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

2 and groundwater

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16

1415 Abstract

- 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 contibute 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

magmatic differentiation, geochemical proxies, sediment provenance, Variscides, accumula tion processes

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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 in the upper earth's crust (1.5-2 µg g⁻¹; Matschullat 1999, Taylor 1964: 1.8 µg g⁻¹ in the continental 43 crust). As can accumulate in rocks to concentrations several orders of magnitude higher than these 44 45 values. The metalloid's fate in the environment is controlled by the prevailing physico-chemical con-46 ditions 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 the the s, 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 carbonato 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 Rüde 2015).

Taylor (1964) cites the average uranium (U) abundance in the continental crust as $2.7 \ \mu g \ g^{-1}$. Thereby, 61 generally higher concentrations are detected in felsic rocks (granite average: 4.8 µg g⁻¹ U) compared to 62 63 mafic lithologies (basalt average: 0.6 µg 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

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. 73 2009). Consequently, drinking water threshold values were broadly lowered in the 1990ies, mostly 74 down to 10 μ 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 occurences in Mexico is given by Armienta and Sego-85 via (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 µg 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 deseases), 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. ~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 µg L⁻¹, German 95 legislation decided on a fixed limitation of 10 µg 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 µg 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 Acharyva 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 µg 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 $\mu g g^{-1}$ As) by Goldberg et al. (1995). Mertens (2000) found an average of 108 $\mu g g^{-1}$ 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 µg L⁻¹ As in groundwater, attributable to mobilization via py-
- 144 rite oxidation, probably triggered by anthropogenic NO_3^- input.



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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.

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 μ 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 μ g g⁻¹. For comparison: the Clarke value for bituminous coal is 9.0 \pm 0.8 μ 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 µg 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 µg g⁻¹ As on average (Clarke value for lignite: 7.4 ± 1.4 µg 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 µg g⁻¹ (Wagner 1999). Heinrichs and Udluft (1999) found that the distribution of extensively elevated As concentrations in Middle 168 169 Franconian (northern Bavaria, area 13) groundwater (up to 150 µg 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 μ g g⁻¹ As that can locally lead to elevated groundwater concentrations when reducing conditions occur (Bayer and 173 174 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 synge-177 netic 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 µg L⁻¹ U in 908 German bottled water 186 samples (maximum: 16 µg 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 µg L⁻¹ U in 2.7% of 965 analyzed wells 189 with a maximum concentration of 86 µg 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 refered to as "active arkoses" (Abele et al. 1962). These syndi-194 agenetic carbonate fluorapatite inclusions in the Keuper aquifer sandstones contain up to 1070 $\mu g g^{-1}$ U and were found to show structurally $(CO_3^{2-}$ substitution in the crystal structure) and radiatively (α -195 196 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 μ 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 µg 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 Pomera-207 nia/NE Germany (van Berk and Fu 2016) and southern Bavaria (area 15, Banning et al. 2013b), 208 drinking water treatment in North Rhine-Westphalia (Banning et al. 2017) or managed aquifer re-209 charge on the island of Heligoland (area 1, Meurer and Banning 2018). The latter is basically a 210 Buntsandstein rock in the North Sea, uplifted by salt tectonics. In the otherwise widely homogeneous 211 red sandstones, Cu- and U-bearing cavity fillings and "fish eyes" – round reduction spots, partly with a 212 black U-rich centre - can be found. They represent the source of geogenic U mainly bound in the car-213 bonate fraction. On Heligoland, brackish water with partly elevated U concentrations is treated via 214 reverse osmosis for use as drinking water. Rain water is irrigated to recharge the aquifer, an artificial 215 accumulation of Buntsandstein debris. The fresh water dissolves part of the geogenic U pool in the 216 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.

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230 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.

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 consoli-
			dated 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

239 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 240 241 a polyethylene vial and irradiated along with flux wires at a thermal neutron flux of 7*1012 n cm⁻² s⁻¹. 242 ²⁴Na 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 ⁶⁰Co 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 μ g g⁻¹ for La, U and As; 0.2 $\mu g g^{-1}$ for Th and 0.1 $\mu g g^{-1}$ for Sc. For quality control, flux wires and control standards were used to 246 247 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.

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 Reves 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).



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. (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 sed-287 iment deposition in both areas.

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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.



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.

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 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.

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.



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), Paleogene (area 5), Cretaceous (area 2) and Lower Triassic (areas 1 and 6) age. Neogene sediments from the 333 334 southern German Molasse basin (area 15) document average La/Sc ratios very closely to the NASC 335 signature.

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

338 The following is hypothesized:

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- 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 prove nance 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, con-

- ditions of redeposition, climate, hydrochemistry and microbiology (let alone anthropogenic
 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 sedimen 348 tary 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 Fig. 5 and Fig. 6, respectively.
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357 **U** (µg g ') **U** (µg g ') **S S S 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. ex-361 cess 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 μ g g⁻¹) of all study area) was not able to accumulate more than 7.2 365 $\mu g g^{-1} U$. 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 concretion-367 ary 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 postsedimentary, i.e.,
Holocene, C_{org}-rich deposits like peat which successively concentrated U from groundwater.

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Fig. 6: As 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).

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 $1.5 \,\mu g \, g^{-1}$ 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 signa391 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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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) af-404 ter ICS (2009). Additionally, major crustal development (supercontinents, left side) after Bahlburg and 405 Breitkreuz (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. capter 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 Breitkreuz 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 (Henningsen 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 line indicated in Fig. 1) 90th percentile values of 3.3-3.5 µg L⁻¹ As with hardly any single values above 435 436 10 µg 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 μ g L⁻¹ As from this area.

The organisation foodwatch collected and published drinking water U data from German federal stateauthorities (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
- Rhine-Westphalia and Saarland are quantitatively below 10 μg L⁻¹ U (2 out of 427 samples in Mecklenburg-Western Pomerania were above that limit) while southern federal states generally exhibit

444 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 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 Breitkreuz 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 Corg-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 BadenBaden, 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.

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 $<1 \ \mu g \ g^{-1} U$ 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.

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, 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 ans 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 sed-524 iment 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.

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.

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