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Geochemistry of the Permian sandstones from the Malužiná Formation in the Malé Karpaty Mts (Hronic Unit, Western Carpathians, Slovakia): implications for source-area weathering, provenance and tectonic setting

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Abstract: The Permian sandstones of the Malužiná Formation in the northern part of the Malé Karpaty Mts are dominantly quartzofeldspathic and quartzolithic in composition with abundant feldspars and volcanic, plutonic igneous and less metasedimentary lithic fragments, indicating the sand grains were derived from a basement uplift and recycled orogen. The Malužiná Formation sandstones have moderate to high SiO_2 contents (68–85 wt. %; on average 76 wt. %), TiO_2 concentrations averaging 0.3 wt. %, Al_2O_3 contents of about 12 wt. %, and Fe_2O_3 (total Fe as Fe_2O_3)+MgO contents of around 2.9 wt. %. The Chemical Index of Alteration (CIA) values for the Permian Malužiná Formation sandstones vary from 45 to 68 with an average of 55, indicating low to moderate weathering of the source area. The bulk chemical composition and selected trace elements preserve the signatures of a felsic and intermediate igneous provenance, and suggest mostly an active continental margin tectonic setting of the source area for the Malužiná Formation sandstones. The Eu/Eu* (~0.78), La/Sc (~7.28), Th/Sc (~2.10), La/Co (~6.67), Th/Co (~1.85), and Cr/Th (~6.57) ratios as well as the chondrite-normalized REE patterns with flat HREE, LREE enrichment, and negative Eu anomalies indicate derivation of the Malužiná Formation sandstones from felsic rock sources. The deposition of the Malužiná Formation sandstones took place in a rifted continental margin environment supplied from collision orogen on a thick continental crust composed of rocks of older fold belts.

Key words: Permian, Western Carpathians, sandstone geochemistry, provenance, tectonic setting.

Introduction

Sandstone geochemistry has a number of important applications (e.g. Potter 1978; Bhatia 1983, 1985; Roser & Korsch 1988; Floyd et al. 1991; McLennan et al. 1993; Dinelli et al. 1999; Getaneh 2002; Lacassie et al. 2004; Rahman & Suzuki 2007; Dey et al. 2009). For instance, major-element chemistry can provide information about the tectonic setting of sedimentary basins, allowing distinction between sandstones derived from oceanic island arc, continental island arc, active continental margin, and passive margin settings (Bhatia 1983; Roser & Korsch 1986; Kroonenberg 1994). Major- and trace-element chemistry have been used to evaluate sedimentation rates and depositional environments in orogenic belts (Sugisaki 1984). Moreover, major-element chemistry has been utilized to infer the original clastic assemblages in deeply buried and altered sedimentary rocks and to help clarify the processes that produced the sediments (Argast & Donnelly 1987). Trace elements also have value in some kinds of provenance studies. (See Boggs 2009, Ch. 7, for discussion of this subject.)

Provenance of the Permian sandstones from the Malužiná Formation in the Malé Karpaty Mts has not as yet been analysed with the geochemical approach. Forasmuch as the Malužiná Formation is a part of the rootless nappe Hronic Unit, we decided to unravel the source-area weathering, provenance, and tectonic setting of the putative source area of the Malužiná Formation sandstones. To this end, we evaluated the major- and trace-element geochemistry of these sandstones, in relation to their mineral composition. The present study supplies new data not only on local geology but also important material for various comparisons and correlations. Finally, our detailed analysis may improve our understanding of the Permian paleogeography and tectonic evolution.

Geological setting

The Late Paleozoic of the Hronicum, defined by Vozárová & Vozár (1981, 1988) as the Ipoltica Group with two lithostratigraphic units of a lower order — the Nižná Boca and the Malužiná Formations, is variably preserved and occurs as tectonically reduced fragments in the basal part of the multi-nappe structure in various regions of the Western Carpathians (Fig. 1a).

The Permian Malužiná Formation overlies the Pennsylvanian Nižná Boca Formation from which it develops gradually without break of sedimentation. The Malužiná Formation ranges from the Cisuralian to the Lopingian in age (Autunian–

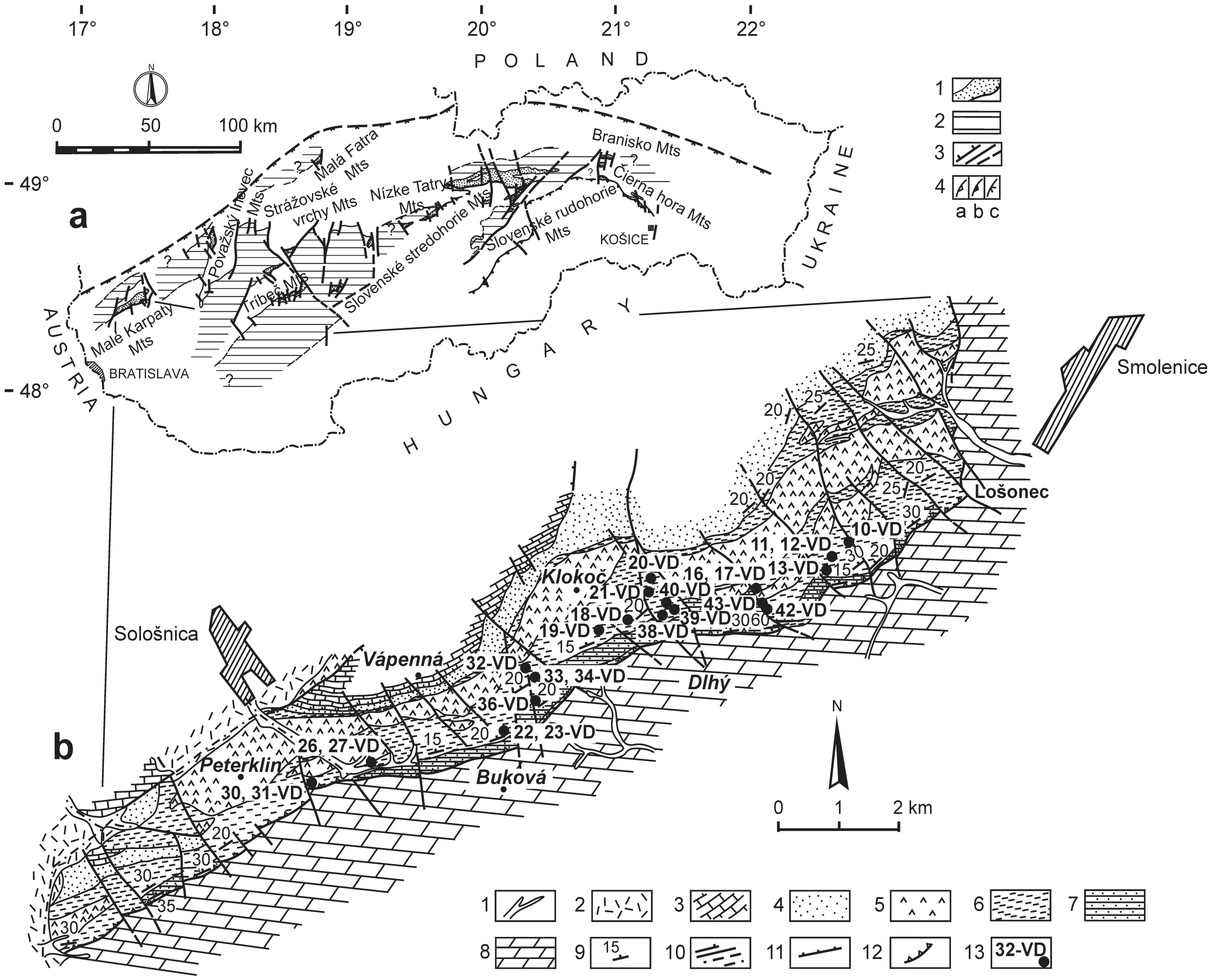

Fig. 1. a — Distribution of the Ipoltica Group in the Western Carpathians (after Vozárová & Vozár 1988). Explanations: 1 — surface occurrences, 2 — established and inferred distribution of the Hronic nappes, 3 — overthrust lines of the Hronic nappes, significant faults and boundaries delimitating distribution of the Ipoltica Group, 4 — significant lines in the Alpine structure of the Western Carpathians: a — Ľubeník-Margecany line, b — Čertovica line, c — Peripieninian lineament. **b** — Late Paleozoic of the Hronicum in the Malé Karpaty Mts (after Vozárová & Vozár 1988). Explanations: 1 — Quaternary sediments, 2 — Tertiary sediments. **Hronicum–Šturec Nappe:** 3 — Middle and Upper Triassic — carbonates, undivided, 4 — Lower Triassic — quartz sandstones, shales, 5 — Late Paleozoic–Permian — andesites, basalts and volcanoclastics (Malužiná Formation), 6 — Late Paleozoic–Permian — conglomerates, sandstones, shales with volcanogenic material admixture (Malužiná Formation), 7 — Late Paleozoic–Stephanian — grey conglomerates, sandstones, shales (Nižná Boca Formation). **Krížna Nappe:** 8 — Mesozoic, undivided. **Others:** 9 — foliation cleavage, 10 — faults, 11 — overthrusts, 12 — overthrust line of nappes, 13 — sample location.

Saxonian–Thuringian according to the Central European local stratigraphic scale) (e.g. Planderová 1973; Planderová & Vozárová 1982; Rojkovič et al. 1992; Vozárová et al. 2005). Lithologically, the Malužiná Formation is characterized by a dominance of siliciclastic sedimentary rocks (polymict conglomerates, sandstones, siltstones, shales) with sporadic chemogenic sediment interbeds (caliches and evaporites) of a variable thickness. There is a significant inner cyclic structure of the sedimentary sequences which are arranged into three regional megacycles. An important phenomenon is the polyphasic synsedimentary andesite-basalt volcanism, represented by rift-related continental tholeiites, in the 1st and 3rd megacycles, comprising huge lava flows generated during two eruption phases (Vozár 1997; Dostal et al. 2003). As estimated from the surface occurrences in the Nízke Tatry Mts and drilling data, the maximum thickness of the Malužiná Formation is 2200–2400 m (Vozárová & Vozár 1988). Volcanics and sediments in the Malužiná Formation are generally very low-grade metamorphosed. The grade of metamorphism did not exceed the diagenesis/anchizone boundary, which is characterized by the pumpellyite-prehnite-quartz mineral association (Vrána & Vozár 1969) and by the illite crystallinity indices from pelites (Plašienka et al. 1989; Šucha 1989; Šucha & Eberl 1992). Lithofacies analyses of the Malužiná Formation sequences, the character of volcanism and the structural arrangement of sediments in the entire megasequence suggest an intracontinental, rift-related type of the original depositional basin. Thus, the depositional environment was continental and was characterized by deltaic-lacustrine and alluvial sub-environments, including micro-environments controlled by arid to semiarid climate (Vozárová & Vozár 1988).

In the northern part of the Malé Karpaty Mts, the Ipoltica Group occupies the area to the SW of Smolenice and Lošonec in a belt 1.5–2.5 km wide, 15 km long, NE–SW-oriented, and extends to the western margin of the mountain range to the S of Sološnica (Fig. 1b). The Mesozoic of the Krížna Nappe is the direct tectonic basement of the Ipoltica Group in the whole area. From the east and west sides of the Malé Karpaty Mts, the geological units are tectonically bordered by the Tertiary faults of NE–SW direction. As a consequence of this tectonic phenomenon, we can interpret the continuation of all geological units (including the Ipoltica Group) into the pre-Neogene basement of the Vienna (western part) and Danube (eastern part) Basins.

Sampling and methods

Twenty-five representative samples of sandstones were collected within the Malužiná Formation in the Malé Karpaty Mts. Sampling spatially covered the whole regional occurrence of the studied lithostratigraphic unit, including its lower and upper parts. The exact locations of sampling sites are shown in Fig. 1b. Medium-grained sandstones were preferentially selected for petrographic and geochemical analyses.

Thin sections of collected samples were prepared and examined by a petrographic microscope. The modal composition of the Malužiná Formation sandstones was reviewed. The petrographic examination and modal analyses of the sandstone samples were carried out following the method of Dickinson (1970). Modal analyses were performed on the thin sections by counting 500 points on each slide using the Gazzi-Dickinson point-counting method. Various types of lithic grains were distinguished on the basis of textural and mineralogical characteristics. Only aphanitic polycrystalline grains were classified as lithic fragments and quartz/feldspar grains larger than 0.06 mm, when occurring within lithic fragments, were counted with the discrete quartz or feldspar component.

In all thin sections, the heavy minerals constitute less than 1 % of the total framework clasts. In order to facilitate the present study, we conducted conventional heavy mineral analysis for ten medium-grained sandstone samples. The 0.063–0.250 mm fraction of the dried samples was sieved out for the heavy mineral analysis. The heavy fraction was separated from the light fraction with the gravity separation method using a heavy liquid (bromoform with a measured specific gravity of 2.8). We point-counted 350 grains in each heavy mineral mount. Problematic opaque and non-opaque heavy minerals were embedded in polished sections and microanalytically determined (EDS). The ZTR index, which is a measure of mineralogical maturity of heavy-mineral assemblages in sandstones, was calculated as a percentage of the combined zircon, tourmaline, and rutile grains among the transparent, non-micaceous, detrital heavy minerals for each sample (Hubert 1962).

Twenty-five sandstone samples of the Permian Malužiná Formation were analysed for major and trace elements by Acme Analytical Laboratories (Vancouver) Ltd., Vancouver, Canada. Major elements were analysed by inductively coupled plasma emission spectrometry (ICP) and trace and rare earth elements (REE) by inductively coupled plasma mass spectrometry (ICP-MS). Loss on ignition (LOI) was determined by heating the samples at 1000 °C for two hours. Sample digestion procedures are similar for both ICP and ICP-MS. Two hundred milligrams of pulverized sample were mixed with 1.5 g of a flux of lithium metaborate and lithium tetraborate in a graphite crucible. Subsequently, the crucible was placed in a muffle furnace and heated to 1050 °C for 15 min. The molten mixture was dissolved in 100 ml of 5% HNO_3 (ACS grade nitric acid diluted in demineralized water). International reference samples (standards) and reagent blanks were added to the sample sequence. At the second stage (sample analysis), sample solutions were aspirated into an ICP emission spectrometer (Jarrel Ash AtomComb 975) or an ICP mass spectrometer (Perkin-Elmer Elan 6000) for the determination of element content. Major elements were determined with accuracy better than 2 % and trace elements with accuracy better than 10 %.

Results

Petrography and mineral composition

A part of the Malužiná Formation sandstones is coloured violet or red owing to the presence of finely disseminated hematite pigment, which occurs as a very thin coating around grains or is infiltrated within the matrix; others are light grey to beige. The sedimentary structure of the Malužiná Formation sandstones is mostly massive and horizontal current laminated, occasionally cross-bedded. Destructive activity is represented by washouts and erosive channel structures associated with a swarm of intraformational claystone- and siltstone clasts. The deformation structures, such as load casts, are frequent.

The sandstones of the Malužiná Formation are typically medium- to coarse-grained and contain high percentages of subangular to angular grains. Sorting of the framework grains ranges from moderately well sorted to poorly sorted (ϕ=0.50 to 2.00) (after Folk 1974; textural comparison chart showing degree of sorting is after Jerram 2001). Thus, the Malužiná Formation sandstones are texturally immature or submature.

The Malužiná Formation sandstones have dominantly quartzofeldspathic composition with predominance of quartz. On the quartz-feldspar-rock fragment (QFR) plot of McBride (1963), these sandstones can be classified as arkose, subarkose, lithic subarkose, and feldspathic litharenite (Fig. 2). Thus, the petrographic classification indicates a group of arkosic sediments for the Malužiná Formation sandstones.

Quartz is the dominant framework grain, constituting an average of 57 % of the rock volume, and occurring as monocrystalline (mean 39.4 %; range 18–64.2 %) and polycrystalline (mean 17.6 %; range 7–29.4 %) grains. Some

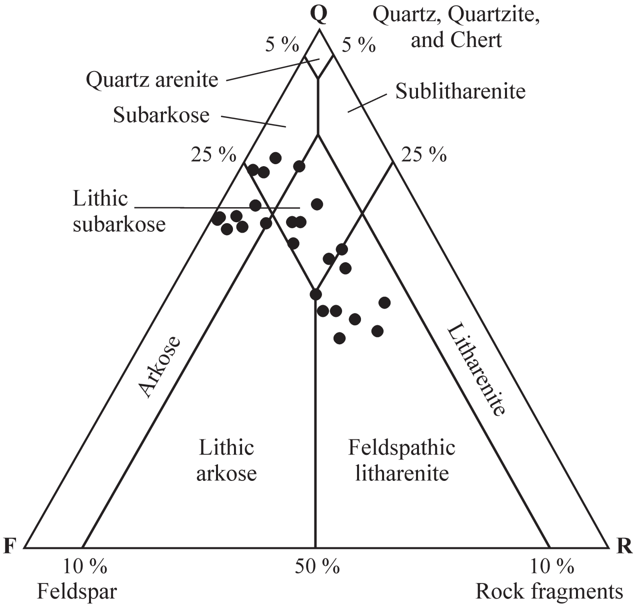

Fig. 2. Classification of the Malužiná Formation sandstones according to McBride (1963). Points within the triangle represent relative proportions of Q (quartz), F (feldspar), and R (rock fragments) end members.

polycrystalline quartz grains display sutured internal boundaries between composite crystals, indicating a probable early stage in development of metamorphic polycrystalline quartz.

Feldspars (orthoclase, microcline, microperthite, plagioclases) constitute around 24.5 % of the total framework grains of the sandstones. Both potassium feldspar (mean 13.3 %; range 6–26 %) and plagioclase (mean 11.2 %; range 3.2–24.4 %) are present in almost equal amounts. Microcline grains have well-developed grid twinning. Many plagioclase grains are characterized by distinctive albite twinning, with twin lamellae that are straight and parallel. The feldspars in the studied sandstones are predominantly fresh and unaltered, but there are a few grains showing some weak degrees of alteration to sericite or kaolinite.

Next in abundance to feldspar, lithic grains make up to 14.4 % of the total framework constituents. Specifically, there are some volcanic (mean 6.8 %; range 0–20.4 %), low-grade metamorphic (mean 3.8 %; range 0–16.4 %), and sedimentary (mean 3.8 %; range 0–16.8 %) rock fragments. Volcanic rock fragments include felsic, intermediate microlithic, basic lathwork, and vitric to vitrophyric grains. Metamorphic rock fragments are grains with tectonite and nonfoliated fabric. The grains with tectonite fabric include metasedimentary fragments of schist, sericite- and quartzose phyllite, paragneiss, and mica schist. The grains with nonfoliated fabric comprise metaquartzite clasts composed mainly of quartz with strongly sutured contacts. Sedimentary rock fragments involve fine-grained sandstone, siltstone, shale or mudstone, and chert.

White mica is generally more abundant than biotite, both constituting on average 1.4 % (range 0–9.6 %) of the total framework grains in the studied sandstones. Biotite grains are usually baueritized.

The sandstones of the Malužiná Formation have very low matrix contents (mean 2.7 %; range 0–10.4 %). These low contents indicate that it is a primary depositional matrix, and not a diagenetic clay. The matrix of the sandstones is slightly recrystallized, changed into a sericite and scarce chlorite aggregate. Quartzose, calcite and ferruginous cements are preserved, but only in a negligible content.

The heavy mineral assemblage in the Malužiná Formation sandstones is characterized by the presence of opaque and non-opaque minerals. The following opaque heavy minerals occur in the studied sandstones: magnetite, ilmenite and hematite (mainly diagenetic in origin). The non-opaque heavy minerals are represented here by three groups: ultrastable (zircon, tourmaline and rutile), stable (apatite and biotite), and moderately stable (titanite and garnet). The average proportion of observed heavy minerals in the studied sandstones is as follows (listed in the decreasing percentage): biotite (29.55 %), magnetite, ilmenite and hematite (27.58 %), titanite (13.86 %), tourmaline (10.21 %), garnet (8.68 %), apatite (5.78 %), zircon (3.93 %), and rutile (0.39 %). The ZTR index varies widely (19.57–59.68 %) among the Malužiná Formation sandstones, but its average value is comparatively low (33.21 %), showing their mineralogical immaturity.

We found only little petrographic evidence of diagenetic features, such as dissolution of feldspar and rock fragments, compaction, reduction of the existing pore space through rearrangements, and rotation and fragmentation of grains resulting in dissolution of quartz grains and cementation. Our observations of only weak diagenetic alterations of feldspars, for example, inconspicuous albitization and other processes, document that the original composition of the Malužiná Formation sandstones was only insignificantly modified. Thus, we exclude considerable diagenetic overprint which could influence the mineral and chemical composition of the studied sandstones.

Chemical composition

The individual major and trace element analyses of the sandstones of the Malužiná Formation from the Malé Karpaty Mts are presented in Table 1.

Major elements

The Malužiná Formation sandstones have moderate to high SiO_2 contents (on average 76 wt. %; range 68–85 wt. %), TiO_2 concentrations averaging 0.3 wt. % (range 0.05–0.63 wt. %), Al_2O_3 contents of about 12 wt. % (range 7.88–14.98 wt. %), and Fe_2O_3 (total Fe as Fe_2O_3)+MgO contents of around 2.9 wt. % (range 0.69–4.67 wt. %). The samples show no marked differences in their major element chemical composition (for details, see Table 1). Variations in the major element geochemistry of the Malužiná Formation sandstones are shown on Harker diagrams (Fig. 3). The linear relationship of TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO, Na_2O, and K_2O with SiO_2 in the Malužiná Formation sandstones is conspicuous in these Harker variation diagrams. In general, SiO_2 increases and TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO, Na_2O, and K_2O decrease in the Malužiná Formation

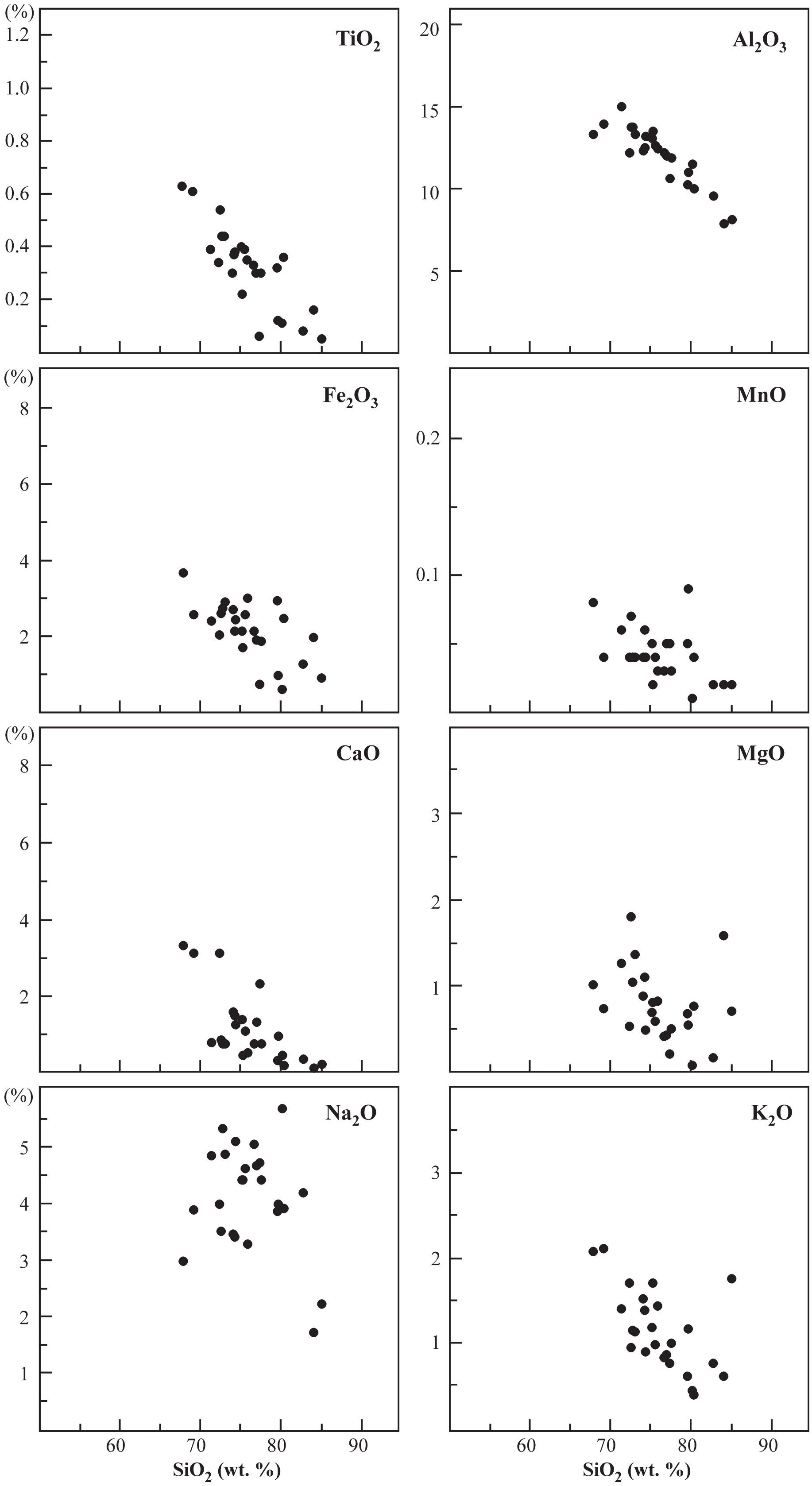

Fig. 3. Harker variation diagrams for the Malužiná Formation sandstones. The increase in SiO_2 reflects an increased mineralogical maturity, i.e. a greater quartz content and a smaller proportion of other detrital grains.

sandstones due to the increase in mineralogical maturity (Fig. 3). This mineralogical maturity is characterized by an increase in the quartz content and a decrease in unstable detrital grains (e.g. feldspar and volcanic rock fragments) in the Malužiná Formation sandstones, which also reflects a stratigraphic trend. The negative correlation of SiO_2 with the other major elements is due to most of the silica being sequestered in quartz, as indicated by Osman (1996). In the present samples, TiO_2 concentrations increase with Al_2O_3, suggesting that TiO_2 is probably associated with phyllosilicates especially with illite (Dabard 1990); Fe_2O_3+MgO are also well correlated with Al_2O_3. The latter correlation implies that these oxides are associated with phyllosilicates, particularly in matrix chlorites (Dabard 1990).

Trace elements

The processes controlling the trace element composition of sedimentary rocks may be investigated using normalization diagrams (spider diagrams). Trace element concentrations of the Malužiná Formation sandstones are in concurrence with the average upper continental crust (UCC) with the exception of Ba, Nb, Sr and Tb contents (Fig. 4). In the present samples, Ba (78–3185 ppm) is strongly enriched in three samples, slightly depleted in most of the samples and strongly depleted only in one sample. The Ba enrichment of the three samples is related to the presence of K-feldspar and barite, occurrence of which was also confirmed by our petrographic observations. Nb (1.7–12.1 ppm) and Tb (0.13–0.97 ppm) are depleted in all studied samples. The Sr content (25.3–460.4 ppm) of the studied sandstones is variable, as there are some slightly enriched, depleted and also strongly depleted samples. This variability is caused by many influences on Sr in low

Table 1: ICP-determined major, trace and rare earth element abundances for the Malužiná Formation sandstones.

Sample	10-VD	11-VD	12-VD	13-VD	16-VD	17-VD	18-VD	19-VD	20-VD	21-VD	22-VD	23-VD
Major elements (wt. %)												
SiO_2	82.73	71.32	75.54	76.94	69.08	72.32	84.02	85.03	77.34	79.57	80.29	79.53
TiO_2	0.08	0.39	0.39	0.3	0.61	0.34	0.16	0.05	0.06	0.12	0.36	0.32
Al_2O_3	9.55	14.98	12.62	12.02	13.94	12.21	7.88	8.11	10.65	11.01	10.01	10.24
Fe_2O_3	1.27	2.41	2.56	1.9	2.57	2.04	1.96	0.9	0.73	0.97	2.47	2.94
MnO	0.02	0.06	0.04	0.05	0.04	0.04	0.02	0.02	0.05	0.09	0.04	0.05
MgO	0.16	1.26	0.58	0.43	0.73	0.53	1.58	0.7	0.21	0.54	0.76	0.67
CaO	0.35	0.77	1.08	1.29	3.1	3.09	0.09	0.21	2.31	0.92	0.18	0.29
Na_2O	4.18	4.83	4.61	4.64	3.88	3.97	1.73	2.22	4.7	3.98	3.89	3.85
K_2O	0.79	1.41	1	0.88	2.12	1.72	0.64	1.76	0.79	1.19	0.41	0.64
P_2O_5	0.05	0.09	0.1	0.08	0.16	0.09	0.04	0.03	0.04	0.05	0.06	0.06
LOI	0.5	2.3	1.3	1.3	3.6	3.5	1.8	0.9	2.4	1.4	1.4	1.3
Total	99.68	99.82	99.82	99.83	99.83	99.85	99.92	99.93	99.28	99.84	99.87	99.89
Na_2O/K_2O	5.29	3.43	4.61	5.27	1.83	2.31	2.70	1.26	5.95	3.34	9.49	6.02
K_2O/Na_2O	0.19	0.29	0.22	0.19	0.55	0.43	0.37	0.79	0.17	0.30	0.11	0.17
Fe_2O_3 + MgO	1.43	3.67	3.14	2.33	3.30	2.57	3.54	1.60	0.94	1.51	3.23	3.61
Al_2O_3/SiO_2	0.12	0.21	0.17	0.16	0.20	0.17	0.09	0.10	0.14	0.14	0.12	0.13
CIA	53	58	54	52	49	47	68	58	45	54	58	58
Trace elements (ppm)												
Sc	1	4	4	4	7	5	2	1	1	1	5	6
V	11	37	42	37	54	38	24	16	8	12	40	38
Co	1.4	9.8	4	2.9	5.6	3.5	4.9	1.8	1.6	2.6	5	4.8
Ni	9.4	13.4	8.2	11.3	10.2	6.3	6.3	7.1	5.6	9.7	10.1	9.3
Cu	14.7	3.5	4.5	12	7.2	38.1	3.7	13.2	2293.7	5.8	33.9	4
Zn	12	80	28	26	34	27	17	15	23	32	27	39
Ga	7	13.7	10.5	10.2	13.6	11.5	6.9	6.9	7.9	9.5	8.5	9.7
Rb	20.5	53	40.9	32.3	77.4	62	22.1	44.6	22.3	33	17.7	28.4
Sr	176	252.2	417.6	460.4	222.1	221.5	25.3	66.7	107.4	116.7	128.8	107.5
Y	7.2	19.9	14.7	15.1	25	18.8	4.5	4.8	8.6	11.4	8.2	14.7
Zr	49.9	252.6	162.7	109.6	342.9	158.4	76.7	43.7	58.7	71.3	90.4	86.2
Nb	1.8	7.4	7	6.3	10.6	6.9	2.7	2	1.7	2.5	6.9	6.1
Cs	0.4	2.1	2.2	1.9	3.6	2.6	1.5	1.5	0.4	0.9	0.8	1.4
Ba	1999	433	266	268	320	441	78	415	3185	541	292	221
Be	1	1	1	2	2	1	1	1	1	2	1	1
Hf	1.6	7.7	5.1	3.6	10.3	4.7	2.3	1	2.1	2.2	2.5	2.6
Ta	0.2	0.6	0.6	0.5	0.9	0.5	0.2	0.2	0.2	0.2	0.4	0.5
W	0.5	0.8	0.9	0.8	1.6	1	1.2	0.5	0.5	0.5	2	0.7
Pb	32.5	5.8	7.8	10.1	3.7	4.8	3.1	5.9	166.9	2.6	8.7	4.6
Th	3.4	10.5	7	6.4	12.2	8.2	4	2.4	3.4	4.1	8.8	7.9
U	0.5	2.2	1.7	1.4	2.9	1.7	0.7	0.8	0.7	0.8	1.4	1
Rare earth elements (ppm)												
La	12.9	46.9	31.4	32.5	40	35.6	10.9	7.4	7.5	13.7	20.3	22.8
Ce	24.8	93.3	57.8	56.4	79	63.9	21.5	16.8	16.7	26.7	43.8	49.4
Pr	3.11	10.09	6.53	6.61	8.95	7.31	2.31	2.02	2.34	3.59	4.36	5.84
Nd	11.8	37.3	24.2	24	33.4	27.8	7.8	7.6	10.1	15.1	15.4	22.4
Sm	2.17	5.68	3.86	4.16	5.98	4.53	1.03	1.47	2.31	2.88	2.36	3.82
Eu	0.52	1.09	0.94	1.02	1.38	1.03	0.19	0.32	0.58	0.83	0.61	0.93
Gd	1.71	4.24	3.02	3.27	5.14	3.66	0.68	1.11	2	2.44	1.66	3.27
Tb	0.27	0.65	0.48	0.55	0.8	0.57	0.13	0.18	0.32	0.4	0.29	0.52
Dy	1.37	3.66	2.77	2.89	4.38	2.96	0.86	0.95	1.57	1.99	1.52	2.73
Ho	0.24	0.7	0.52	0.55	0.83	0.6	0.16	0.17	0.3	0.38	0.29	0.51
Er	0.61	2.03	1.49	1.54	2.39	1.72	0.51	0.44	0.8	0.98	0.81	1.33
Tm	0.09	0.31	0.22	0.23	0.37	0.24	0.08	0.07	0.11	0.15	0.13	0.21
Yb	0.59	2.02	1.46	1.41	2.32	1.64	0.58	0.44	0.69	0.86	0.86	1.33
Lu	0.08	0.29	0.21	0.2	0.35	0.24	0.09	0.07	0.1	0.13	0.13	0.2
ΣREE	60.26	208.26	134.9	135.33	185.29	151.8	46.82	39.04	45.42	70.13	92.52	115.29

temperature depositional environments (Fairbridge 1972). For instance, the distribution of Sr can be affected by the presence of Ca, fractionation of Sr can result from the weathering of feldspars, particularly plagioclase, and additional Sr can be incorporated in diagenetic carbonate, as also noticed in the Malužiná Formation sandstones. K and Rb have a trend comparable to that of Nb (Fig. 4). The two former elements are mainly hosted in micas and K-feldspar (Heier & Billings 1970); thus, alteration of these minerals will dominate the fractionation of these elements. The high field strength elements (e.g. Hf, Zr, Y) generally show consistent interrelationships, as do the large ion lithophile elements (Th and U) and selected rare earth elements (La, Ce, Nd, Sm, Tm, and Yb), though clear relationships are sometimes not completely obvious between them (Fig. 4).

Table 1: *Continued from previous page.*

Sample	26-VD	27-VD	30-VD	31-VD	32-VD	33-VD	34-VD	36-VD	38-VD	39-VD	40-VD	42-VD	43-VD
Major elements (wt. %)													
SiO_2	74.22	67.83	72.71	72.97	75.25	75.85	74.03	72.52	74.29	76.6	75.14	77.52	80.11
TiO_2	0.37	0.63	0.44	0.44	0.22	0.35	0.3	0.54	0.38	0.33	0.4	0.3	0.11
Al_2O_3	12.51	13.31	13.73	13.3	13.48	12.46	12.31	13.74	13.19	12.18	13.08	11.89	11.47
Fe_2O_3	2.15	3.66	2.75	2.89	1.71	2.99	2.71	2.6	2.42	2.15	2.14	1.86	0.61
MnO	0.06	0.08	0.04	0.04	0.02	0.03	0.04	0.07	0.04	0.03	0.05	0.03	0.01
MgO	1.09	1.01	1.03	1.36	0.8	0.81	0.88	1.8	0.48	0.41	0.68	0.49	0.08
CaO	1.47	3.3	0.75	0.74	0.42	0.5	1.57	0.83	1.23	0.75	1.36	0.72	0.42
Na_2O	3.4	2.97	5.29	4.86	4.41	3.27	3.45	3.5	5.08	5.03	4.41	4.4	5.66
K_2O	1.4	2.08	1.16	1.15	1.71	1.45	1.53	0.97	0.92	0.85	1.2	1.01	0.46
P_2O_5	0.09	0.16	0.1	0.1	0.06	0.09	0.09	0.06	0.1	0.09	0.11	0.07	0.04
LOI	3.1	4.8	1.9	2	1.8	2.2	3	3.3	1.8	1.5	1.3	1.6	0.9
Total	99.86	99.83	99.9	99.85	99.88	100	99.91	99.93	99.93	99.92	99.87	99.89	99.87
Na_2O/K_2O	2.43	1.43	4.56	4.23	2.58	2.26	2.25	3.61	5.52	5.92	3.68	4.36	12.30
K_2O/Na_2O	0.41	0.70	0.22	0.24	0.39	0.44	0.44	0.28	0.18	0.17	0.27	0.23	0.08
Fe_2O_3 + MgO	3.24	4.67	3.78	4.25	2.51	3.80	3.59	4.40	2.90	2.56	2.82	2.35	0.69
Al_2O_3/SiO_2	0.17	0.20	0.19	0.18	0.18	0.16	0.17	0.19	0.18	0.16	0.17	0.15	0.14
CIA	56	50	55	56	58	61	55	62	53	54	54	55	52
Trace elements (ppm)													
Sc	5	8	6	6	3	4	5	9	5	4	5	3	1
V	45	54	57	49	28	36	28	48	36	28	28	18	8
Co	8	8.5	6.4	8.6	4.3	4.3	4	12	4.2	2.9	4.1	3.8	0.8
Ni	8	15.1	12	18.7	14.2	13.1	13.2	15.9	9.4	7	8.2	7.8	5.4
Cu	3.3	2.7	3.6	3.8	2.5	5.7	5	1.6	5.1	3.3	5.9	2	3.2
Zn	33	37	59	84	16	22	28	62	28	23	39	20	5
Ga	11.8	13.7	14	12.8	12.4	11.5	11.9	13.8	11.6	10.5	12.2	10.1	8.2
Rb	51.4	86.4	43.4	43.1	49.4	44.9	46.8	45	33.7	32.4	43.8	37.5	12.6
Sr	102.2	126	217.8	223.3	109	110.8	126.2	152.7	438.6	242.1	370.2	268.3	252.3
Y	19	30.7	16.1	15.7	11.3	11.5	18	17.8	14.7	15	16.5	12.6	7.5
Zr	198.4	354.8	179.9	213.4	136.8	132.5	96.6	169.8	129.9	118.4	159.9	134.7	83.6
Nb	7.6	12.1	8.6	8.3	4.7	5.9	5	12.1	7.2	7.3	7.5	6.8	2.4
Cs	4	7.9	2.4	2.6	1.9	1.4	1.7	4.2	1.5	1.4	2.3	1.7	0.6
Ba	245	316	328	226	492	257	544	338	228	390	328	212	1175
Be	2	2	1	1	1	1	1	1	1	1	1	1	1
Hf	6.3	10.5	4.9	5.9	3.8	3.3	2.7	4.6	3.6	3.7	4.7	3.7	2.2
Ta	0.6	1	0.6	0.7	0.4	0.5	0.5	1	0.7	0.9	0.7	0.7	0.2
W	1.5	2.3	1.2	1.1	0.6	0.9	0.8	1.4	1	1.1	1	0.9	0.5
Pb	6.7	15.3	7.9	5.1	2.2	10.2	12.9	7.9	7	5	4.7	4.2	4.3
Th	8	14.5	7.8	8.9	6.9	6	4.9	8.9	6.7	7	8.7	6.3	5.9
U	2.2	2.5	2.7	1.9	1	1.2	1.1	2.1	1.9	1.5	1.9	1.4	0.9
Rare earth elements (ppm)													
La	22.6	30.6	21.2	24.6	23.2	15.3	21	28.5	39	39.1	37.8	21	19.7
Ce	46.4	66.6	44.2	53.4	51.7	32.7	33.6	53.6	63.2	70.3	67.3	42.6	38.5
Pr	5.31	7.61	5.19	5.92	5.73	3.72	4.66	6.4	6.97	7.69	7.61	4.97	4.53
Nd	20.3	29.6	20.4	23.1	21.6	14.8	17.7	24.8	23.4	28.6	28.1	17.6	17.1
Sm	4.09	6.33	3.67	4.15	3.28	2.56	3.35	4.09	3.78	4.29	4.46	3.28	2.68
Eu	0.93	1.29	0.82	0.95	0.75	0.62	1.05	0.92	1	0.98	1.04	0.79	0.67
Gd	3.63	5.78	3	3.39	2.39	2.22	3.2	3.41	3.07	3.36	3.47	2.63	2.02
Tb	0.61	0.97	0.5	0.56	0.36	0.34	0.49	0.54	0.45	0.49	0.52	0.42	0.27
Dy	3.16	5.16	2.61	2.81	2.01	2	2.73	3.03	2.44	2.42	2.82	2.32	1.37
Ho	0.69	1.03	0.57	0.55	0.37	0.43	0.54	0.58	0.48	0.5	0.6	0.44	0.24
Er	1.94	3.05	1.68	1.57	1.15	1.39	1.59	1.75	1.46	1.43	1.72	1.31	0.63
Tm	0.31	0.44	0.27	0.25	0.17	0.21	0.25	0.27	0.22	0.22	0.27	0.2	0.1
Yb	1.98	2.9	1.69	1.55	1.11	1.31	1.46	1.85	1.38	1.39	1.65	1.12	0.53
Lu	0.29	0.41	0.25	0.24	0.16	0.2	0.23	0.27	0.21	0.2	0.25	0.17	0.09
ΣREE	112.24	161.77	106.05	123.04	113.98	77.8	91.85	130.01	147.06	160.97	157.61	98.85	88.43

The trace element relationships illustrate the chemical coherence and uniformity of the Malužiná Formation sandstones.

Rare earth elements

The rare earth elements (REE) concentrations of the Malužiná Formation sandstones are shown as chondrite-normalized patterns in Fig. 5. The sandstones have REE contents, ranging between 39–208 ppm with an average of 114 ppm, comparable to average UCC (143 ppm; Taylor & McLennan 1985). The chondrite-normalized REE distribution patterns are about the same for all Malužiná Formation sandstones and are similar to that of the average Post-Archean Australian Shale (PAAS; Taylor & McLennan 1985). The sandstones

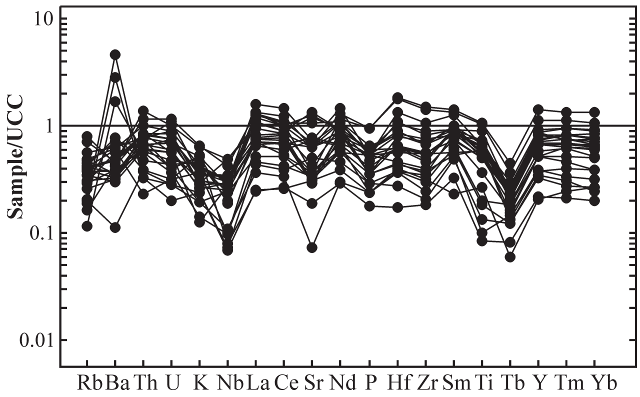

Fig. 4. Multi-element diagram of the Malužiná Formation sandstones normalized to the composition of the average upper continental crust (UCC). The elements are arranged from left to right in order of increasing compatibility in a small fraction melt of the mantle. The average UCC data are from Taylor & McLennan (1981).

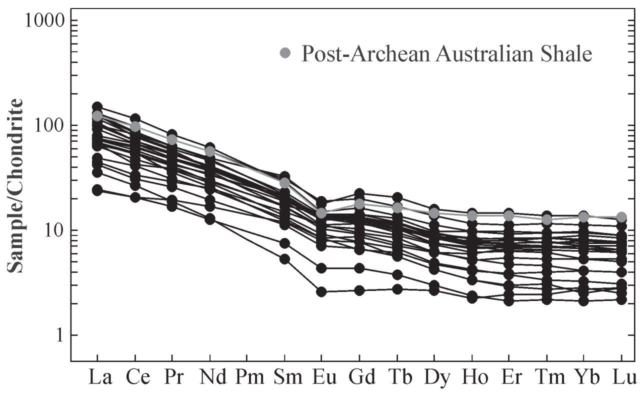

Fig. 5. Chondrite-normalized REE diagram for sandstone samples from the Malužiná Formation. Note the similarity in the patterns with LREE enrichment, flat HREE distributions and the ubiquitous negative Eu-anomaly. REE chondrite-normalizing factors are from Boynton (1984). Post-Archean Average Australian Shale values from Taylor & McLennan (1985).

show slight LREE-enriched and relatively flat HREE patterns with negative Eu anomalies (Fig. 5). Negative Eu anomalies are only very slightly marked.

Discussion

Sorting and weathering effects

The Th/U ratio in most upper crustal rocks is typically about 3.5 to 4.0 (McLennan et al. 1993). During sedimentation, U is readily oxidized to the soluble U^{6+} state and may be lost to ore deposits, leading to an elevation in the Th/U ratio. Thus, Th/U ratios may be useful in interpreting sedimentary recycling histories (McLennan et al. 1990). In sedimentary rocks, Th/U values higher than 4.0 may indicate intense weathering in source areas or sediment recycling, meaning derivation from older sedimentary rocks (Asiedu et al. 2000; Rahman & Suzuki 2007). Th/U ratios in the Malužiná Formation sandstones range from 2.9 to 7.9, with an average of 4.9, indicating the derivation of these sediments from unequally weathered fragments of the upper crust. The Th/U versus Th plot for the Malužiná Formation sandstones (Fig. 6) shows a typical distribution similar to the average values of fine-grained sedimentary rocks reported by Taylor & McLennan (1985) and follows the normal weathering trend (McLennan et al. 1993). The trend of depleted mantle sources in a few samples is derived from the addition of detrital material from the eroded synsedimentary continental tholeiites. This is also documented by the presence of basic volcanic rock fragments in our samples and by the occurrences of the Malužiná Formation sandstones along with basic volcanics and their tuffs which have a tholeiite magmatic trend (Fig. 1b; Vozár 1997; Dostal et al. 2003).

Since a number of heavy minerals are dominated by elements that are trace elements in most sedimentary rocks (e.g. Zr in zircon, REE in monazite and allanite), it is possible to evaluate the role of heavy mineral concentration during sedimentary sorting (McLennan 1989). The sedimentary sorting and recycling can be monitored by a plot of Th/Sc against Zr/Sc (McLennan et al. 1993). A simple positive correlation between Th/Sc and Zr/Sc ratios is exhibited by first-cycle sediments, whereas there is a substantial increase in Zr/Sc with far less increase in Th/Sc in recycled sediments (Asiedu et al. 2000; Rahman & Suzuki 2007). However, if first-cycle sediments are derived from largely plutonic sources, they could also show a trend of increased Zr/Sc and almost constant Th/Sc (Roser & Korsch 1999). On the Th/Sc versus Zr/Sc diagram, the Malužiná Formation sandstones follow a general trend which is consistent with that of first-cycle sediments (Fig. 7). This suggests their direct derivation from igneous and, according to our thin-section observations, also from metamorphic rocks. From Figs. 6 and 7 it can be, therefore,

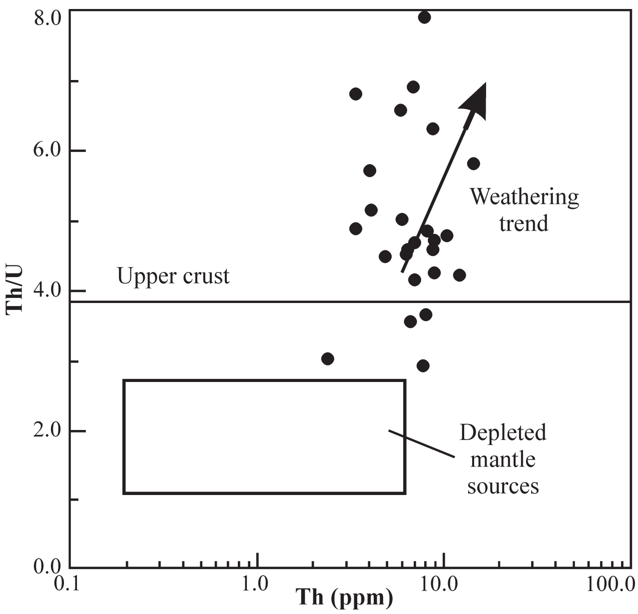

Fig. 6. Plot of Th/U versus Th for the Malužiná Formation sandstones (after McLennan et al. 1993).

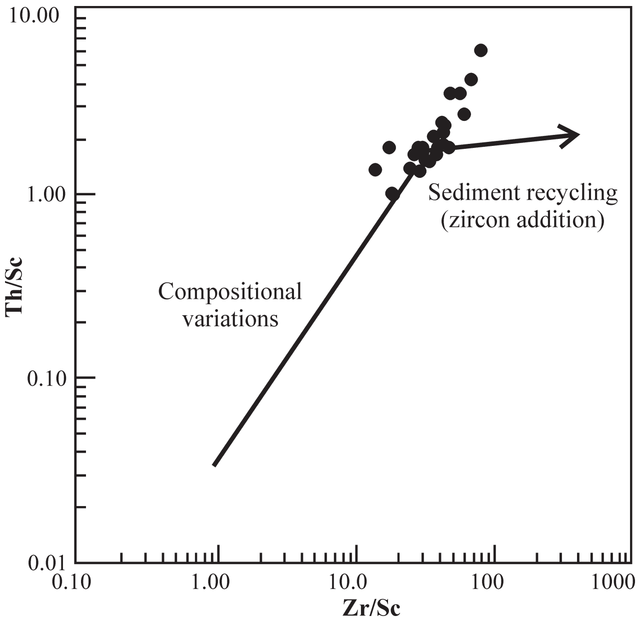

Fig. 7. Plot of Th/Sc versus Zr/Sc for the Malužiná Formation sandstones (after McLennan et al. 1993). Analysed sandstone samples, which are less affected by sedimentary sorting and recycling, show a simple correlation for these ratios. This relationship is interpreted as due to the compositional variations of the provenance.

inferred that the bulk of the Malužiná Formation sandstones were directly derived from igneous and metamorphic rocks that had undergone some degree of weathering.

Nesbitt & Young (1982, 1984, 1989) introduced a chemical index of alteration (CIA), which provides a means of quantifying the degree of weathering (chemical alteration) to which silicate materials have been subjected. The CIA is calculated according to $CIA=[(Al_2O_3)/(CaO^*+Na_2O+K_2O+Al_2O_3)]\times100$, where the oxides are expressed as molar proportions and CaO* is CaO in silicates only (as opposed to that in phosphates or carbonates). However, if $CaO<Na_2O$, then the molecular CaO is accepted as approximate CaO* (McLennan 1993). This applies to all studied Malužiná Formation sandstones. To calculate a reliable CIA, a rock needs to contain less than 75 wt. % SiO_2 and less than 1 wt. % CaO. Both these conditions are met for the majority of the studied sandstones (Table 1), making our interpretation of the CIA values reliable. High CIA values (i.e. 76–100) indicate intensive chemical weathering in the source areas. Conversely, low CIA values (i.e. 50 or less) indicate the near absence of chemical alteration or unweathered source areas, and consequently might reflect cool and/or arid conditions (Fedo et al. 1995). Low CIA values can also be interpreted as a result of an extremely high erosion rate. The CIA values for the Malužiná Formation sandstones vary from 45 to 68, with an average of 55, indicating low to moderate chemical weathering of the source area. Consequently, they reflect arid conditions and an extremely high erosion rate. The average CIA value (55) of the Malužiná Formation sandstones is comparable to those of feldspar (50), unweathered felsic plutonic and volcanic rocks (45–55) as well as the UCC (50) (Fedo et al. 1995). The CIA values of the studied sandstones are also plotted in the Al_2O_3–(CaO^*+Na_2O)–K_2O (A–CN–K) diagram (Fig. 8), which may express much of the chemical variation resulting from weathering. Unweathered rocks cluster along the left-hand side of the plagioclase-K-feldspar join line in the A–CN–K system (Nesbitt & Young 1984). The weathered material moves away from the source rocks along a line subparallel to the Al_2O_3–(CaO^*+Na_2O) join due to prior removal of Ca and Na in preference to Al and K (Fig. 8). The composition of the source rocks can also be predicted back along the trend. All the samples studied here plot a little away from the plagioclase-K-feldspar join line and parallel to the Al_2O_3–(CaO^*+Na_2O) edge, supporting the conclusion that the Malužiná Formation sandstones were derived from an intermediate igneous source terrain in general. Although the effect of post-depositional processes in altering the mineralogy and chemistry cannot be completely neglected, both the textural and the chemical immaturity of the investigated sandstones strongly suggest that their bulk chemistry, including the Na_2O enrichment (Table 1), was inherited from the source area.

The Rb/Sr ratios of sediments also monitor the degree of source-rock weathering (McLennan et al. 1993). During weathering (and in many cases, diagenesis), there is a substantial increase in the Rb/Sr ratio of most rocks. This is because Rb^+, a large alkali trace element (1.72 Å for 12-fold

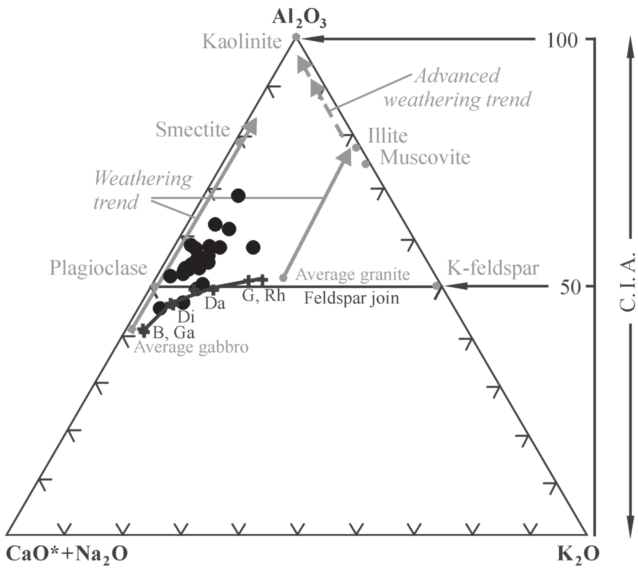

Fig. 8. The Malužiná Formation sandstones plotted on the Al_2O_3–(CaO^*+Na_2O)–K_2O diagram (A–CN–K) after Nesbitt & Young (1984, 1989) and Fedo et al. (1995). The relation between the CIA scale (Nesbitt & Young 1982) and the triangle is shown on the right side of the diagram. The A–CN–K diagram shows the weathering trends for average granite and average gabbro. The advanced weathering trend for granite is also shown. The solid line linking crosses is the compositional trend in pristine average igneous rocks (data of Le Maitre 1976). **B** — basalt, **Ga** — gabbro, **Di** — diorite, **Da** — dacite, **G** — granite, **Rh** — rhyolite. The horizontal solid line is the plagioclase-K-feldspar join. The data are plotted as molar proportions and the compositions of plagioclase, K-feldspar, muscovite, illite, kaolinite and smectite are shown. Modal carbonate cement is trivial, however, and the calculated proportions are thus close to actual values. CaO* represents the CaO associated with the silicate fraction of the sample.

coordination), is more readily retained on exchange sites of clays than the smaller Sr^{2+} (1.26 Å for eight fold coordination). The Malužiná Formation sandstones have an average Rb/Sr ratio of 0.29, and this value is close to that of the average upper continental crust (0.32) but significantly lower than the average Post-Archean Australian Shale (0.80; McLennan et al. 1983). This suggests that the degree of source area weathering was most probably low to moderate rather than intense.

The Al–Ti–Zr ternary diagram monitors the effects of sorting processes (Garcia et al. 1994). On this diagram, mature sediments consisting of both sandstones and shales show a wide range of TiO_2/Zr variations, whereas immature sediments of sandstones and shales show a more limited range of TiO_2/Zr variations (Asiedu et al. 2000). On the Al–Ti–Zr diagram, the Malužiná Formation sandstones are confined in the centre with a limited range of TiO_2/Zr variations, suggesting poor sorting and rapid deposition of the studied sandstones (Fig. 9). This is completely corroborated by their sedimentary structures and mineral composition.

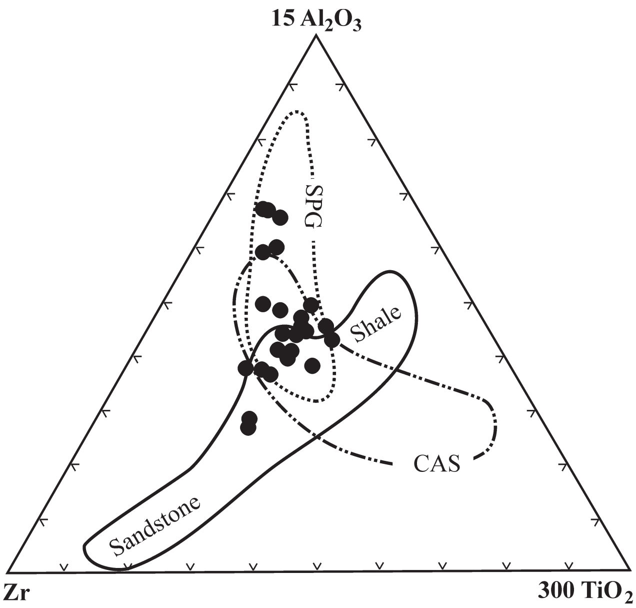

Fig. 9. Al–Ti–Zr plot for the Malužiná Formation sandstones. The solid contour refers to the observed range of compositions in clastic sediments. CAS refers to the fields of calc-alkaline suites and SPG refers to fields of strongly peraluminous granites (after Garcia et al. 1994).

Source-rock compositions and provenance

As apparent from the Results section and the previous chapter, the mineral and chemical composition of the Malužiná Formation sandstones is a record of characteristics of the source area. Therefore, whole-rock geochemistry of the investigated sandstones can be used as a suitable tool for unravelling their provenance. Our following interpretations based on chemical composition are in agreement with petrographic analysis which indicates that the detrital constituents of the Malužiná Formation sandstones were derived from a basement uplift and recycled orogen tectonic provenance (Fig. 10). These petrographical features imply a source area in which granitic and gneissic rocks plus sedimentary and metasedimentary rocks dominated, while andesitic to basaltic volcanic rocks were much less abundant.

The Malužiná Formation sandstones have high K_2O and Rb concentrations and a uniform K/Rb ratio of 242 that lies close to a typical differentiated magmatic suite or "main trend" with a ratio of 230 (Fig. 11; Shaw 1968). This feature emphasizes

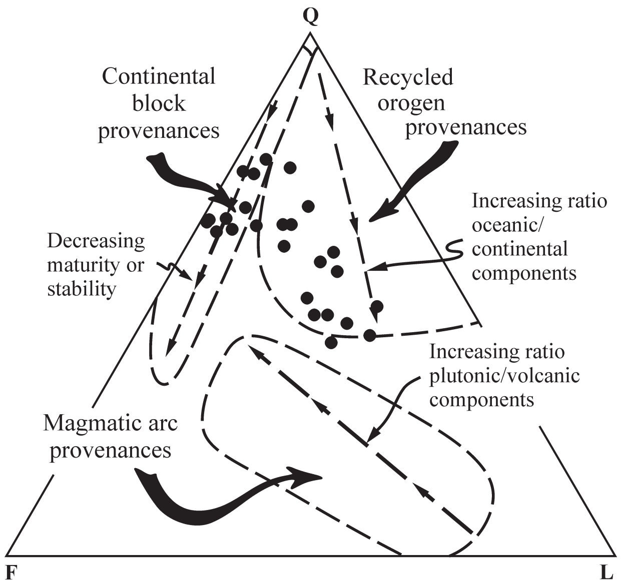

Fig. 10. Triangular QFL plot showing framework modes for the Permian Malužiná Formation sandstones: Q is total quartzose grains, including monocrystalline Qm and polycrystalline Qp varieties; F is total feldspar grains; L is total unstable lithic fragments. Provenance fields from Dickinson & Suczek (1979).

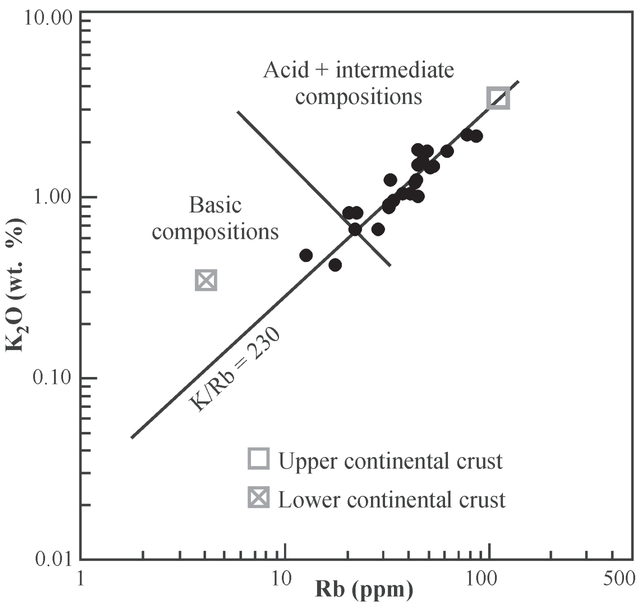

Fig. 11. Distribution of K and Rb in the Malužiná Formation sandstones relative to a K/Rb ratio of 230 (= main trend of Shaw 1968). Average upper and lower continental crust from Taylor & McLennan (1985).

the chemically coherent nature of the sandstones and derivation mainly from acid to intermediate magmatic rocks. As mentioned above, the original material of the Malužiná Formation sandstones was only slightly weathered and was deposited rapidly. Therefore, there was no further redistribution in or component removal from the original material. The uniform K/Rb ratio indicates that diagenesis and very low-grade metamorphism was isochemical in the Malužiná Formation, and there was no or very little elemental redistribution.

A plot of La/Th against Hf (Fig. 12) provides a useful tool for bulk rock discrimination between different arc compositions and sources (see also Asiedu et al. 2000). Felsic composition-dominated arcs have low and uniform La/Th ratios (less than 5) and Hf contents of about 3–7 ppm. With the progressive unroofing of the arc and/or incorporation of sedimentary basement rocks, the Hf content increases via the release of zircon (Floyd & Leveridge 1987). The compositions of the Malužiná Formation sandstones suggest derivation mainly from felsic igneous rocks with minor mafic input (Fig. 12). This minor mafic input is also documented by the scarce occurrences of basic lathwork rock fragments in the framework

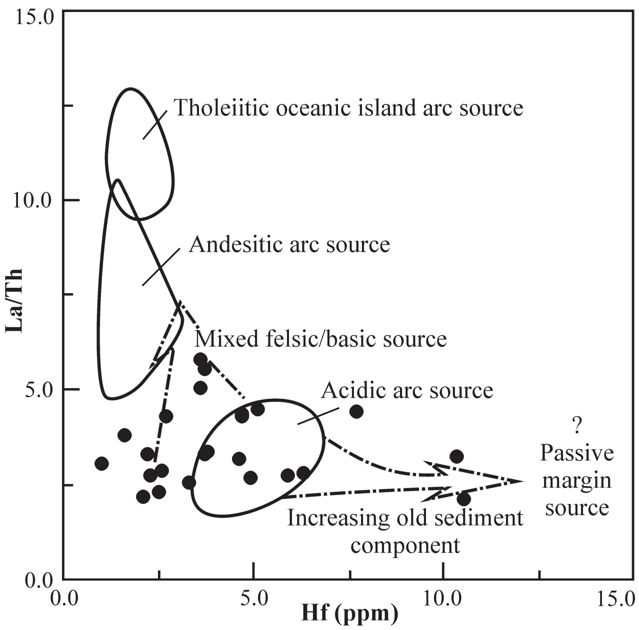

Fig. 12. Plot of La/Th versus Hf for the Malužiná Formation sandstones (compositional fields are after Floyd & Leveridge 1987).

of the studied sandstones. Only two samples have Hf concentrations above 10 ppm, which is much higher than considered to be typical of felsic rocks. This may be indicative of a passive margin tectonic setting and a sedimentary source, which is well-documented by our observations of sedimentary rock fragments in thin sections from these sandstones.

The ferromagnesian trace elements Cr, Ni, Co, and V show a generally similar behaviour in magmatic processes, but they may be fractionated during weathering (Feng & Kerrich 1990). Very high levels of Cr and Ni have been used by various authors (e.g. Hiscott 1984; Wrafter & Graham 1989) to infer an ultramafic provenance for sediments. The elevated values of Cr (>150 ppm) and Ni (>100 ppm) and a ratio of Cr/Ni between 1.3–1.5 are diagnostic of ultramafic rocks in the source region (Garver et al. 1996). Higher Cr/Ni ratios probably indicate derivation of these elements from mafic volcanic rocks (Garver & Scott 1995). The Malužiná Formation sandstones have low levels of Cr (14–109 ppm; on average 43 ppm) and Ni (5–19 ppm; on average 10 ppm), and Cr/Ni ratio of 4.61. This may suggest either a minor amount of mafic input into the depositional system or else that trace elements could have travelled into the depositional basin as adsorbed ions on clays (McCann 1991). Vanadium concentrations (8–57 ppm; on average 33 ppm) of the Malužiná Formation sandstones are relatively higher than the levels commonly recorded in sediments (about 20 ppm), and given that V is concentrated in mafic rocks, they suggest some mafic input into the depositional system (McCann 1991). On the other hand, the slightly higher content of vanadium in our samples may also be a result of concentration of heavy minerals.

The high field strength elements (HFSE) such as Zr, Nb, Hf, Y, Th are preferentially partitioned into melts during crystallization (Feng & Kerrich 1990), and as a result these elements are enriched in felsic rather than mafic sources. These elements are thought to reflect provenance compositions as a consequence of their generally immobile behaviour (Taylor & McLennan 1985). The REE and Sc also give an indication of source compositions because of their relatively low mobility during sedimentation (Bhatia & Crook 1986). REE and Th abundances are higher in felsic than in mafic igneous source rocks and in their weathered products, whereas Co, Sc, and Cr are more concentrated in mafic than in felsic igneous rocks and in their weathered products. Mafic and felsic source rocks differ significantly in their ratios of Eu/Eu*, La/Sc, Th/Sc, La/Co, Th/Co, and Cr/Th and hence provide useful information about the provenance of sedimentary rocks (e.g. Cullers

Table 2: Range of elemental ratios of the Permian Malužiná Formation sandstones compared to elemental ratios in sediments derived from felsic rocks, mafic rocks, and in the upper continental crust.

Elemental ratio	Malužiná Formation sandstones (n = 25)	Ranges in sediments from felsic sources[1]	Ranges in sediments from mafic sources[1]	Upper continental crust[2]
Eu/Eu*	0.64–0.97	0.40–0.94	0.71–0.95	0.63
La/Sc	3.17–19.70	2.50–16.3	0.43–0.86	2.21
Th/Sc	0.98–5.90	0.84–20.5	0.05–0.22	0.79
La/Co	2.22–24.63	1.80–13.8	0.14–0.38	1.76
Th/Co	0.74–7.38	0.04–3.25	0.04–1.40	0.63
Cr/Th	1.67–15.86	4.00–15.0	25.00–500	7.76

[1] — After Cullers et al. (1988), Cullers (1994, 2000), and Cullers & Podkovyrov (2000). [2] — After Taylor & McLennan (1985) and McLennan (2001).

et al. 1988; Cullers 1994, 2000; Cullers & Podkovyrov 2000). In this study, the Eu/Eu*, La/Sc, Th/Sc, La/Co, Th/Co, and Cr/Th values of the Permian Malužiná Formation sandstones are more similar to values for sediments derived from felsic source rocks than to those for mafic source rocks (Table 2), suggesting prevalent derivation from felsic source rocks. The higher LREE/HREE ratios and negative Eu anomalies (0.64–0.97) of the Malužiná Formation sandstones also bear the characteristics of felsic source rocks (after Taylor & McLennan 1985; Wronkiewicz & Condie 1989).

A discriminant function diagram has been proposed by Roser & Korsch (1988) to distinguish between sediments whose provenance is primarily mafic (first-cycle basaltic and lesser andesitic detritus), intermediate (dominantly andesitic with subordinate rhyolitic and dacitic detritus) or felsic igneous (acid plutonic and volcanic detritus) and quartzose sedimentary (mature polycyclic quartzose detritus). Their study was based upon 248 chemical analyses in which Al_2O_3/SiO_2, K_2O/Na_2O and $Fe_2O_{3(tot)}+MgO$ proved the most valuable discriminants. A plot of the first two discriminant functions based upon the oxides of Ti, Al, Fe, Mg, Ca, Na and K most effectively differentiates between the four provenances (Fig. 13). In this diagram, the majority of the Malužiná Formation sandstones plot on the felsic igneous provenance field suggesting that the source area for the Malužiná Formation sandstones had an average felsic composition. Using the ratio discrimination diagram in which discriminant functions are based upon the ratios of TiO_2, $Fe_2O_{3(tot)}$, MgO, Na_2O and K_2O all to Al_2O_3 (Fig. 14), the Malužiná Formation sandstones plot in the felsic and intermediate igneous provenance fields. This distribution may indicate a significant contribution of detritus

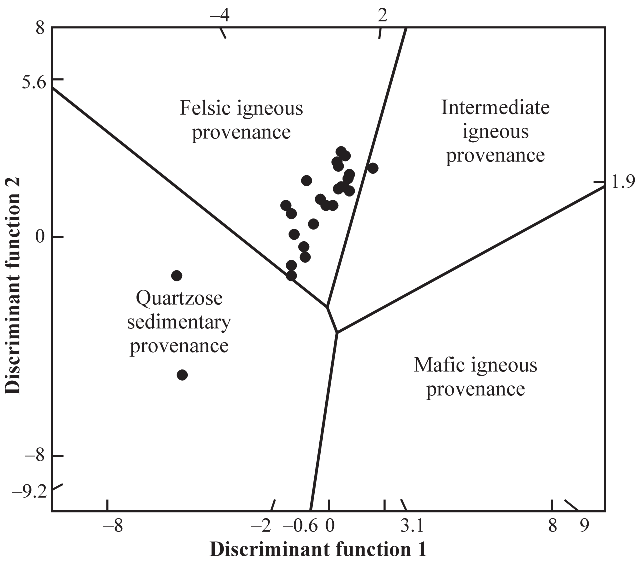

Fig. 13. Discriminant function diagram using major elements for the provenance signatures of the Malužiná Formation sandstones (diagram after Roser & Korsch 1988). Fields for predominantly mafic, intermediate and felsic igneous provenances are shown with the field for a quartzose sedimentary provenance. The Malužiná Formation sandstones plot in the felsic igneous provenance field demonstrating that they are derived from a silicic crystalline (plutonic-metamorphic) terrain with a lesser intermediate-acid volcanic component.

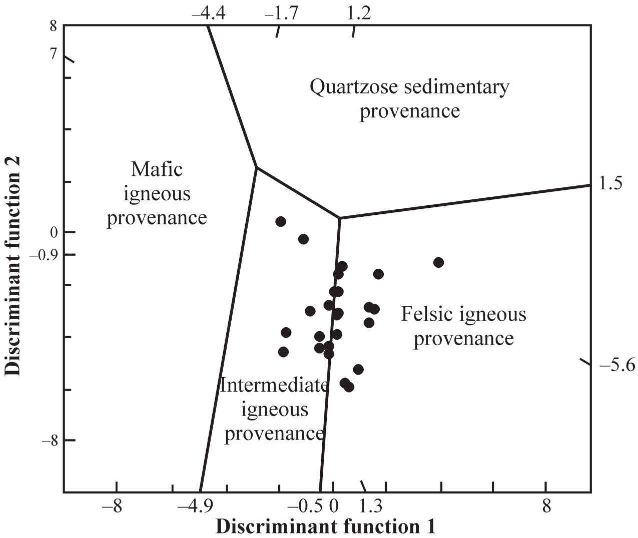

Fig. 14. Discriminant function diagram using major element ratios for the provenance signatures of the Malužiná Formation sandstones (diagram after Roser & Korsch 1988). Fields for dominantly mafic, intermediate and felsic igneous provenances are shown with the field for a quartzose sedimentary provenance.

from continental transform boundaries or rifted continental margins. Both these tectonic settings expose deep-seated plutonic rocks with dominant feldspathic detrital material.

Figure 4 shows a multi-element diagram of the Malužiná Formation sandstones normalized to the average UCC (Taylor & McLennan 1981). The figure shows that, with the exception of the high Ba values and low Nb, Sr and Tb values, the Malužiná Formation sandstones have compositions similar to those of the average UCC and PAAS. This feature indicates that the sandstones were derived mainly from the upper continental crust, for which granitic composition is characteristic. As discussed earlier, the high Ba values for the Malužiná Formation sandstones reflect a significant presence of K-feldspar.

Tectonic setting of source area

The mineralogy of the Malužiná Formation sandstones clearly indicates their derivation from predominantly acid igneous rocks, with less admixture of clastic detritus from synsedimentary acid to intermediate/basic volcanic rocks and from low-grade metasedimentary rocks. According to the interpretations of Dickinson & Suczek (1979), Dickinson et al. (1983) and Ingersoll (1990), these types of clastic detritus may be derived from uplifted basement blocks or a rifted continental margin (Fig. 10). The latter tectonic setting and rapid erosion and transport are also well-documented by the compositional diagnostic features of the Malužiná Formation sandstones, which include the lowest polycrystalline/monocrystalline quartz ratios, the lowest content of lithic fragments, and nearly equal amounts of plagioclase and alkali feldspars.

Although most studies of tectonic setting of the source area have relied on interpretations based upon sandstone mineralogy, several studies have shown that major- and trace-element geochemistry also reflect provenance differences that depend upon tectonic setting (e.g. Bhatia 1983; Bhatia & Crook 1986; Roser & Korsch 1986; Skilbeck & Cawood 1994). Both trace elements (particularly relatively immobile elements such as La, Y, Th, Zr, Hf, Nb, Ti, and Sc) and major elements have proved to be useful in studies of the tectonic setting of the source area.

The SiO_2 content and K_2O/Na_2O ratios in sandstones appear to be particularly sensitive indicators of geotectonic setting of the source area. Roser & Korsch (1986) present a chemical model, based on K_2O/Na_2O ratios and SiO_2 content, for discriminating the tectonic setting of the source area (Fig. 15). By using these chemical parameters, they were able to discriminate between samples from three major tectonic settings: passive margin (PM), active continental margin (ACM), and oceanic island arc margin (ARC). Some overlaps occur between the composition fields shown in Fig. 15, but overall the discriminating power of the technique appears to be reasonably good (Armstrong-Altrin & Verma 2005; Boggs 2009). On a K_2O/Na_2O versus SiO_2 diagram, the Malužiná Formation sandstones may be classified as having an active continental margin provenance (Fig. 15). Hence the Malužiná Formation sandstones may represent quartz-intermediate sediments derived from a tectonically active continental margin adjacent to active plate boundaries.

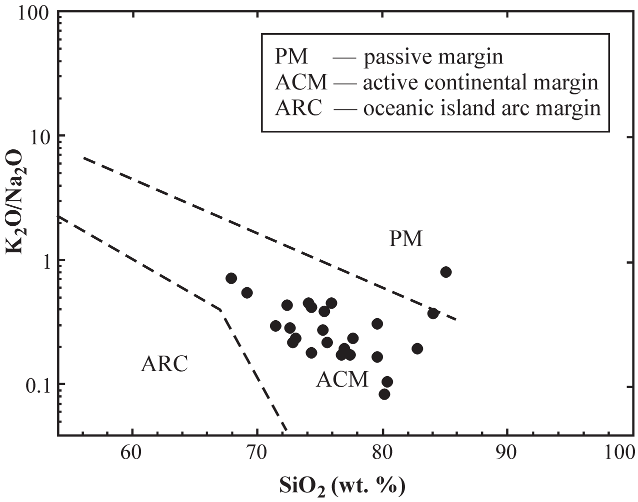

Fig. 15. Tectonic discrimination diagram of Roser & Korsch (1986) for the Permian Malužiná Formation sandstones.

Sandstones from oceanic island arc, continental island arc, active continental margin, and passive margin settings are variable in composition, particularly in their $Fe_2O_{3(tot)}+MgO$, Al_2O_3/SiO_2, K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ contents. Bhatia (1983) used this chemical variability to discriminate between the different tectonic settings on a series of bivariate plots, two of which are shown in Fig. 16. On these plots, most of the Malužiná Formation sandstones fall in the general area of active continental margin field (Fig. 16).

Bhatia & Crook (1986) identified the elements La, Th, Zr, Nb, Y, Sc, Co and Ti as the most useful in discriminating between sandstones from different tectonic environments. Distinctive fields for four environments — oceanic island arc, continental island arc, active continental margin and passive margin — are recognized on bivariate plots of La vs. Th, La/Y vs. Sc/Cr, Ti/Zr vs. La/Sc and the trivariate plots La–Th–Sc, Th–Sc–Zr/10 and Th–Co–Zr/10. On a Ti/Zr vs. La/Sc plot (Fig. 17), the Malužiná Formation sandstones again plot mainly in the field of active continental margin sediments. This distribution suggests that substantial amounts of detritus were derived from acid igneous rocks of a dissected magmatic arc and from granite-gneisses and siliceous volcanics of an uplifted

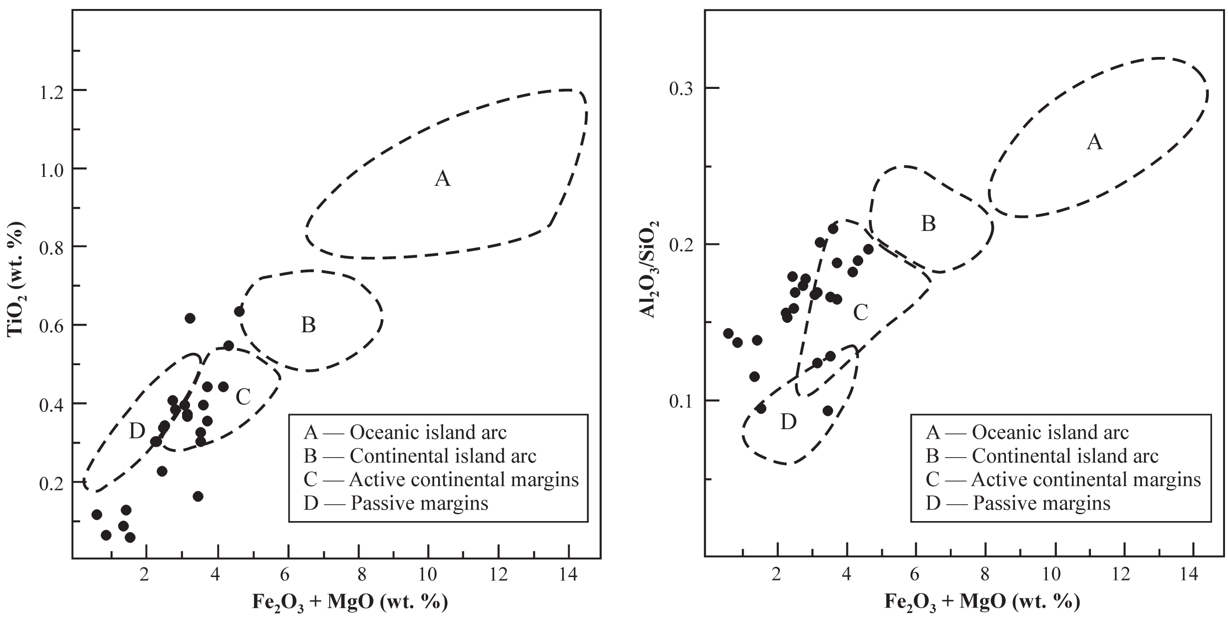

Fig. 16. Major element composition plots of the Malužiná Formation sandstones for tectonic setting discrimination (after Bhatia 1983). Plot of TiO_2 and Al_2O_3/SiO_2 versus Fe_2O_3+MgO. (Fe_2O_3 represents total iron as Fe_2O_3.) Dashed lines mark the major fields representing various tectonic settings.

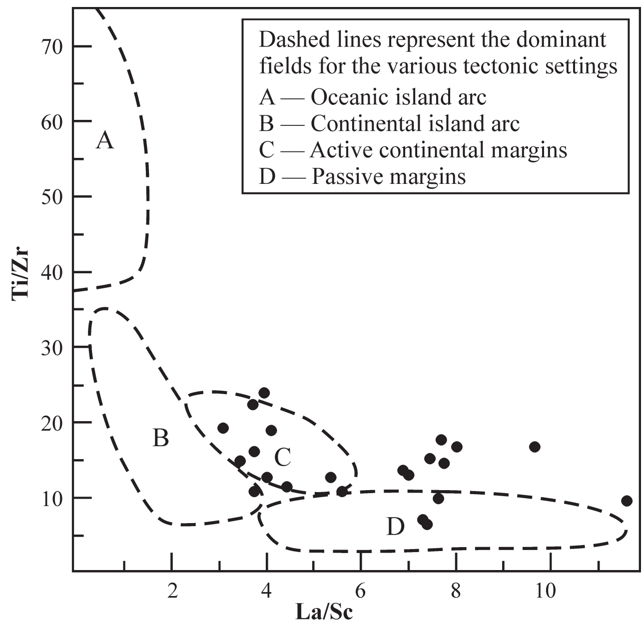

Fig. 17. Ti/Zr versus La/Sc plot of the Malužiná Formation sandstones for tectonic setting discrimination (after Bhatia & Crook 1986).

basement. The original depositional basin of the Malužiná Formation sandstones was probably developed on a rifted thick continental crust behind an active continental margin. This tectonic setting can also comprise rocks of older fold belts. The present interpretation is in good agreement with previous studies (Vozárová & Vozár 1988; Vozár 1997; Dostal et al. 2003).

Paleogeographical reconstruction

The Permian sedimentary basin of the Malužiná Formation originated as a consequence of post-Variscan extensional tectonics. It was a part of a large geodynamic zone connected with the internal part of the Variscan orogenic domain, in which rift-related and strike-slip continental post-orogenic basins were developed during the Pennsylvanian-Permian period (Vozárová et al. 2009). Relics of the volcano-sedimentary Malužiná Formation sequences are present in the Western Carpathians within the basal part of the Hronicum rootless nappe system. The mineral composition and geochemistry of the Malužiná Formation sandstones permitted us to interpret the character of the original basement rocks. With respect to our results, the Malužiná rift system originated on a high-grade crystalline core complex penetrated with huge masses of syn- and late-orogenic igneous rocks, what is characteristic for the Variscan terranes of the Central Western Carpathians (Biely et al. 1996; Vozárová et al. 2009 and references therein). The axial part of the former rift-trough is designated by the occurrences of continental tholeiites, from which a variable amount of clastic grains were derived into the former sedimentary basin. The small admixture of low-grade metasedimentary lithic fragments could be derived from the Variscan orogenic zone. Based on these facts we suppose that the Hronicum rift-related basin originated on the continental crust parallel to the Variscan orogenic belt.

Conclusions

The geochemistry of the Permian sandstones from the Malužiná Formation in the Malé Karpaty Mts was studied to determine their source-area weathering, provenance, and the tectonic setting of the source area.

The Permian Malužiná Formation sandstones have dominantly quartzofeldspathic and quartzolithic composition with predominance of quartz. They are classified as arkose, subarkose, lithic subarkose, and feldspathic litharenite. The Malužiná Formation sandstones contain abundant feldspars, volcanic, fine-grained igneous (aplitic) and metasedimentary lithic grains, indicating that the detrital constituents were derived from a basement uplift and recycled orogen tectonic provenance.

The CIA values for the Permian Malužiná Formation sandstones vary from 45 to 68 with an average of 55, indicating low to moderate chemical weathering of their source area. Consequently, they reflect arid conditions and an extremely high erosion rate. The average CIA value (55) is a little above than that of the CIA value (50) of the upper continental crust.

Eu/Eu*, La/Sc, Th/Sc, La/Co, Th/Co and Cr/Th ratios indicate derivation of these sandstones from felsic source rocks. In the same way, the predominantly felsic composition of the Malužiná Formation sandstones is supported by the REE plots. Thus, the existence of huge complexes of mafic/ultramafic rocks in the source region is most unlikely.

The geochemical characteristics preserve the signatures of a felsic and intermediate igneous provenance for the Permian Malužiná Formation sandstones. This is in good agreement with framework mineralogy. Tectonic discrimination diagrams suggest mostly an active continental margin setting for the Malužiná Formation sandstones.

The Malužiná Formation sandstones were derived especially from fault-bounded, uplifted basement areas in continental-block provenances, where high relief and rapid erosion of uplifted sources gave rise to quartzofeldspathic sands of classic arkosic character. The Malužiná Formation sandstones could have been accumulated in basins related to transform ruptures of continental blocks, incipient rift blocks, or zones of wrench tectonism within continental interiors.

The Malužiná rift system originated on a high-grade crystalline core complex penetrated with huge masses of syn- and late-orogenic igneous rocks, as characteristic for the Variscan terranes of the Central Western Carpathians. A variable amount of clastic grains were derived from the continental tholeiites into the former sedimentary basin. The small admixture of low-grade metasedimentary lithic fragments could be derived from the Variscan orogenic zone. We suppose that the Hronicum rift-related basin originated on the continental crust parallel to the Variscan orogenic belt.

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