

ON POSSIBLE ORIGIN OF BACKGROUND CONTENTS OF HEAVY METALS AND METALLOIDS IN THE SUBSURFACE PENNSYLVANIAN TÉSENY METASANDSTONES, SW HUNGARY

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Abstract: Potentially toxic trace elements such as chromium, cobalt, arsenic and antimony exist in many sediments and sedimentary rocks, and therefore require an understanding of their occurrence, distribution and accumulation in the geologic environment. Ten trace elements (Sc, Cr, Co, Rb, Cs, Hf, Th, U, As and Sb) were quantified by neutron activation analysis in drill core samples comprising medium to very coarse-grained sandstones from the Pennsylvanian molasse Tésény Metasandstone Formation (TMF), SW Hungary. The results reveal a large range of the local background levels of these trace elemental concentrations. With regard to the toxic heavy metals and metalloids, the total Cr concentrations in the sandstone samples have a range of 15–150 mg/kg with a median of 47 mg/kg. Cobalt is present in the range of 7–19 mg/kg (median 9 mg/kg). Arsenic and antimony concentrations vary between 2 and 40 mg/kg (median 5 mg/kg) and between 0.4 and 2.5 mg/kg (median 0.8 mg/kg), respectively. Trace elemental geochemistry of the samples reflects the immature petrographic composition of the TMF sandstones, corresponding to a felsic source area, and the presence of abundant illite±muscovite. Additionally, the relatively enhanced As and Sb contents in some samples could be related to hydrothermal activity in the region. Trace elemental concentrations of the TMF samples are comparable to those of world-average siliciclastic sedimentary rocks indicating that the potentially toxic heavy metal contents of the TMF do not significantly affect the groundwater quality in the region. Water-rock interactions at the marginal area of the Drava depression, however, may contribute some metalloids to groundwaters if the hydrogeochemical conditions are favourable for their release into solution.

Keywords: sandstone, heavy metals, metalloids, local natural background, sulfide minerals, vein system

1. INTRODUCTION

The contamination of sedimentary aquifer systems by potentially toxic metals and metalloids is recognized as a global environmental problem (Matschullat, 2000; Filella et al., 2002; Appelo & Postma, 2009; Rowland et al., 2011). Many environmental geochemists have recognized correlations between the geographic distribution of diseases and the presence of toxic elements in the geologic environment (Filella et al., 2002; Smedley & Kinniburgh, 2002; Varsányi & Ó.Kovács, 2006). Therefore, quantification of trace elements, including certain toxic elements, in sedimentary aquifers and associated rocks is very essential to elucidate the variability of natural concentrations, and to establish

the environmental levels of various elements, in order to outline areas of potential toxicity. Thus, numerous publications have been dedicated to chemical behaviour of potentially toxic heavy metals and metalloids in natural systems and in industrial areas (e.g. Giurginca et al., 2010; Gjoka et al., 2010; Horiacu et al., 2010; Nagy-Korodi et al., 2011).

In the last few years, a countrywide geochemical map of surface and near surface rocks was prepared by the Geological Institute of Hungary (Fügedi, 2004; Gondi et al., 2004; Fügedi et al., 2007). Additionally, the geochemical background levels of different elements and the extent of accumulation of toxic elements were also established (Fügedi, 2004; Fügedi et al., 2007). Unfortunately, however, very little is known about the origin of such

elements in the shallow subsurface rocks in southern Transdanubia, SW Hungary, forming the marginal area of the Drava depression (Figs. 1 and 2) where slightly elevated levels of As in its groundwaters were also detected (Gondi et al., 2004; Ujević et al., 2010).

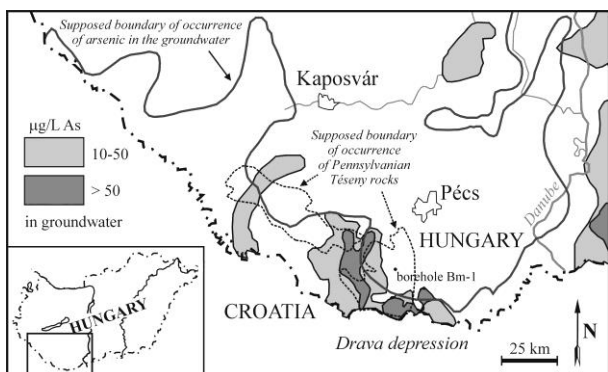


Figure 1. The map of the arsenic groundwater occurrences in SW Hungary modified after Gondi et al. (2004) with geological data of Kassai (1983)

The studied siliciclastic metasedimentary rocks belong to the coal-bearing Pennsylvanian continental sequence called Téseny Metasandstone Formation (TMF; based on the renewed nomenclature of the Palaeozoic Subcommittee of the Stratigraphic Commission of Hungary, 2011), occurring subsurface in the area between the Mecsek and Villány Mountains (Jámbor, 1969; Hetényi & Ravaszné Baranyai, 1976; Kassai, 1983; Varga et al., 2007). The TMF rocks are mainly impermeable, and therefore, groundwater flows in the fractures, joints and cleavage planes. On the other hand, the TMF is generally overlain by Pannonian (Upper Miocene and Pliocene) and Pleistocene siliciclastic sediments (Jámbor, 1969; Hetényi & Ravaszné Baranyai, 1976), including important aquifer systems.

The TMF consists of terrigenous clastics (anthracitic slate, metasandstone, and metaconglomerate) that were deposited in fluvial and alluvial swamp environments; its total thickness is estimated to be about 1500 m (Jámbor, 1969; Hetényi & Ravaszné Baranyai, 1976; Varga et al., 2007).

The objectives of the present study are to characterize the trace element chemistry (Sc, Cr, Co, Rb, Cs, Hf, Th, U, As and Sb) of the TMF using neutron activation analysis, to determine the local background contents for a number of potentially toxic trace elements such as heavy metals and metalloids and to discuss their origin in a regional framework.

2. MATERIALS AND METHODS

A total of seventeen medium to very coarse-grained sandstone drill core samples from three

exploration boreholes (Bogádmindszent Bm-1, Diósvizlő Dv-3 and Siklósbodony Sb-1) penetrating TMF rocks were collected for the present study (Fig. 2). Chemical analysis of trace elements were performed by neutron activation analysis (NAA) at the XRAL Laboratories (Accredited Laboratory No. 456, SGS Geochemical Laboratories), Canada. Detection limits for the trace elements discussed in this paper are the follows (in mg/kg): Scandium (1), Chromium (10), Cobalt (5), Rubidium (30), Cesium (3), Hafnium (1), Thorium (0.5), Uranium (0.5), Arsenic (2), Antimony (0.2). As a quality control, duplicate analyses were performed on selected samples.

3. RESULTS AND DISCUSSION

3.1. Total concentrations of selected trace elements in the studied samples

The results of the NAA analysis and summary statistics for the analyzed elements are presented in table 1. The median value is independent of outliers; therefore, it is used as the preferred statistical parameter instead of the arithmetic mean in this study.

In the TMF sandstone samples, Sc is present in the range of 2–12 mg/kg with a median value of 6 mg/kg. Chromium, a potential health hazard, is detected in all samples at levels of 15–150 mg/kg. The TMF samples have median Cr content of 47 mg/kg. Cobalt, a certain toxic heavy metal, is only detected in eight of the samples studied, and it is present in the range of 7–19 mg/kg (median 9 mg/kg). Rubidium contents vary between 38 and 166 mg/kg (median 110 mg/kg). Cesium varies between 4 and 26 mg/kg (median 8 mg/kg) in all but one sample. Hafnium is present in the range of 2–9 mg/kg (median 3 mg/kg), while Th and U vary between 5.7 and 15.0 mg/kg (median 8.0 mg/kg), and between 1.3 and 5.6 mg/kg (median 2.4 mg/kg), respectively. With regard to the metalloids that cause chronic toxicological effects, arsenic shows a high variability. Its concentrations range from 2 to 40 mg/kg with a median of 5 mg/kg, while Sb levels range from 0.4 to 2.5 mg/kg with a median of 0.8 mg/kg.

3.2. Trace element content versus reference values for geochemical background

The relative abundance of the elements studied in different terrestrial systems is given in table 2. Additionally, the chemical data acquired from the TMF of different boreholes mentioned above are normalized to the upper continental crust (UCC) composition (McLennan, 2001), and these normalized ratios are shown in figure 3.

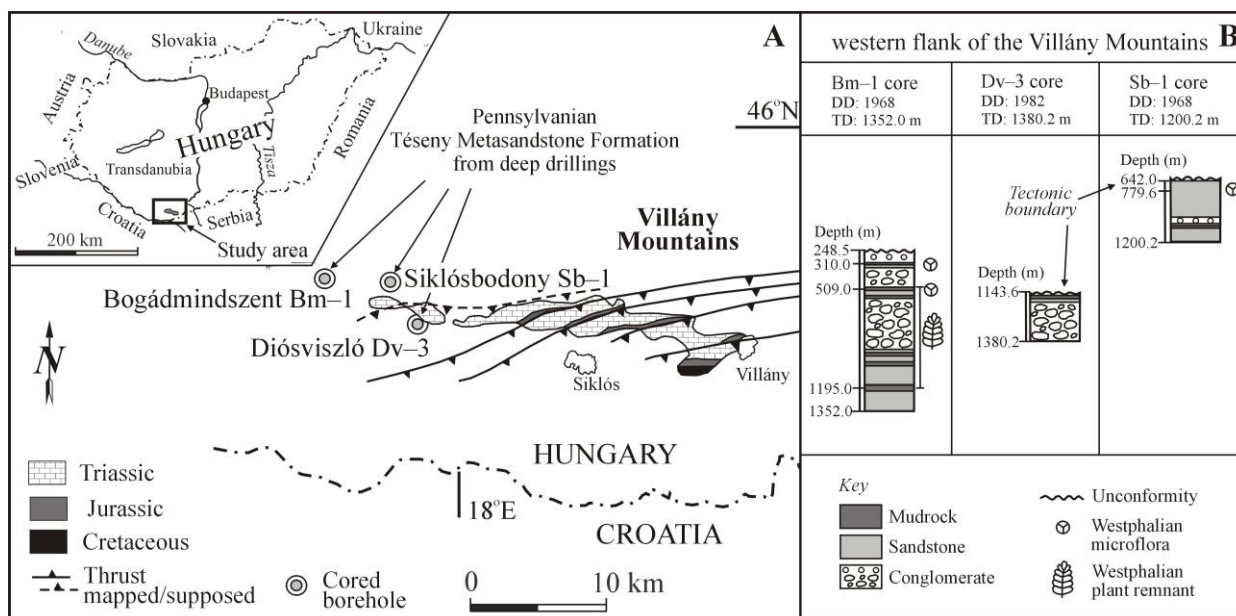


Figure 2. A) Simplified geologic map of the Villány area (S Transdanubia, Hungary) showing the localities where samples were collected for this study. B) Schematic lithologic logs of the boreholes, showing the stratigraphic relationships of the cores studied and the position of the investigated section within the hole. Modified after Varga et al. (2007). DD = date of drilling; TD = total depth below the surface. *Note:* Top of the TMF is at a depth of ~40–50 m below the surface near the village of Téseny (not shown)

Table 1

Elemental concentrations (in mg/kg) and descriptive basic statistics of the trace element contents in the TMF sandstone samples. Blank fields indicate that the element is not present above minimum limit of detection.

	Sc	Cr	Co	Rb	Cs	Hf	Th	U	As	Sb
Bm-1/2	3	20		150	4	2	9	2	3	0.5
Bm-1/5	8	34	7	85		4	6	2	2	0.4
Bm-1/6	2	15		110	4	2	7	2	3	0.5
Dv-3/1	12	150	9	160	12	9	15	4	20	1.4
Dv-3/2	5	47	9	127	14	3	10	4	40	0.7
Dv-3/3	5	35		38	8	2	7	2	5	1.0
Dv-3/4	11	87	10	66	10	3	13	2	10	1.1
Dv-3/5	6	27		81	8	2	7	3	3	0.8
Dv-3/6	5	30		115	7	3	6	3	8	0.6
Dv-3/7	6	58		127	17	3	10	2	5	2.3
Dv-3/8	6	49		139	26	3	10	2	3	1.5
Dv-3/9	5	29		108	26	2	7	1	3	0.8
Dv-3/10	7	63		98	7	4	11	2	21	2.5
Dv-3/11	10	61	9	166	25	4	8	3	15	1.6
Sb-1/4	11	51	19	60	5	3	6	3	2	0.7
Sb-1/5	9	34	12	120	8	3	6	6	24	1.4
Sb-1/6	7	47	8	64	4	3	8	2	5	0.6
minimum	2	15	7	38	4	2	6	1	2	0.4
maximum	12	150	19	166	26	9	15	6	40	2.5
range	10	135	12	128	22	7	9	5	38	2.1
mean	7	49	10	107	12	3	9	3	10	1.1
standard deviation	2.9	31.6	3.8	37.0	7.9	1.6	2.6	1.1	10.6	0.6
median	6	47	9	110	8	3	8	2	5	0.8

Table 2

Typical elemental concentrations (in mg/kg) for the upper continental crust (UCC) and in different types of siliciclastic sedimentary rocks together with the geochemical backgrounds of the silicate and carbonate rock covered catchment areas in the Mecsek and Villány Mts. (SW Hungary)

Material*	Sc	Cr	Co	Rb	Cs	Hf	Th	U	As	Sb
UCC (1)	7	35	11.6	110	5.8		10.3	2.5	2.0	0.31
UCC (2)	13.6	83	17	112	4.6	5.8	10.7	2.8	1.5	0.2
UCC (3)	14	92	17.3	84	4.9	5.3	10.5	2.7	4.8	0.4
Shales	15–19.5	104–127	20–26	125–163	5.2–6.0	4.6–6.6	12.3–14.6	2.9	3–13	1–2
Sandstones	2.0	30	2.5	25		3.1	4.0	1.1	0.5–4.1	
Greywackes	14–16	75–88	15–20	72–90	2.2	3.5–3.8	8.8–9.0	1.7–2.0		
Background (1)		19	8.2						5.3	0.38
Background (2)		21	8						6.6	0.5

*UCC values were used from (1) Wedepohl (1995), (2) McLennan (2001) and (3) Rudnick & Gao (2003); shale, sandstone and greywacke data come from Condie (1993), Wedepohl (1995), Matschullat (2000), McLennan (2001), Filella et al. (2002) and Smedley & Kinniburgh (2002); additionally, background data for (1) silicate and (2) carbonate rock covered catchment areas come from Fügedi et al. (2007)

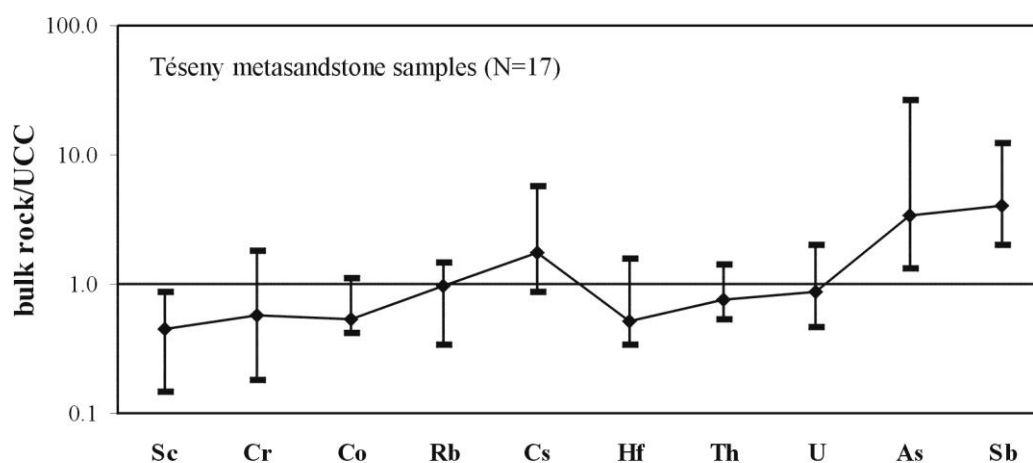


Figure 3. Upper continental crust (UCC)-normalized (McLennan, 2001) distribution of trace elements for the TMF sandstone samples. The bar represents minimum–maximum range, the diamond represents the median

Compared to the UCC (McLennan, 2001), the TMF sandstone samples are depleted in transition metals (TTEs), including Sc, Cr and Co, although variations are broad (Fig. 3). With respect to the large ion lithophile elements (LILEs), the samples have similar Rb contents and they are slightly enriched in Cs relative to the UCC. The concentrations of the high field strength elements (HFSEs) such as Hf, Th and U are generally lower in the sandstone samples compared with those of the UCC (McLennan, 2001). On the other hand, the samples are significantly enriched in As and Sb (Fig. 3).

Concentrations of trace metals, including toxic elements such as Cr and Co, in the sandstone samples are generally within the normal global ranges represented by the different UCC compositions (Wedepohl, 1995; McLennan, 2001; Rudnick & Gao, 2003). Additionally, these values are comparable to world-average siliciclastic sedimentary rock TTE,

LILE and HFSE concentrations (Tab. 2). Although the TMF samples are slightly enriched in trace metals (except for Hf) relative to the average chemical composition of Phanerozoic cratonic sandstones (Condie, 1993), these differences are probably due to the quartz dilution effect. The immature TMF sandstone samples, which have a median SiO₂ content of 78.9 wt% (Varga et al., 2007), have higher trace element concentrations than more mature cratonic sandstones (SiO₂ content of 91.5 wt%; Condie, 1993), because of their lower detrital quartz contents.

The concentration of As in sedimentary rocks is typically in the range of 5–10 mg/kg (Smedley & Kinniburgh, 2002), i.e. slightly above average terrestrial abundance represented by the upper continental crust composition (Wedepohl, 1995; McLennan, 2001; Rudnick & Gao, 2003). Sands and sandstones tend to have the lowest concentrations, reflecting the low metalloid contents of their dominant

minerals: quartz and feldspars. Average sandstone As concentrations are around 4 mg/kg (Smedley & Kinniburgh, 2002), although other work (Matschullat, 2000) gave a lower average value of 0.5–1.0 mg/kg (Tab. 2). The concentration of Sb in sedimentary rocks is generally in the range of 0.2–2 mg/kg (Filella et al., 2002). In TMF subsurface rocks, elevated As and Sb contents (up to 40 and 2.5 mg/kg, respectively) in some samples reflect heterogeneous distribution of metalloid-bearing phases. However, none of the samples shows anomalous high local background concentrations of naturally-occurring As and Sb (Tab. 1).

3.3. Origin of local background

Many studies have noted that Sc, Cr, Cs, Hf and Th are least affected by sedimentary processes, and they are transferred dominantly into the clastic sedimentary record during continental erosion (Taylor & McLennan, 1985; Condie, 1993; McLennan, 2001). Scandium, Cr, Co, Hf and Th are generally immobile under surface conditions (Taylor & McLennan, 1985). Therefore, these elements inherit the characteristic features of their source areas, and they are particularly useful indicators of the provenance of siliciclastic sedimentary rocks (Cullers, 1995; Bauluz et al., 2000; Lee, 2002). On the other hand, the Cr, Hf, Th and U contents of sandstones are also affected by heavy mineral fractionation (e.g. chromite, zircon and monazite; Bauluz et al., 2000; McLennan, 2001; Lee, 2002). In general, Rb and Cs concentrations in many siliciclastic sedimentary rocks reflect the K-bearing mineral content, such as K-feldspar, muscovite and illite (Taylor & McLennan, 1985; McLennan, 2001; Lee, 2002). Naturally elevated concentrations of As and Sb in sedimentary rocks are either related to sulfide minerals (e.g. arsenopyrite, stibnite and pyrite), or associated with high metalloid contents in organic matter, as well as in Fe oxides and oxyhydroxides that form coatings on mineral grains (Matschullat, 2000; Filella et al., 2002; Smedley & Kinniburgh, 2002).

Previous petrological and geochemical studies have shown that the TMF sandstones are poorly to moderately sorted litharenite and arkose. They are composed of variable amounts of quartz, feldspar, micas, chlorite, clays, Fe oxides and lithic grains such as quartz-rich metamorphic, acidic to intermediate volcanic, granitoid and siliciclastic rock fragments (Hetényi & Ravaszné Baranyai, 1976; Varga & Szakmány, 2004; Varga et al., 2007). The ubiquitous depletion of compatible elements such as Sc, Cr and Co together with the relatively low HFSE contents

indicates a felsic source area of the TMF (Fig. 3). The relatively high medians of Rb and Cs in this formation reflect the presence of abundant detrital muscovite and a high proportion of illite±muscovite in the clay-mineral assemblage (Varga & Szakmány, 2004; Varga et al., 2007; Varga, 2009).

On the other hand, petrographic features of some sandstone samples reflect extensive hydrothermal alteration with concomitant pyritization (Varga & Szakmány, 2004). Therefore, the possible source of As and Sb could be the sulfide minerals contained in these rocks (Fig. 4). In addition to the hydrothermal sulfide indications, aplite dykes (quartz + K-feldspar ± chlorite veins) also occur in the rock body (Jámbor, 1969; Hetényi & Ravaszné Baranyai, 1976). Furthermore, a well-developed fracture network filled by dominantly silicate minerals (e.g. K-feldspar, quartz, epidote, chlorite) and, subsequently, carbonates (± quartz) can be found in the drill core TMF samples (Fig. 5). Occasionally, opaque grains (pyrite?) also occur in the silicate veins.

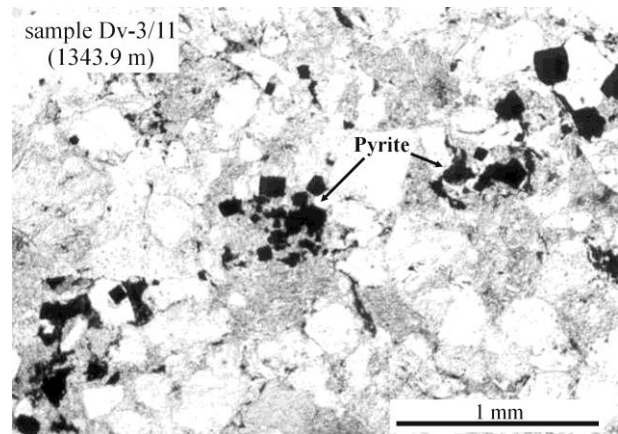


Figure 4. Petrographic evidence for pyritization (thin section photomicrograph, 1N)

Aplite dykes together with silicate and quartz-carbonate veins are also documented in the neighbouring polymetamorphic rock body of the Baksa Gneiss Complex, SW Hungary (Fintor et al., 2009, 2010, 2011; Fintor, 2011). Detailed investigation of Ca-Al silicate vein network revealed a characteristic diopside → epidote ± clinozoisite → sphalerite → albite ± K-feldspar → chlorite ± adularia ± prehnite → pyrite → calcite fracture-filling mineral succession (Fintor et al., 2010, 2011). These veins contain only minor amounts of pyrite; chalcopyrite and sphalerite grew sporadically in nonore minerals, like epidote, diopside, chlorite, quartz and calcite. Nevertheless, pyrite grains show significant As content that varies between 330 and 2830 mg/kg. According to the results of Fintor et al. (2011), high trace element content of pyrite crystals together with

their Co/Ni ratio approximately 1–5 support a postmagmatic hydrothermal origin of the veins. Additionally, Fintor et al. (2009) and Fintor (2011) proved that there was a paleohydrological communication between the crystalline basement and the Pennsylvanian TMF sedimentary rocks during the cementation phase resulted in quartz-carbonate veins.

The petrographic similarities of the aforementioned Ca-Al silicate vein systems in the TMF with those that are characteristic in the case of the neighbouring Baksa Gneiss Complex indicate that further research would be useful to reveal probable genetic relationships between them.

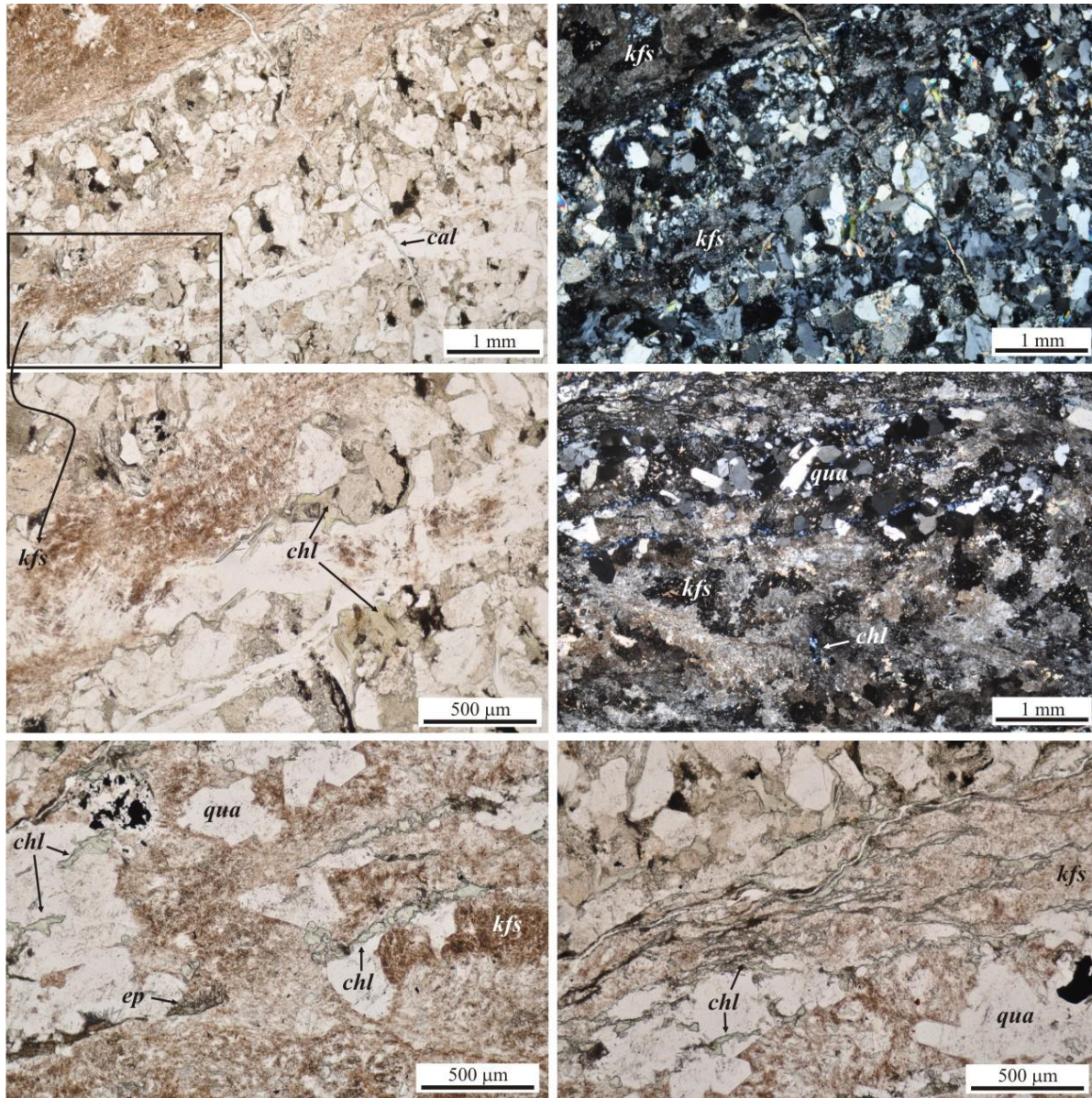


Figure 5. Crosscutting vein network in the TMF sandstone sample, drill core Bogádmindszent Bm-1, 1062.1–1062.3 m (kfs: K-feldspar; chl: chlorite; cal: calcite; qua: quartz; ep: epidote); collection of the Geological Institute of Hungary

3.4. Environmental significance of bedrocks with As-bearing pyrite in the study area

Both As and Sb are considered to be toxic in the environment at low levels (Matschullat, 2000; Filella et al., 2002; Smedley & Kinniburgh, 2002; Smedley et al., 2005). Furthermore, the oxidation of As-bearing pyrite is regarded as an important process

that supplies As into groundwater systems (Smedley & Kinniburgh, 2002; Appelo & Postma, 2009).

The most probable groundwater As sources in the Pannonian Basin are deeper sediments from the Middle and Upper Pleistocene (Varsányi & Ó.Kovács, 2006; Ujević et al., 2010; Rowland et al., 2011). In the Drava depression, the spatial distribution of the total As concentrations is not homogenous (Ujević et al.,

2010 and references therein). Reductive dissolution of Fe oxides, desorption of As from Fe oxides and/or clay minerals as well as competition for the sorption sites with organic matter and phosphate could be the principal mechanisms that control As mobilization. In addition, water residence time and different water use practices can also influence As concentrations in the groundwater (Ujević et al., 2010). However, a few wells (Drava aquifer, Vinogradi well field) with high As concentrations exhibit higher SO_4^{2-} concentrations which might be related to As-rich pyrite oxidation (Ujević et al., 2010 and references therein).

Aquifer recharge in the Drava depression is dominantly influenced by infiltration of meteoric water (Ujević et al., 2010) which is commonly very dilute, oxidizing, saturated with CO_2 and is thus potentially acidic in nature (Worden & Burley, 2003). According to the results of Worden & Burley (2003), basin-scale water flow can take place at any stage during the evolution of a sedimentary basin. In the early stages of basin formation large-scale water flow is usually driven by topographic head which is well documented from continental basins bounded by mountain ranges where groundwater influx can penetrate for kilometres into sedimentary sequences.

Erosional unconformities allow meteoric water influx at the basin margins (Worden & Burley, 2003); therefore, in theory, water-rock interactions at the marginal area of the Drava depression could contribute some metalloids to groundwater bodies if the geochemical and hydrogeological conditions are favourable for their release into solution. Nevertheless, a better comprehension of the local and regional factors responsible for the As enrichment in groundwater is necessary and will be the aim of future research.

4. CONCLUSIONS

Trace elemental geochemistry of the Pennsylvanian Téseny Metasandstone Formation (Hungary) deposited in fluvial and alluvial swamp environments reveals a large range of the background levels of trace metal and metalloid concentrations. With regard to the certain toxic heavy metals and metalloids, Cr, Co, As and Sb contents range from 15 to 150 mg/kg (median 47 mg/kg), from 7 to 19 mg/kg (median 9 mg/kg), from 2 to 40 mg/kg (median 5 mg/kg), and from 0.4 to 2.5 mg/kg (median 0.8 mg/kg), respectively. These concentrations are within the normal global ranges; however, some TMF samples have naturally elevated As and Sb contents reflecting hydrothermally altered, pyritized rocks. Our results indicate that the potentially toxic metalloid

content of the TMF may affect the groundwater quality of the study area if the hydrogeochemical conditions are favourable.

ACKNOWLEDGEMENTS

The Mecsek Ore Environment Co. (Pécs, Hungary) made the core samples available for study. This research has been supported by the Hungarian Scientific Research Found (OTKA; No. PD 83511), and it was additionally supported by the János Bolyai Research Scholarship of the HAS (AV). Valuable comments of the two anonymous reviewers are highly appreciated.

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