# Provenance and early diagenetic processes of the Ordovician Šárka Formation at Praha – Červený vrch Hill (Barrandian, Czech Republic)

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A bstract. Shales and siliceous nodules from Praha – Červený vrch Hill (Middle Ordovician, Šárka Formation, Barrandian area) were studied by chemical and X-ray phase analyses as well as by K-Ar age dating to specify their formation and provenance. White micas occurring as detrital components within the shales of the Šárka Formation reveal a Neoproterozoic (Cadomian) K-Ar age ( $599 \pm 12$  Ma) of the source rocks. The enrichment of heavy rare earth elements (HREE) over light rare earth elements (LREE), high Th/U ratios, and a distinct kaolinite content in the shales of the Šárka Formation point to strong chemical weathering of the source area in pre-Middle Ordovician times. Major element data indicate a passive margin setting for these shales, whereas trace element data and discriminant function analysis display the inherited island arc signature of the Neoproterozoic basement. Very low sulphide sulphur (S<sub>pyrite</sub>) and organic carbon (C<sub>org</sub>) contents as well as the depletion in Fe and Mn are interpreted as a tracer for oxic bottom-water conditions during deposition and transport of these elements by bottom currents. The growth of the siliceous nodules is supposed to be connected with the replacement of former sediment by SiO<sub>2</sub> and with leaching of most elements simultaneously with the enrichment in Mn, Ca, Co, Pb, Y and HREE.

Key words: Middle Ordovician, Šárka Formation, diagenesis, clastic micas, Prague Basin

### Introduction

In fine-grained clastic sediments, geochemical methods provide decisive information about their provenance and formation history. The chemical composition of such sediments is controlled by interaction of provenance, weathering, transport, deposition and diagenetic processes (Rollinson 1993, Johnsson 1993). The REE are considered to be immobile during weathering, hydrothermal overprint and low-grade metamorphism. Together with immobile trace elements, such as Th, Sc, Cr, Zr, Co, they reflect the provenance of clastic sediments (Bhatia 1985, Bhatia and Crook 1986, Cullers et al. 1988, McLennan et al. 1990). Major element contents of sandstones and mudstones were used for discriminating geotectonic settings by Bhatia (1983), Roser and Korsch (1986, 1988). The extent of weathering as a process modifying the provenance signals of the source rocks can be estimated by distinct elements and their ratios, e.g., Al<sub>2</sub>O<sub>3</sub> content, Th/U ratio, REE patterns (Nesbitt and Young 1989, Nesbitt et al. 1990, McLennan et al. 1993). The availability of oxygen during subaqueous deposition of shales under non-marine, normal oxic marine, and euxinic bottom-water conditions can be distinguished by the S<sub>pyrite</sub>/C<sub>org</sub> ratio (Raiswell and Berner 1986, Leventhal 1995, Lyons et al. 2000).

K-Ar age determinations on detrital white micas represent another appropriate tool for provenance analysis. The radioactive decay of <sup>40</sup>K to <sup>40</sup>Ar (e.g., Faure 1986) permits ascertaining the last cooling of the measured micas below their blocking temperature ( $350 \pm 50$  °C after

Purdy and Jäger 1976). In sediments unaffected by thermal events, the age calculated from the isotopic composition of detrital minerals corresponds to the cooling age of the source rock.

Combining the data obtained by these diverse methods, the source area and the weathering processes leading to the origin of shales of the Šárka Formation are to be characterized. Neoproterozoic rocks as a potential source of the Early Palaeozoic sediments were analysed for comparison.

Sampling was carried out in a temporary excavation at Červený vrch Hill in Prague (Fig. 2) and in the Jezírko Quarry at Dobříš. The number of samples is small and does not have systematic character. However, the application of several modern analytical methods yields reliable information on the provenance and formation of the studied rocks.

#### **Geological setting**

The Šárka Formation was deposited during the latest Arenigian to early-middle Llanvirnian times, Darriwillian (sensu Fatka et al. 1996) in the Prague Basin (Barrandian area, see Fig. 1). The largest part of the Šárka Formation is dominated by shales and silty shales. Black shales with > 1 % C<sub>org</sub> prevail in the central parts of the basin, while sedimentary iron ores are present in onshore settings (Havlíček in Chlupáč et al. 1998). Within the shales, irregularly distributed horizons of nodules form spatially restricted lo-



Fig. 1. Geological sketch-map of the Barrandian area and stratigraphic column of the Ordovician after Kraft et al. (1999).

cal occurrences. Accumulations of volcanic and volcaniclastic rocks are related especially to the Komárov Volcanic Complex during the Lower and Middle Ordovician, including the Šárka Formation (e.g., Chlupáč and Kukal 1988, Petránek 1991, Chlupáč et al. 1998).

## Methods

The mineralogical composition of shales of the Šárka Formation and of the associated siliceous nodules was investigated using light microscopy and X-ray phase analysis. The latter method has been performed in the mineralogical laboratories at Freiberg University of Mining and Technology, Germany. The total of all crystalline phases was recalculated to 100 %. Depending on the structure and matrix, the detection limit is specified between 0.5 and 5 wt%. Mineral phases were quantified by the Rietveld method on the basis of the published crystal structure data (Tab. 1).

Whole-rock major and trace element analyses were obtained on three samples of shales, two siliceous nodules, and one sample of tuffitic rock (Fig. 2) by fusion ICP and ICP-MS, respectively (Tabs. 2, 3). The contents of carbon and sulphur were determined on three shale samples by INAA (Tab. 4; all Activation Laboratories Ltd., Ancaster, Canada). Three samples from Neoproterozoic fine-grained sandstones

taken in the Jezírko Quarry at Dobříš (Štěchovice Group) were analysed for comparison (see Tabs. 2, 3).

K-Ar age dating of detrital white micas from sample Šárka 01 (see Fig. 2, Tab. 5) was performed in the Geowissenschaftliches Zentrum der Universität Göttingen,

Tab. 1. Mineral phases [wt%] recognized by X-ray phase analysis



Germany. Sample preparation as carried out at the University of Göttingen is described by Wemmer (1991). Details on K determination, measurement of Ar isotopic composition, and the mode of age calculation were given by Ahrendt et al. (2001).

Sample	System	Lithostratigraphy	Quartz	Anatase	Rutile	Calcite	Kaolinite	$\Sigma$ 2:1 layer silicates
CV03	Ordovician	Šárka Formation	20	1	1	_	23	55 [2M <sub>1</sub> muscovite and mixed layer illite/smectite ordered (~75% illite) in a ratio of 1:1]
CVP01	Ordovician	Šárka Formation	87	_	_	1	2	10 (2M <sub>1</sub> muscovite and mixed layer illite/smectite ordered in a ratio of 1:1)

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			SiO	Al <sub>2</sub> O <sub>2</sub>	Fe,O,	MnO	ΜαΟ	CaO	NacO	K,O	TiO.	P,O,	IOI	TOT
Chronostratigraphy Lithos	Lithos	tratigraphy	%	72.03 %	1 2 0 3 %	%	% %	%	%	% %	% %	دمع %	%	2
			68.1	20.9	0.76	0.004	0.15	0.06	0.07	0.59	0.876	0.13	8.56	100
			58.6	26.0	1.04	0.004	0.67	0.12	0.71	4.35	1.069	0.11	7.24	6
Ördanision Šáda Par	Йźль, Пос		57.6	25.0	2.81	0.008	0.82	0.29	0.93	3.60	1.067	0.15	7.84	100
Urdovician Sarka Forn	Sarka Forn	nation	56.8	24.7	3.37	0.016	0.82	0.36	0.98	3.53	1.024	0.14	8.09	96
			91.0	4.6	1.01	0.011	0.13	0.47	0.17	0.75	0.197	0.09	1.74	100
			87.9	4.2	2.46	0.057	0.13	0.39	0.15	0.52	0.176	0.10	2.47	6
			69.0	13.7	4.88	0.062	2.02	1.13	3.64	2.31	0.535	0.11	2.49	6
Neoproterozoic Štěchovice Group	Štěchovice Group	0	62.3	15.5	7.01	0.107	2.80	1.48	2.94	3.00	0.670	0.15	4.07	6
-	4		62.4	16.5	6.96	0.103	2.82	0.58	3.35	3.00	0.678	0.17	3.39	100

#### Results

#### Middle Ordovician, Šárka Formation

Volcaniclastic rocks at the base of the section (see Budil et al. 2003, this volume) represent a tuffitic mixture containing several detrital minerals (quartz, white micas, zircon) and fine-grained matrix composed of redeposited volcanic and clastic material. The position close to a fault zone and the very light colour apparent in the field as well as grains with corroded rims and altered minerals observable in thin section characterize the very strong alteration of these rocks. Chemical composition of one sample of the volcaniclastic rocks (CV 02) is listed in Tab. 2 and Tab. 3. The overlying sedimentary part of the studied section contains dark grey to black shales partly with an admixture of mica as well as a horizon with siliceous nodules.

Shales: The fine-clastic samples of the Šárka Formation are classified as shales by the diagram of Herron (1988; Fig. 4). The shales of the Šárka Formation contain detrital quartz with a grain size up to 150  $\mu$ m and detrital micas (predominantly white micas and very rare dark micas) up to 400  $\mu$ m long. The detrital grains are arranged in thin laminae generally oriented parallel to the bedding planes (Fig. 3a). The mineralogical composition was determined by X-ray phase analysis (for results see Tab. 1) and demonstrates a distinct kaolinite content.

The  $S_{pyrite}/C_{org}$  ratio is used to characterize the depositional environment of sediments. Leventhal (1995) differentiates between freshwater, normal marine, and euxinic depositional conditions. Black shales expected to be deposited under euxinic bottom-water conditions should feature high sulphide sulphur (> 1%). The sulphate sulphur of the measured shales (Tab. 4) is beneath the detection limit; it is therefore impossible to calculate the sulphide sulphur from total sulphur. However, the total sulphur and consequently the sulphide sulphur as well are clearly below 1 %. Anoxic bottom-water conditions causing pyrite precipitation can be therefore ruled out for the analysed samples. The dark grey shales are not typically enriched in trace elements like Cr, V, Cu, and Co; the Corg content of 0.05–0.06 % also indicates "normal" shales ( $C_{org}$ content in black shales 1-10 %). Compared with PAAS (Fig. 6D), Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, and CaO are depleted.

The latest tectonothermal history of the source area is recorded in the K-Ar isotopic composition of detrital white micas reflecting the last cooling of the source rocks. In sample Šárka 01 micas are up to 400  $\mu$ m long and chiefly occur on bedding planes. They do not show a strong alignment; therefore they are of detrital nature. The K-Ar age of Šárka 01 is 599 ± 12 Ma (Tab. 5). Accordingly, the detrital micas of the Šárka Formation are derived from a Neoproterozoic source area. The source rocks consist most probably of micaschists, gneisses or granites, which underwent their last higher-grade overprint or emplacement during Panafrican/Cadomian orogenic processes.

Siliceous nodules of the Šárka Formation: Chemical analyses (Tab. 2) of the concretions show a very high  $SiO_2$ 

Sample	Rock type	Chronostratigraphy	Lithostratigraphy	>	Sc	Cr	Co	ïZ	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	ЧN
CV 02	tuffite			106	8	109	0	0	0	0	34	4	13	28	587	28	137	18
CV 03				139	19	144	2	0	46	0	37	3	0	186	316	29	128	21
CV 04	shale		r x	143	20	149	5	0	48	79	37	ю	13	190	201	33	139	22
CV 05		Urdovician	Sarka Formation	140	20	140	7	41	50	122	35	4	20	185	172	33	135	21
CVP 01	•			34	4	52	5	0	20	0	~	7	0	39	49	52	35	S
CVP 02	concretion			28	4	48	12	0	22	91	7	6	11	29	39	50	28	4
DOBŘÍŠ 01	fine			102	16	115	13	46	43	77	17	2	0	74	164	19	186	10
DOBŘÍŠ 02b	grained	Neoproterozoic	Štěchovice Group	121	17	106	25	57	72	137	22	2	22	111	149	22	173	12
DOBŘÍŠ 04b	sandstones			123	16	100	15	61	58	115	22	2	0	110	126	21	145	12
Sample	Rock type	Chronostratigraphy	Lithostratigraphy	Sn	Sb	Cs	Ba	Hf	Та	M	Π	Pb	Bi	Th	n	Mo	Ag	In
CV 02	tuffite			5	4	3	207	4	1	4	1	23	0	14	2	0	0	0
CV 03				9	4	6	484	4	2	3	1	13	0	21	3	0	0	0
CV 04	shale		L	9	1	6	521	4	2	3	1	13	0	23	3	0	0	0
CV 05		Urdovician	Sarka Formation	8	1	6	510	4	2	3	1	17	0	22	3	0	0	0
CVP 01				3	0	2	238	1	0	0	0	25	0	6	1	0	0	0
CVP 02	concretion			5	2	2	85	1	0	0	0	29	0	5	1	0	0	0
DOBŘÍŠ 01	fine			3	1	3	719	5	1	0	1	16	0	8	2	0	0	0
DOBŘÍŠ 02b	grained	Neoproterozoic	Štěchovice Group	4	3	7	633	5	1	2	-	25	0	6	3	0	0	0
DOBŘÍŠ 04b	sandstones			4	3	9	556	4	1	2	1	19	0	10	3	0	0	0
Sample	Rock type	Chronostratigraphy	Lithostratigraphy	La	Ce	Pr	ΡN	Sm	Eu	Gd	τb	Dy	Но	Er	Tm	Yb	Lu	
CV 02	tuffite			53.5	103.6	12.52	48.9	10.0	2.35	8.0	1.3	6.6	1.3	3.4	0.58	3.2	0.49	
CV 03				62.7	121.3	13.54	49.4	8.8	1.94	6.3	1.1	5.6	1.2	3.4	0.62	3.3	0.51	
CV 04	shale			63.6	122.8	13.65	50.1	9.3	2.02	6.8	1.2	6.2	1.3	3.7	0.64	3.5	0.53	
CV 05		Ordovician	Sarka Formanon	62.0	118.4	13.45	50.2	9.2	2.04	6.8	1.2	6.5	1.4	3.8	0.64	3.6	0.54	
CVP 01				15.0	29.4	3.38	13.0	4.5	1.53	9.9	2.1	10.6	1.8	4.5	0.71	3.4	0.49	
CVP 02	collicientoli			14.6	28.0	3.07	11.6	4.2	1.46	9.7	2.1	10.5	1.9	4.6	0.70	3.6	0.52	
DOBŘÍŠ 01	fine			17.4	37.4	4.42	16.9	3.6	0.94	3.2	0.6	3.4	0.8	2.1	0.37	2.1	0.35	
DOBŘÍŠ 02b	grained	Neoproterozoic	Štěchovice Group	30.7	59.3	6.49	25.0	4.8	1.20	4.1	0.8	4.0	0.9	2.5	0.42	2.4	0.40	
DOBŘÍŠ 04b	sandstones			29.0	58.3	6.27	23.9	4.6	1.09	3.9	0.7	3.9	0.8	2.5	0.42	2.5	0.41	

Tab. 3. Trace element amounts in the sampled rocks



Fig. 3a, b. Microphotographs (XPL) showing the occurrence of detrital quartz and micas a) in the shales and b) in a silicious concretion of the Šárka Formation.

Table 4. Sulphur and carbon contents in the shales

SAMPLE	System	Lithostratigraphy	TOTAL C %	GRAPHITIC C %	ORGANIC C %	CO <sub>2</sub> %	S %	$SO_4 \%$	S/C <sub>org</sub>
CV 03	Ordovician	Šárka Formation	0.45	0.38	0.05	< 0.05	0.03	< 0.05	0.6
CV 04	Ordovician	Šárka Formation	0.47	0.39	0.05	< 0.05	0.03	< 0.05	0.6
CV 05	Ordovician	Šárka Formation	0.51	0.40	0.06	< 0.05	0.03	< 0.05	0.5

content (~ 90 %). Therefore, they are interpreted as recrystallized cherts. Detrital quartz grains with corroded rims (up to 150 µm in diameter) and detrital micas (up to 250 µm long) in the chert concretions represent remnants of the former sediment (Fig. 3b), which was replaced by the formation of the concretions in an early diagenetic stage. The replacing matter was opal or carbonate (see Kukal 1962), later replaced by opal. The opal substance is now transmuted to quartz. The siliceous concretions are plotted along with the shales (Fig. 4) in the Herron's (1988) diagram, which is actually established for terrigenous clastics, to show the chemical effect of the detrital minerals. The concretions are characterized as sublitharenite/Fe-rich sand. In spite of the high SiO<sub>2</sub> content there is a pronounced proportion of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> pointing to relics of clay minerals and micas. Further evidence for these detrital



Fig. 4. Chemical classification scheme for terrigenous clastic sediments after Herron (1988).

components is the detection of kaolinite (2 wt%) and three-layer minerals (10 wt%) by X-ray phase analysis (Tab. 1). The chemical composition of the siliceous concretions is normalized to the shales of the Šárka Formation to emphasise the depletion in most elements in the nodules (Fig. 5). SiO<sub>2</sub>, MnO, CaO, Co, Pb and the HREE including Y (except Yb and Lu) are enriched in the concretions, compared to the shales (Tab. 3). At the time there is no clear explanation for such an effect. The growth of the concretions took place obviously before the first compaction, because most of the relictic components are not aligned (Fig. 3b). Consequently, we suppose an early diagenetic origin of the nodules.

#### Neoproterozoic sandstones of the Štěchovice Group

Thin sections of Neoproterozoic sediments of the Štěchovice Group reveal immature fine-grained sandstones containing quartz, plagioclase, orthoclase, dark and white mica, heavy minerals, some opaque substances, and clay-sized matrix. The absence of unstable lithic fragments can be explained by the small grain size and diagenetic alteration. The components are mostly angular, indicating a short transport. Immaturity is confirmed by the classification as shale/wacke (Fig. 4) in the diagram of Herron (1988).

The geochemical composition of clastic sediments reflects the degree of weathering and recycling, and, on the other hand, the provenance. Major and trace element data on sediments of the Middle Ordovician Šárka Formation and the Neoproterozoic Štěchovice Group are treated together to emphasise similarities and differences.

Ar - Isotopic	Abundance	Spike - Isot	opic Composition	Decay Co	onstants [1/a]:	Potassiu	n	
<sup>40</sup> Ar :	99.6000 %	<sup>40</sup> Ar :	0.0099980 %	$\lambda_{\epsilon}$ :	5.810E-11	<sup>40</sup> K :	0.011670%	
<sup>38</sup> Ar :	0.0630 %	<sup>38</sup> Ar :	99.9890000 %	$\lambda_{\beta}$ :	4.962E-10	K <sub>2</sub> O/K :	0.8302	
<sup>36</sup> Ar :	0.3370 %	<sup>36</sup> Ar :	0.0009998 %	$\lambda_{tot}$ :	5.543E-10	Atomic Weight	[g/mol]:	
Standard Ter	mperature Press	ure (STP)				tot Ar :	39.9477	
0°	° C; 760 mm Hg			Mola	ır Volume	<sup>40</sup> Ar :	39,9624	
Normal A	Normal Atmosphere (DIN 1343)			[ml] :	22413.8	tot K :	39,1027	
273,15K; 1013,25 mbar								-
Sam	ıple	Spike [ No. ]	K2O [ Wt. % ]	<sup>40</sup> Ar <sup>-</sup> [ nl/g ] S	* <sup>40</sup> Ar * TP [%]	Age [ Ma ]	2s-Error [ Ma ]	2s-Error [%]
Šárka 01 - detr (for sample loca	rital muscovite ation see Fig. 2)	2769	3.77	86.360	0 99.35	598.9	12.2	2.0

Tab. 5. Data on K-Ar analysis and geochronology of a white mica concentrate taken from sample Šárka 01

The SiO<sub>2</sub> vs. K<sub>2</sub>O/Na<sub>2</sub>O diagram of Roser and Korsch (1986) characterizes the geotectonic setting of the source area of the clastic sediments. This diagram is related to the maturity of the sediment. Mature, PM-indicating clastics are derived from stable continental blocks and deposited in several types of basins including rift basins, whereas more immature ACM-proving sediments are delivered from mixed sources and stored on or adjacent to active plate margins and in strike-slip settings (Roser and Korsch 1986). Shales of the Šárka Formation, evidencing deposition in a passive margin setting (PM), are clearly differentiated from the Neoproterozoic rocks showing an active margin/continental island arc (ACM) signature (Fig. 6b).

The ternary plot of Bhatia and Crook (1986) dealing with discriminatory trace elements is actually compiled on the basis of the geochemical composition of greywacke samples. The Th-La-Sc diagram displays an island arc signature for the Precambrian and Middle Ordovician sediments (Fig. 7b). The discriminant function diagram of Roser and Korsch (1988) characterizes the provenance of the analysed rocks as an intermediate igneous one (Fig. 7a).

Weathering and recycling processes of the source rocks accompanied by U solution are reflected in the resulting terrigeneous clastics and can be estimated by the Th/U ratio (McLennan et al. 1993). Generally, shales are depleted in U, and their Th/U ratio is elevated above upper crustal igneous values of 3.5–4.0. Whereas the shales of the Šárka Formation with Th/U values of ~ 7 point to strong weathering and recycling of the source rocks, the Neoproterozoic fine-grained sandstones show Th/U ratios like the upper crust (Fig. 6a). Furthermore, exogenous processes are responsible for the enrichment in LREE over HREE (McLennan et al. 1993). Fig. 6c shows chondrite-normalized REE patterns of the Dobříš sandstones and the sediments of the Šárka Formation. Both rocks feature similar ratios with enhanced LREE, but the absolute REE content in the shales is higher due to the lower grain size.

# **Discussion and conclusions**

The content of kaolinite in the shales of the Šárka Formation, as well as the high Th/U ratio and the REE patterns evidence strong weathering processes. However, the interpretation of the age of weathering is difficult. Starke (1970) reported a drill core from the Rügen island (Germany), where Llanvirnian-Llandeilian shales contain up to 30 % kaolinite, although the overlying Silurian graptolite shales display only a few percent of kaolinite. Furthermore, the same author described a high kaolinite content in the Upper Ordovician Lederschiefer Formation of Thuringia. Highly mature Tremadocian sandstones in Saxo-Thuringia were interpreted as a result of uplift and intensive Late Cambrian weathering of Cadomian rocks (Linnemann and Romer 2002), which were finally deposited in a rift setting and reach a thickness of > 2000 m (Linnemann and Heuse 1998). In the Barrandian, the Tremadocian and Arenigian sediments (silicites, shales, conglomerates, sandstones) achieve a thickness of up to 300 m. The coarser clastic rocks contain many unstable lithic fragments indicating only a short



Fig. 5. Chemical components of the concretions normalized to the shales of the Šárka Formation.

transport (Chlupáč et al. 1998). The immature conglomerates and sandstones should be derived from relatively fresh sources close to the site of deposition, whereas the more mature shales of the Šárka Formation can be acquired from more distant regions, which underwent intensive and particularly extensive chemical weathering. Paleomagnetic studies of Krs et al. (1986, 1987) suggest a low paleolatitude for the Middle–Late Cambrian and Early Ordovician of the Barrandian, which is in good agreement with intense weathering processes. Assuming related but not synchronous geotectonic conditions for the Barrandian and the Saxo-Thuringian, the content of kaolinite in the shales of the Šárka Formation is interpreted as a relic of fossil (pre-Middle Ordovician) weathering processes in the source area and not as an effect of recent alterations. Petránek (1991) demonstrated the unfixing of iron and manganese in sediments with anoxic pore water conditions, the diffusion of Fe<sup>2+</sup> and Mn<sup>2+</sup> to the sediment/water interface and their removal by streaming bottom water. The studied shales of the Šárka Formation show very low contents of C<sub>org</sub> and S<sub>total</sub> and a depletion in Fe<sub>2</sub>O<sub>3</sub> and MnO compared to PAAS. The S/C ratio of 0.5–0.6, actually pointing to normal marine bottom-water conditions, could be also an expression of the removal of degraded C<sub>org</sub> ( $\rightarrow$ CO<sub>2</sub>) and sulphate ( $\rightarrow$ H<sub>2</sub>S) as well as reduced bivalent iron and manganese ions by bottom currents. If pH < 5, FeS cannot be precipitated (Fetter 1994). In such acidic environment, the formation of siliceous nodules and the depletion in Fe, Mn and H<sub>2</sub>S during progressive degradation of organic matter can take place simultaneously in an early diagenetic stage.



Fig. 6. a – Th/U versus Th plot after McLennan et al. (1993); b – Provenance diagram for sandstones and mudstones after Roser and Korsch (1986); PM, passive continental margin; ACM, active continental margin including continental island arcs; ARC, oceanic island arc; c – Chondrite-normalized REE patterns (normalizing values from Taylor and McLennan 1985); d – Average element contents of analysed samples normalized to PAAS (normalizing values from Taylor and McLennan 1985).

The latest thermal event in the source area of the shales of the Šárka Formation was determined at  $599 \pm 12$  Ma. The mica compound of sample Šárka 01 (Tab. 5) contains only 3.77 wt.% K<sub>2</sub>O but the K<sub>2</sub>O content in pure muscovite is about 10 %. This means that other minerals such as paragonite or chlorite were measured besides muscovite. These minerals do not contain K, and therefore do not affect the calculated age. Ahrendt et al. (1998) found K-Ar ages of 612–585 Ma in the Middle Cambrian to uppermost Ordovician clastic sediments of the Barrandian. The K-Ar isotopic composition of the white mica-bearing shale of the Šárka Formation shows a cooling age within this range.

Recent U-Pb age data on detrital zircons of the Neoproterozoic Dobříš Conglomerate (Dörr et al. 2002) demonstrate magmatic activity in the source area of these sediments at least at 585-568 Ma. However, the scarcity of granite boulders (Chlupáč 1993) and the absence of metamorphic pebbles in the Dobříš Conglomerates exclude repeated recycling of the Neoproterozoic sediments of the Štěchovice Group as the major source of Palaeozoic siliciclastics. The large supply of detrital white mica during several Cambro-Ordovician periods is rather realized by crystalline basement. Trace elements and discriminant function analysis reflecting an island arc signature in the Middle Ordovician shales and in the Neoproterozoic sediments of the Štěchovice Group point to the same geotectonic setting of their source rocks. The top of the Cadomian island arc composed of sediments and volcanics was probably eroded and deposited during the Neoproterozoic, whereas the shales of the Šárka Formation were supplied from the same but deeply eroded source (plutons). Therefore, the trace elements of the Middle Ordovician shales display an inherited island arc signature of the Cadomian source rocks. Major element data of the shales of the Šárka Formation demonstrate a passive margin setting during the Middle Ordovician with derivation of the clastic material from stable continental blocks.

The most probable depositional setting of the Šárka Formation is a rift basin, which consists of (1) zones with sedimentary iron ore deposits in shallower parts, (2) transitional zones indicating normal marine sediments / bottom currents (studied shales of the Šárka Formation), and (3) zones with euxinic marine conditions in the central part of the basin. Considering the depletion in Fe and Mn, the shales of the Šárka Formation could act as a part of the iron source for the ore deposits. The transport to the coast can be realized by upwelling.

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Fig. 7. Provenance diagrams of the Šárka Fm. shales show inherited signatures of the Neoproterozoic continental island arc. a – Ternary Th-La-Sc plot after Bhatia and Crook (1986); b – Discriminant function diagram after Roser and Korsch (1988);

 $\begin{array}{l} \mbox{Discriminant function I} = -1.773 \ \mbox{TiO}_2 + 0.607 \ \mbox{Al}_2 \mbox{O}_3 + 0.76 \ \mbox{Fe}_2 \mbox{O}_{3(total)} \ -1.5 \ \mbox{MgO} + 0.616 \ \mbox{CaO} + 0.509 \ \mbox{Na}_2 \mbox{O} - 1.224 \ \mbox{K}_2 \mbox{O} - 9.09; \end{array}$ 

Discriminant function II =  $0.445 \text{ TiO}_2 + 0.07 \text{ Al}_2\text{O}_3 - 0.25 \text{ Fe}_2\text{O}_{3(\text{total})} - 1.142 \text{ MgO} + 0.438 \text{ CaO} + 1.475 \text{ Na}_2\text{O} + 1.426 \text{ K}_2\text{O} - 6.861.$ 

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