U and associated concentrations in groundwater derived from water-
181 rock-interaction in Germany were scarce until about ten years ago. In contrary, the environmental
182 impact of former extensive U mining, especially in Eastern Germany, has been characterized in detail
183 (e.g. Wolkersdorfer 1996, Winkelmann et al. 2001, Baborowski and Bozau 2006). More recently, the
184 inventory of geogenic background U in groundwater attracted more attention due to the new drinking
185 water limitation. Birke et al. (2010) found a median of $0.17 \mu\text{g L}^{-1}$ U in 908 German bottled water
186 samples (maximum: $16 \mu\text{g L}^{-1}$). They statistically found that Triassic sandstone and crystalline base-
187 ment aquifers (mainly Black Forest) represent the main hosts for elevated groundwater U. Hessian
188 environmental authorities detected concentrations above $10 \mu\text{g L}^{-1}$ U in 2.7% of 965 analyzed wells
189 with a maximum concentration of $86 \mu\text{g L}^{-1}$, elevated values were ascribed to geogenic input from
190 Triassic rocks or Holocene peat deposits (HLUG 2008). For the SW German federal state of Baden-
191 Württemberg, Liesch et al. (2015) found groundwater U concentrations controlled by geology with
192 highest mean values associated to Upper Triassic aquifers. Uraniferous Upper Triassic sediments are
193 also known from northern Bavaria and referred to as “active arkoses” (Abele et al. 1962). These syndi-
194 agenetic carbonate fluorapatite inclusions in the Keuper aquifer sandstones contain up to $1070 \mu\text{g g}^{-1}$
195 U and were found to show structurally (CO_3^{2-} substitution in the crystal structure) and radiatively (α -
196 recoil damage from U decay) enhanced mineral solubility. Extraction experiments indicated U release
197 to groundwater during weathering: apatite alteration was identified as the responsible mechanism for
198 widespread groundwater U concentrations in the region (16% of wells $>10 \mu\text{g L}^{-1}$) (area 13, Banning
199 and Rüde 2015). Further north, the Keuper aquifer system hosts dolomitic inclusions instead of phos-

200 phates. Mineralogical and extraction data revealed that also this facies has a significant potential to
201 release U to groundwater (area 12, Steffanowski and Banning 2017); the two uraniferous facies con-
202 trol the geogenic U groundwater problem in northern Bavaria. The subsurface of the “Mechernich
203 Triassic triangle” in the far west of Germany consists of Buntsandstein sediments. Groundwater in this
204 Lower Triassic aquifer contains up to 56 $\mu\text{g L}^{-1}$ U, with 7% of all samples in the study dataset exceed-
205 ing the German guideline value (area 6, Schindler et al. 2016). Further studies describe anthropogenic
206 mobilisation of geogenic subsurface U pools by agricultural activity in Mecklenburg-West Pomerania/NE Germany (van Berk and Fu 2016) and southern Bavaria (area 15, Banning et al. 2013b),
207 drinking water treatment in North Rhine-Westphalia (Banning et al. 2017) or managed aquifer re-
208 charge on the island of Heligoland (area 1, Meurer and Banning 2018). The latter is basically a
209 Buntsandstein rock in the North Sea, uplifted by salt tectonics. In the otherwise widely homogeneous
210 red sandstones, Cu- and U-bearing cavity fillings and “fish eyes” – round reduction spots, partly with a
211 black U-rich centre – can be found. They represent the source of geogenic U mainly bound in the car-
212 bonate fraction. On Heligoland, brackish water with partly elevated U concentrations is treated via
213 reverse osmosis for use as drinking water. Rain water is irrigated to recharge the aquifer, an artificial
214 accumulation of Buntsandstein debris. The fresh water dissolves part of the geogenic U pool in the
215 sandstones, leading to U groundwater peaks during low tide.

217 This work revisits and extends nine earlier regional studies which unravelled geogenic As and/or U
218 accumulation processes in aquifers with different geological and stratigraphical background, and their
219 timings in geological history. These aquifers were hydrogeochemically, mineralogically and genetical-
220 ly characterized, they are actually or potentially affected by naturally elevated groundwater
221 concentrations of As and/or U. Besides the major importance of the obtained results on a regional
222 scale and global transferability based on comparable conditions between single areas, more may be
223 learned from geochemical comparison of all study areas and their distribution in space and time.
224 Therefore, the impact of sediment provenance and the spatio-temporal development of Europe on geo-
225 genic As and U distribution are evaluated in this study. Geochemical proxies derived from so far
226 unpublished trace element data will be assessed to characterize the studied sediments’ provenance,
227 combine the results with the earlier As/U-focused studies, and derive a geodynamic explanation for
228 large-scale natural As and U distribution in Germany.

229

230 **2 Materials and Methods**

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

235

236 Table 1: overview of investigation areas and samples used in this study (in stratigraphical order, cf. Fig. 1 for
 237 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

238

239 All samples were ground to powder grain size and analysed for bulk rock trace element geochemistry
 240 using Instrumental Neutron Activation Analysis (INAA). A sample aliquot of 1 g was encapsulated in
 241 a polyethylene vial and irradiated along with flux wires at a thermal neutron flux of $7 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$.
 242 ^{24}Na was allowed to decay for 7 days. Subsequently, the samples were counted on a high purity Ge
 243 detector with resolution of better than 1.7 KeV for the 1332 keV ^{60}Co photopeak. These analyses were
 244 performed by ISO 17025:2017-accredited Activation Laboratories Ltd., Ancaster, Ontario/Canada. For
 245 the trace element data presented here, analytical detection limits were $0.5 \mu\text{g g}^{-1}$ for La, U and As; 0.2
 246 $\mu\text{g g}^{-1}$ for Th and $0.1 \mu\text{g g}^{-1}$ for Sc. For quality control, flux wires and control standards were used to
 247 compare decay-corrected activities to a calibration developed from certified international reference
 248 materials: DMMAS 108, 108-B, 111 or 119. One standard was run for every 11 samples. Replicates
 249 and blanks were analysed to check accuracy and precision of the data.

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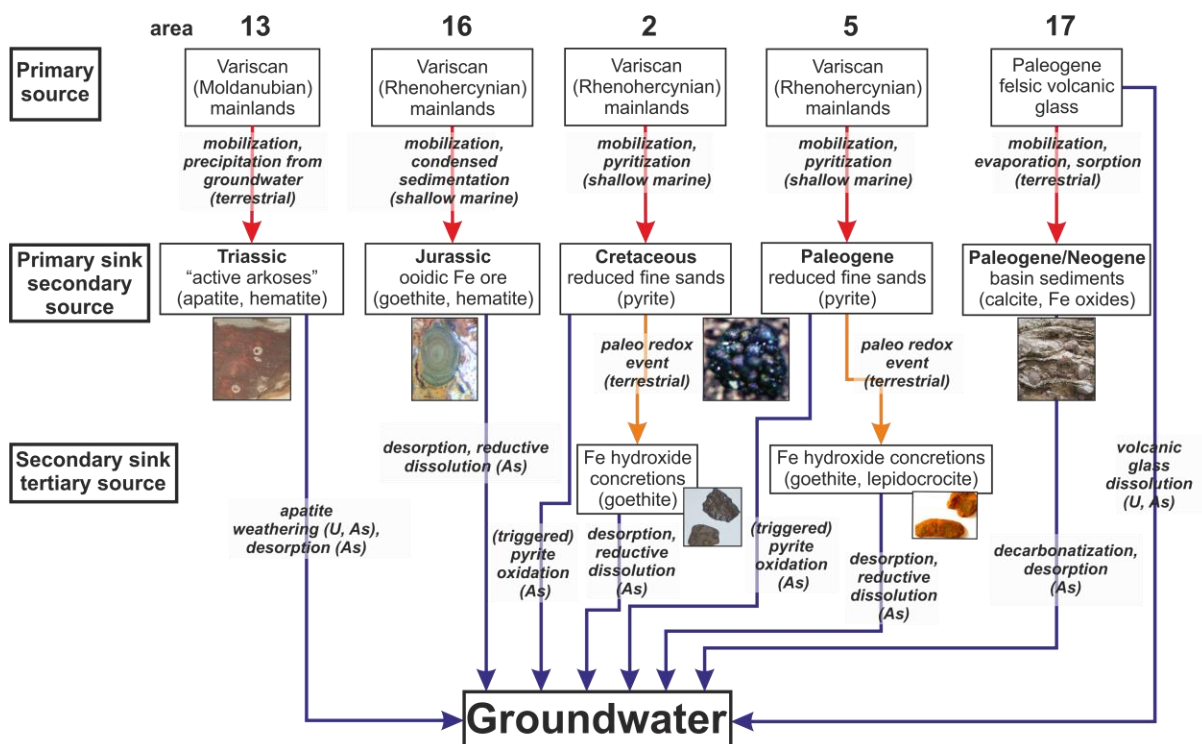
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252 3 Results and Discussion

253 3.1 Regional significance and comparative overview

254 Important outcomes from five of the nine regional studies evaluated in the course of the present work
 255 are visualized in Fig. 2 whereby As and U sources and sinks structures including mobilization and
 256 immobilization processes in the studied areas are assessed. Studies 13, 16, 2 and 5 mentioned in Fig. 2
 257 were conducted in different parts of Germany (Fig. 1, chapter 1.3). Study 17 (Banning et al. 2012)
 258 discovered elevated groundwater As and U concentrations in the Villa de Reyes Graben, San Luis
 259 Potosí/central Mexico and succeeded in unravelling their common occurrence as well as the evolution
 260 of both elements' geochemical signatures. Absolute concentrations, inter-elemental behaviour and
 261 geochemical proxies supported the aforementioned view that both U and As are incompatible elements
 262 in magmatic differentiation and therefore accumulated in felsic lithologies. Dissolution of volcanic
 263 glass was identified as the main common release mechanism of U and As in the volcano-sedimentary
 264 Mexican basin. It represents input from a common source into groundwater, supported by geochemical
 265 signatures (e.g., normalized REE patterns) in volcanic rocks, basin fill sediments and groundwater
 266 (Banning et al. 2012). While As and U can both occur in groundwater of sedimentary basins, it be-
 267 came obvious that in most samples, only one of the trace elements showed high concentrations. This is
 268 explainable by separation due to redox heterogeneity in the aquifer, or by additional preferential input
 269 from secondary sedimentary sources (in this case preferential As over U input due to desorption from
 270 Fe (hydr)oxides and decarbonatization from caliche deposits).

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272

273 Fig. 2: Graphical overview of As and U sources and sinks structures including mobilization and immobilization
274 processes in some of the studied areas. Area 13: Banning and Rüde (2015), area 16: Banning and Rüde
275 (2010), area 2: Banning et al. (2013), area 5: Banning and Rüde (2010), area 17: Banning et al. (2012).

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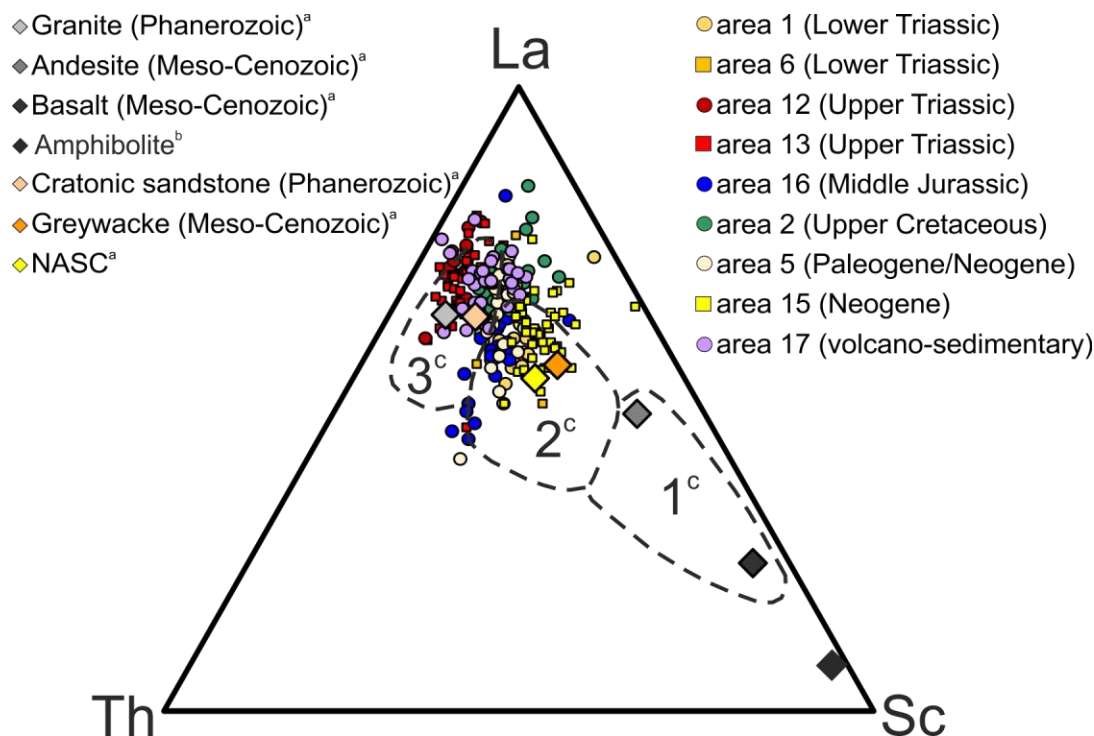
277 Figure 2 indicates that trace element accumulation processes and reservoirs can be of different orders
278 such that spatio-temporal structure models of sources and sinks, and transfer processes between them,
279 can be developed for a given area. The choice of study areas representing a variety of geological back-
280 grounds and evolution make approaches and obtained results transferable to other regions. Sandstone-
281 hosted uraniferous phosphates (area 13), shallow marine ooidic Fe ores (area 16), reduced glauconit-
282 ic/pyritic marine sandy sediments (areas 2 and 5) and felsic volcano-sedimentary basins (area 17) are
283 widespread geological environments worldwide and often share genetic and geochemical characteris-
284 tics. This is especially supported by striking similarities between the studies in Cretaceous and
285 Paleogene sediments (areas 2 and 5) exhibiting close analogies not only in geological situation and
286 development but also in As distribution and behaviour in spite of a time span of ~50 Ma between sedi-
287 ment deposition in both areas.

288

289 **3.2 Geodynamic model for large-scale natural As and U distribution in Germany**

290 Besides the major importance of the obtained results on a regional scale and global transferability
291 based on comparable conditions between single areas, more may be learned from general geochemical
292 comparison of all study areas and their distribution in space and time. Therefore, the impact of sedi-
293 ment provenance and the spatio-temporal development of Europe on geogenic As and U distribution
294 are evaluated in the following. Geochemical proxies are assessed to characterize the studied sedi-
295 ments' provenance and combine the results with the As and U accumulation processes derived in
296 earlier studies. Figure 3 illustrates a ternary plot of La-Th-Sc to deduce source rock geochemistry and
297 tectonic setting of the studied sediments.

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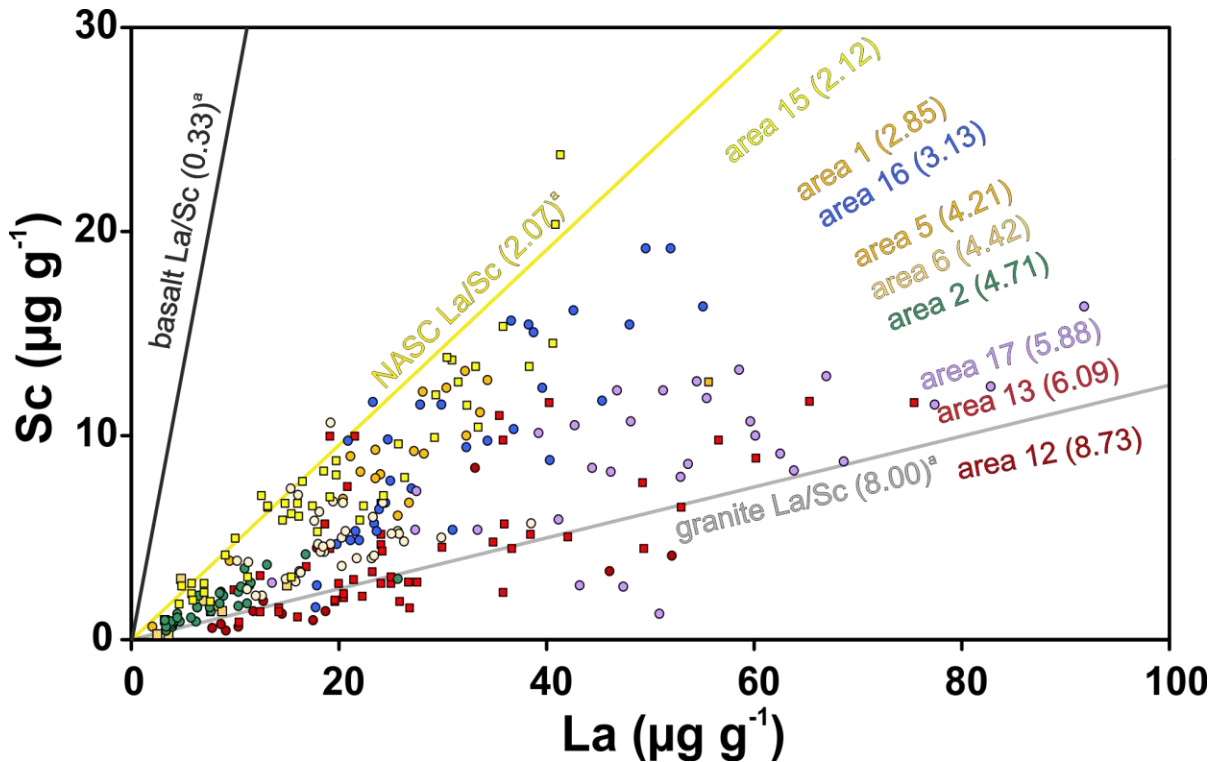
Fig. 3: La-Th-Sc plot of all studied sediment samples (cf. Fig. 1 for study area allocation). For comparison, plots of typical lithologies were implemented after ^aCondie (1993) and ^bCullers (1994). Furthermore, fields in the diagram after ^cBhatia and Crook (1986) indicate provenance rock tectonic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

307 Most studied sediments plot in a rather dense cloud near the La corner of the diagram. Regarding the
308 distal position of the samples from standard amphibolite, basalt and andesite (characterized by higher
309 contents of compatible Sc) and the proximity to granite (higher degree of incompatible La and Th), a
310 generally rather felsic provenance is obvious for all sediments (Fig. 3). Also in comparison to NASC,
311 the North American Shale Composite (representative of upper crustal sediments; e.g., Gromet et al.
312 1984), the majority of samples plot in the more felsic range and are in this respect rather comparable
313 to typical cratonic sandstone plotting within the data aggregation.

314 Concerning tectonic setting of the provenance sensu Bhatia and Crook (1986), most samples indicate
315 derivation from continental margins with an overlap to the field of continental island arcs (Fig. 3), thus
316 reflecting the tectonic configuration of Variscan central Europe as will be discussed later on. Sediment
317 origin from oceanic island arcs can be excluded which was expectable regarding the choice of study
318 areas.

319 To better differentiate between the single study areas with regard to geochemical provenance, a binary
320 plot of incompatible La vs. compatible Sc is presented in Fig. 4.

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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 ^aCondie (1993).

327 The observation of geochemical proxies indicating rather felsic provenance, also in comparison to
328 average upper crustal sediment (NASC), is supported by the binary plot (Fig. 4). In spite of partly
329 considerable scattering (R^2 of the nine data subsets: 0.11-0.72), differences between the single study
330 areas become evident. Upper Triassic sediments from areas 12 (La/Sc ratio derived from trendline
331 equation: 8.73) and 13 (6.09) as well as volcano-sedimentary basin filling from San Luis Potosí (area
332 17, 5.88) exhibit clearly more felsic provenance than marine sediments of Jurassic (area 16), Paleo-
333 gene (area 5), Cretaceous (area 2) and Lower Triassic (areas 1 and 6) age. Neogene sediments from the
334 southern German Molasse basin (area 15) document average La/Sc ratios very closely to the NASC
335 signature.

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

338 The following is hypothesized:

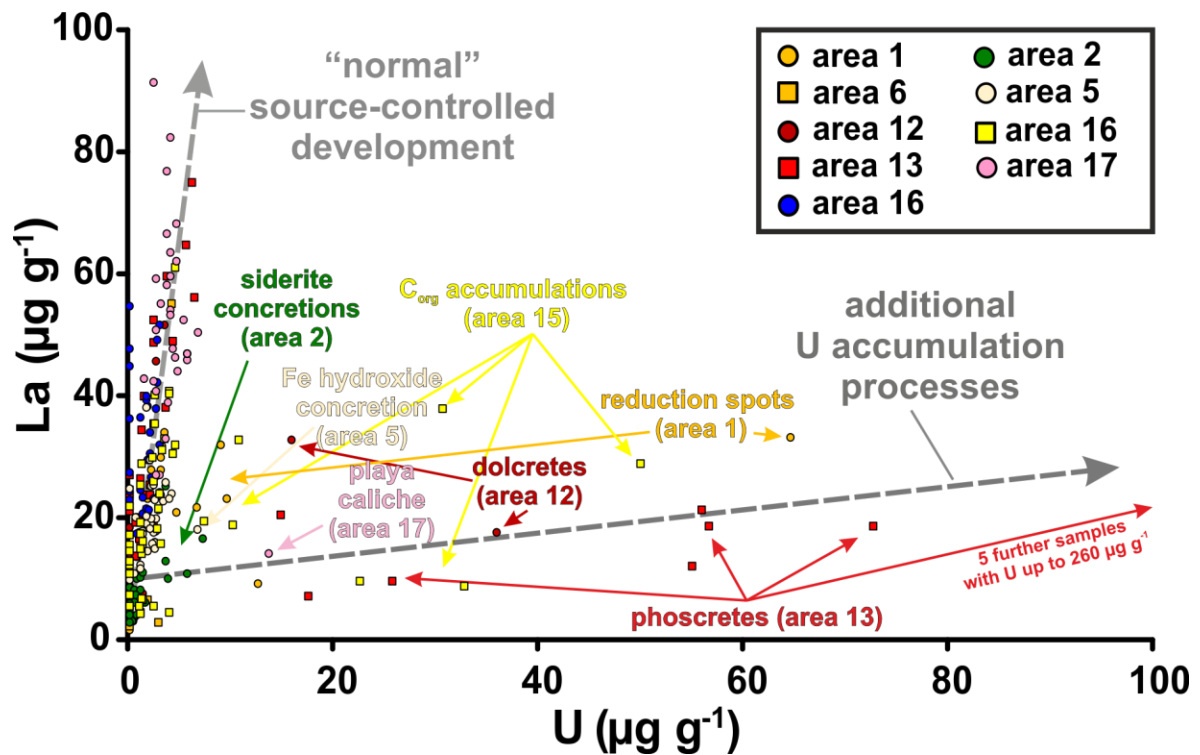
- 339 a) Sedimentary environments potentially fostering As enrichment require above-average (i.e.,
340 above NASC) felsic provenance to assure sufficient supply of the incompatible trace element.
- 341 b) Sedimentary environments potentially fostering U enrichment require highly felsic prove-
342 nance to assure sufficient supply of the (more) incompatible trace element, i.e. highly felsic
343 origin is a prerequisite for sedimentary systems to create both, high As *and* U. Of course, con-

344 ditions of redeposition, climate, hydrochemistry and microbiology (let alone anthropogenic
345 activity) control potential final groundwater concentrations.

346 c) Classical geochemical proxies like those presented here may serve as pre-diagnostic tools to
347 characterize geochemical provenance (and thus, primary trace element sources) of sedimentary
348 areas potentially affected by As and/or U.

349 In an effort to combine this approach and the previously discussed As/U accumulation processes, plots
350 of La vs. U and La vs. As are presented as Fig. 5 and Fig. 6, respectively.

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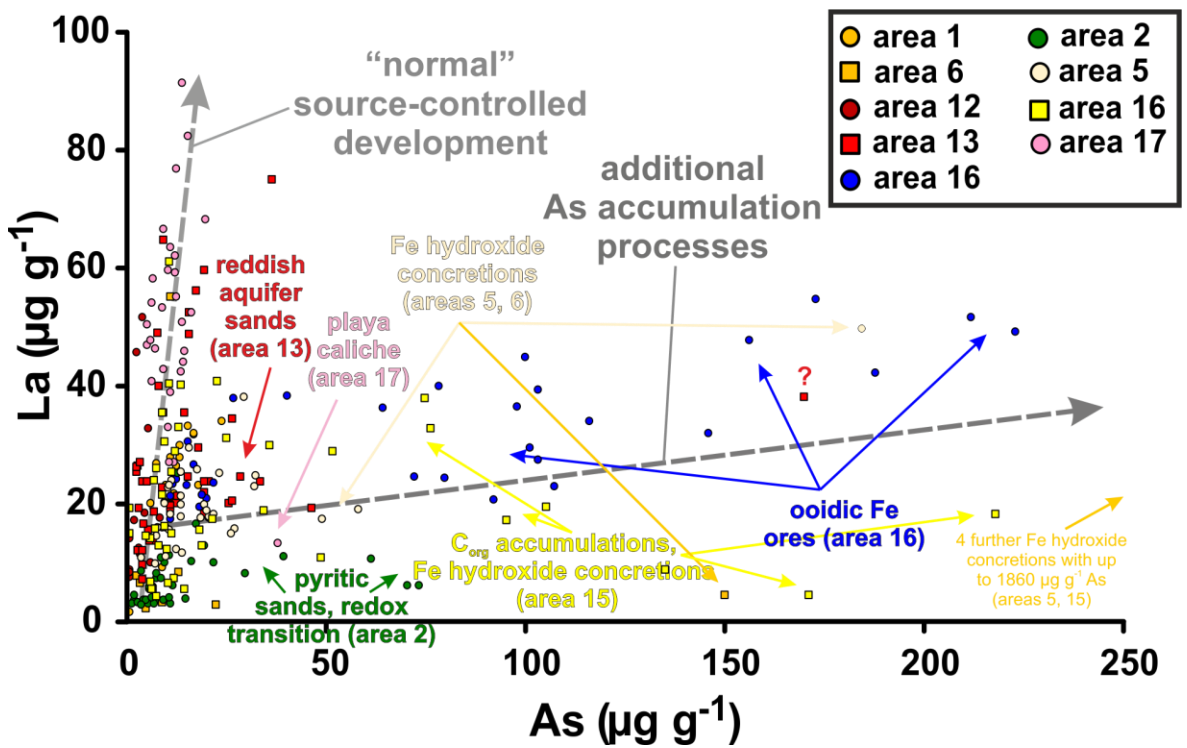
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Fig. 5: U vs. La scatter plot for all studied sediments (cf. Fig. 1 for study area allocation), and secondary U accumulation mechanisms in sediment basins (cf. Fig. 2 and chapter 1.3).

358 The majority of samples in Fig. 5 exhibit a development along a positively trending line interpreted to
359 represent “normal” source (i.e. provenance)-controlled behaviour. Here, common successive increase
360 of both incompatible trace elements is obvious. Offsets from this “background” development, i.e. excess
361 U, reflect additional sedimentary enrichment processes in the different areas. Slight accumulation
362 was found in siderite concretions within Cretaceous fine sands (area 2). Uranium sorption to the purest
363 Fe hydroxide concretion in oxidized sands of the Lower Rhine Embayment (area 5, this sample has the
364 singular highest As content (1860 µg g⁻¹) of all study area) was not able to accumulate more than 7.2
365 µg g⁻¹ U. This finding supports the hypothesis that a more felsic provenance is needed for sufficient U
366 supply – U availability was just too low in the Paleogene sediments such that not even this concretionary
367 best option for accumulation could be taken advantage of. Evaporative concentration accounts for

368 elevated U contents in relic playa lake caliches (area 17). Apatite precipitation from U-bearing
 369 groundwater on former playa carbonates resulted in high U contents in phoscretes (area 13), also the
 370 more proximal original dolcretes (area 12) show some U accumulation. Very localized reducing condi-
 371 tions lead to punctual U hot spots in Lower Triassic sandstone on Heligoland (area 1), this
 372 phenomenon is also known from e.g., Switzerland (Hofmann 1990, Burkhalter 1995). Uranium accu-
 373 mulation in Neogene sediments (area 15) is almost exclusively observed in postsedimentary, i.e.,
 374 Holocene, C_{org} -rich deposits like peat which successively concentrated U from groundwater.

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377 Fig. 6: As vs. La scatter plot for all studied sediments (cf. Fig. 1 for study area allocation), and secondary U
 378 accumulation mechanisms in sediment basins (cf. Fig. 2 and chapter 1.3).
 379

380 Similar observations can be made in the As vs. La plot (Fig. 6) – a provenance-driven “background”
 381 development is overlain by different additional As concentration processes occurring in the studied
 382 sediment basins: sorption to Fe hydroxide coatings of silicate aquifer material (areas 6 and 13), accu-
 383 mulation in ooidic Fe ores during condensed sedimentation (area 16), fixation in pyrite and subsequent
 384 redistribution to redox transition zones and Fe hydroxide concretions (areas 2 and 5), enrichment by
 385 evaporation in playa caliches (area 17), concentration by sorption to organic material and in Fe(III)
 386 concretions (area 15). Jurassic ooidic Fe ores (area 16) with high As values only yield U contents of
 387 $1.5 \mu\text{g g}^{-1}$ on average although depositional environment and potential host phases seem suitable for
 388 higher accumulation. Again, U availability in the sediment provenance is suggested to be the limiting
 389 factor for this phenomenon. Compared to the U-La plot (Fig. 5), the trend of “normal” source-
 390 controlled development between As and La for all samples appears less distinct. Obviously, the signa-

391 ture of the more incompatible U regarding geochemical provenance proxies is clearer. Moreover, addi-
 392 tional redistribution processes after sediment deposition (like paleo redox events) seem to
 393 preferentially fractionate As, thereby altering primary geochemical signals.

394 To pursue these observations and possibly further support the formulated hypotheses, the stratigraph-
 395 ical and spatial distribution of the study areas will be assessed in the following and set in relation to
 396 their sediment provenance areas. Figure 7 offers an overview of the study areas' stratigraphical situa-
 397 tion and the plate tectonic framework.

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Super-continents	ERA	PERIOD	AGE (Ma)
EURASIA/ AFRICA and others	CENO- ZOIC	NEOGENE	23.03 15
		PALEOGENE	5, 17
PANGAEA break-up ↑ ↓ growth ↑ GONDWANA and others	MESOZOIC	CRETACEOUS	65.05 ± 0.3 2
		JURASSIC	145.5 ± 4.0 16
		TRIASSIC	199.6 ± 0.6 12, 13
		PERMIAN	251.0 ± 0.4 1, 6
	PALEOZOIC	CARBONIFEROUS	299.0 ± 0.8
		DEVONIAN	359.2 ± 2.5
		SILURIAN	416.0 ± 2.8
		ORDOVICIAN	443.7 ± 1.5
CAMBRIAN	488.3 ± 1.7		

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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 Breitzkreuz (1998) is indicated.

407 The stratigraphical distribution of studied elevated sedimentary As in Germany reflects affected units
 408 ranging from Carboniferous to Neogene in age. A clustering of cases in Permo-Triassic is conspicuous
 409 which includes Germany's most significant As (and U) problem area in Northern Bavaria (areas 12,

410 13). Sediments from these periods often represent cratonic sandstones (cf. Fig. 3) derived from weath-
411 ering of the then young Variscan massifs. Surveys of groundwater U conducted so far identified the
412 Triassic as “hot spot” age for affected aquifers (Birke et al. 2010, Kurth 2010, HLUG 2008, LGL and
413 LfU 2007; cf. chapter 1.3). Likewise, an overview of As in German groundwater (Heinrichs and Udluft
414 1996) reports elevated concentrations mainly in Permo-Triassic aquifers. During that time, the for-
415 mation climax of the supercontinent Pangaea as a result of the collision between Laurasia and
416 Gondwana was reached (Bahlburg and Breitzkreuz 1998, Fig. 7). This process was accompanied by the
417 Variscan Orogeny representing a mountain-building event, relics of which are found today as e.g., the
418 Rhenish Massif, the Black Forest or the Bohemian Massif in Germany and neighbouring countries.
419 Denudation of the orogen and transport of resulting material to sediment basins started in the Upper
420 Carboniferous. Concluding from Fig. 7, only stratigraphies younger than that appear to be affected by
421 elevated As. Moreover, the upper limit of a stratigraphical “window” of sedimentary As occurrences
422 seems to be defined by the end of the Neogene period. Possible explanations for that must be sought in
423 the spatio-temporal geological development of Germany.

424 Figure 1 illustrates the spatial distribution of studied sedimentary As as well as Variscan terrains and
425 thick Quaternary overburden. It becomes evident that all known cases of elevated sedimentary As in
426 Germany are located south of the thick unconsolidated Quaternary cover governing geology and land-
427 scape of northern Germany (except for the Triassic rock island Heligoland, area 1, which is not
428 covered by Quaternary). These mostly Pleistocene glacial and periglacial deposits with main prove-
429 nance areas in northern and northeastern Europe (Henningesen and Katzung 2002) obviously did not
430 bring a significant As (or U) potential along. Not only would these observations explain the northern
431 boundary of As study areas (Fig. 1) but also raise expectations concerning better shallow groundwater
432 quality with respect to As and U in northern Germany. Indeed, Kunkel et al. (2004) characterized nat-
433 ural groundwater quality in Germany and found in an evaluation of a large As dataset (n=1661) from
434 sand and gravel aquifers of the North German Plain (widely identical with the area north of the red
435 line indicated in Fig. 1) 90th percentile values of 3.3-3.5 $\mu\text{g L}^{-1}$ As with hardly any single values above
436 10 $\mu\text{g L}^{-1}$ in different aquifer depth intervals of up to 50 m below ground surface. Supporting this in
437 their earlier survey, Heinrichs and Udluft (1996) do not report on geogenic groundwater concentra-
438 tions in exceedance of 10 $\mu\text{g L}^{-1}$ As from this area.

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

445 Another observation from Fig. 1 is the close spatial relation of most conducted sedimentary As and U
446 studies to Variscan terrains in Germany supporting a relation between Variscan geology and trace

447 element distribution as was already suspected from stratigraphy (Fig. 7). Differences between sedi-
448 mentary occurrence of As and U in the single studied areas in this work can be derived from the
449 distribution of Variscan granites and support the hypotheses on degree of provenance felsicity formu-
450 lated earlier: Upper Triassic sediments from northern Bavaria (areas 12, 13) derive from weathering of
451 the Bohemian Massif which belongs to the Moldanubian section of the European Variscides (like main
452 parts of Black Forest and Vosges) representing the most metamorphic part with abundant felsic intru-
453 sions (Krebs 1976, Bahlburg and Breitzkreuz 1998) while Cretaceous and Paleogene sediments (areas
454 2, 5) originate from the Rhenohercynian Variscan section with low degree of metamorphism and
455 widely absent granitic intrusions (Fig. 1). At first glance, it seems surprising that the Jurassic sedi-
456 ments (area 16), being located in direct vicinity to the Moldanubian granite-rich Black Forest and
457 Vosges (Fig. 1) do neither show highly felsic provenance (Fig. 4) nor elevated U potential (Fig. 5).
458 Nevertheless, the Moldanubian crystalline terrains did not serve as sediment provenance but were
459 submerged during the Middle Jurassic (Ziegler 1990), sediment (and Fe/As, but no U) input was ac-
460 complished from the Rhenish Massif (Sauer and Simon 1975) and thus, from the Rhenohercynian – a
461 provenance of lower felsicity.

462 To crosscheck this hypothesis, a short review of another basin that actually received its sedimentary
463 filling from weathering of the Black Forest was conducted. Within the range of this Moldanubian ter-
464 rain, only few rather small sedimentary basins filled with Upper Carboniferous to Permian material
465 fulfill this condition, the biggest of which is the one around Baden-Baden in the northern Black Forest
466 (Henningsen and Katzung 2002). Stefanian (Upper Carboniferous) partly C_{org}-rich arkoses and sand-
467 stones in that area, underlain by granite and derived from erosion of the proximal granitic young
468 Variscan mountains, host several sedimentary U anomalies prospected in the past, the most significant
469 of which is the deposit Müllenbach (Kneuper et al. 1977). The mineralization is of the roll-front type,
470 main U carriers are uraninite and coffinite, bulk U₃O₈ contents of several wt.% are known. Arsenic is
471 present in concentrations of up to 3000 µg g⁻¹, mainly as arsenopyrite. Kneuper et al. (1977) also
472 found a positive correlation between As and U in the sediments. The authors genetically suggest
473 common U and As precipitation from groundwater with trace elements primarily mobilized from
474 Black Forest granites. This development is thus very similar to the one described here for Triassic
475 phoscretes (area 13). Also Permian sediments in that basin partly show common enrichment of both U
476 and As (Plinninger and Thuro 1999). Hydrothermal U mineralizations within granites are known from
477 the southern Black Forest, e.g., near Menzenschwand. This site is the type locality of several second-
478 ary U-As minerals, one of which – Nielsbohrite [(KUO₂)₃(AsO₄)(OH)₄*H₂O] – was described by
479 Walenta et al. (2009). These studies clearly underline Black Forest granites' high source potential for
480 both U and As. The receiving sediment basins in the area are probably too small (in comparison to
481 e.g., the South German Keuper Basin) to account for significant postdepositional redistribution pro-
482 cesses and prominent groundwater As and U problems. Nevertheless, elevated U concentrations in
483 Black Forest mineral waters are known (Birke et al. 2010). Moreover, the thermal springs of Baden-

484 Baden, recharged by meteoric waters circulating in the regional granites, show high As concentrations
485 of 200 $\mu\text{g L}^{-1}$ on average; U presence is documented by U-bearing amorphous thermal Mn hydroxides
486 and opaline sinters (Rüde 1996). In consequence, this short overview of a second Moldanubian massif
487 fully supports the model of Variscan control over geogenic As and U distribution in Germany devel-
488 oped in the present work.

489 One exception among the existing studies of sedimentary As in Germany probably without Variscan
490 influence should be mentioned: Bayer (1997) states that partly high As concentrations (up to
491 1900 μg^{-1}) in Fe-rich sections of the Bavarian molasse basin, esp. Badenean sands (area 14 in Fig. 1),
492 originate, like the sediments themselves, from weathering of the Alpine Mountains; As is believed to
493 primarily derive from mineralized zones in the eastern Alps. Uranium concentrations are low in the Fe
494 concretions, Bayer (1997) detected $<1 \mu\text{g g}^{-1}$ U in all his samples. According to the genetic model
495 developed in the present work, this data argues for a primary trace element source of moderately high
496 felsicity not able to supply sufficient U for enrichment in sediments. This source indeed is likely to be
497 found in the eastern Alps which, in contrast to the central and western parts of the orogen, do not host
498 significant granitic intrusions (Gwinner 1971). Nevertheless, several occasions of elevated U are
499 known in groundwater and sediments from the range of the Miocene molasse basin (e.g. LGL and LfU
500 2007). An explanation for that can be given by another paleogeographical observation: after deposition
501 of the Badenean sands, sediment provenance changed for the eastern and northern parts of the basin.
502 During the subsequent Sarmatian and Pannonian, clastic material and groundwater supply were partly
503 accomplished from the Bohemian Massif (Unger 1989) – a provenance of high felsicity with proven
504 ability to produce U enrichment in associated sediment basins.

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

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

517

518 **4 Conclusions**

519 Geological evolution, expressed by geochemical proxies, can explain trace element distribution on
520 different temporal and spatial scales, and help understand and forecast the occurrence of actual and
521 potential groundwater quality problem areas. Trace element abundance was shown to directly reflect
522 supraregional and intra-basinal geological evolution. The distribution of areas with elevated As and U
523 in Germany is large-scale widely determined by Variscan and Quaternary geology. Geochemical sedi-
524 ment provenance controls elevated As (felsic provenance) and U (highly felsic provenance) supply to
525 sedimentary environments, whereby the different Variscan sections are decisive. Thus, magmatic geo-
526 chemistry based on incompatibility of U and As is the ultimate control of trace element supply to
527 sedimentary systems where subsequent intra-basinal processes of trace element accumulation, redistri-
528 bution and eventually remobilization to groundwater take place and create the present-day situation.

529 The present work contributes to a deeper understanding of the interplay between geological history
530 (magmatic and sedimentary), geochemistry, mineralogy, hydrogeology and hydrochemistry with re-
531 spect to potentially hazardous geogenic trace elements, focussing on the still little understood situation
532 in Germany. Increased comprehension of occurrence and behaviour of not only anthropogenic but also
533 natural contaminants on a global scale will be necessary in the future in view of growing awareness
534 regarding health impacts along with more stringent drinking water limitations, and continuously more
535 severe population pressure on water resources, especially under climate change conditions.

536
537

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547
548

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