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Paleogeography of the Cretaceous karst in the light of geochemical methods

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Abstract. Grain-size, trace and major elements of red clays and bauxites of Cretaceous age, forming the infilling of karstic traps in Middle/Uppper Triassic carbonates were analysed. The aim of the work is to answer open paleogeographical questions: 1. autochthony or allochthony of the infillings, 2. their facial characteristics, 3. characterize the source areas, 4. contribute to the question of the age of the infillings.

Key words: karstic traps infillings, major and trace elements

Introduction

Karst sediments of Cretaceous age are conserved only rudimentary in different kinds of karst depressions. The sedimentary traps represent a scale of different karst hollows/fissures, widened by karst dissolution, shallow doline-like and deeper, canyon-like depressions. This study covers the geochemistry of the karstic traps infillings. (Fig. 1)

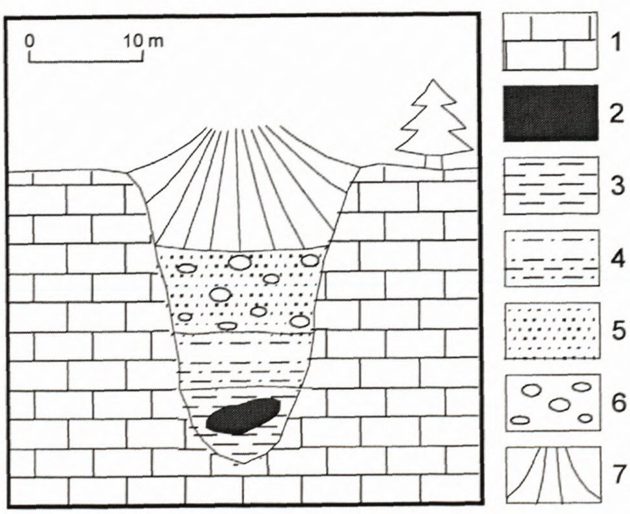

Fig. 1 Schematic cross-section of a canyon-like depression W of Brezová pod Bradlom
1 – Hauptdolomite (Norian), 2 – bauxite, 3 – bauxitic clay, 4 – kaolinic clay, 5 – illitic/smectitic clay (pre-Upper Cretaceous), 6 – Valchov Conglomerate (Upper Cretaceous), 7 – debris

Methods

The infillings of karstic traps -red ferrugineous clays or silty clays and rather rare lens-shaped boehmite-kaolinite bauxite- were analysed in regard of grain-size distribution, clay minerals, trace and major elements.

The grain size of the samples was determined by the pipet method for three grain–size fractions.

The mineralogical composition of the samples studied was determined by means of X-ray diffraction. Philips PW 1710 diffractometer was used to this purpose. Whole-rock powdered preparations and separated samples <2μm were examined. Prior to separation of fractions by the sedimentation method, the samples were prepared by ultrasonic disintegration. The suspension obtained was coagulated and finally transformed into homoionic Na form by 1 M solution of NaCl. The excess of salt was removed by washing with distilled water, and the process was checked by means of chloride ions, using $AgNO_3$.

Preparation for X-ray diffraction analysis were prepared by sedimentation of clay suspension (10 mg.cm^{-2}) on glass slides. The specimens were analysed in their natural state and after saturation with ethylene glycol vapour for 8 hours at a temperature of 60° C.

Major elements were analysed on the X-ray spektrometer Philips PW 1410/20 (X-ray tube with Rh anode, gas flow detector with Ar/CH_4=90/10 filling, LiF200 and TlAP crystals). The samples were analysed in the form of solid solution with $Li_2B_4O_7$.

Trace elements were determined by optical emission spectroscopy (using the spectrograph PGS-2 in ultraviolet and visible ranges). The results were checked by the analysis of the standard samples KK (kaolinite Karlovy Vary) and TB (slate).

Aim of the work

The Paleoalpine collision caused partial stabilization leading to the individualization of the Central Western Carpathians (CWC) into quasiplatform basement and to the subsequent geocratic regime (Činčura, 1988). Surface and near subsurface zones of the basement were composed to a great extent of carbonate complexes. Favourable lithology, tectonics and climate conditioned the origin of the Cretaceous, Paleolpine karst. The lower boundary of the Paleoalpine karst period is age-determined by the gradual emergence and termination of the marine deposition in the main tectonic units of the

Western Carpathians (Činčura & Köhler, 1995). The pre-Gosau and/or pre-Paleogene karst is developed on the carbonate complex of Middle/Upper Triassic age of the Hronic and Silicic superficial nappe systems. The presence of the Paleoalpine karst period is proved mainly by different corrosional karst forms and partly also by karst sediments-infillings of karstic traps.

The aim of our work is above all to answer open paleogeographical questions:

1. autochthony or allochthony of the infillings of the karstic traps, 2. facial characteristics of the infillings, 3. characteristics of source areas, 4. contribute to the question of the age of the infillings.

Analytical results and discussion

1. Autochthony versus allochthony. Limestones (Gutenstein, Annaberg, Reifling, Wetterstein) of Middle/Upper Triassic age, surrounding the infillings of the karstic traps have low insoluble residua contents, which is a characteristic feature of shelf carbonates where the supply of clastic material is minimal. Insoluble residues of the Gutestein, Annaberg, Reifling and Wetterstein Limestones in Malé Karpaty Mts. consist exclusively of clay material (Lintnerová et al., 1988). Similar results were obtained also from other localities. Red clays/silty clays occurring in the karstic traps represent a two- to three component system in which the clay fraction is predominant (up to 75-80%). The content of silt particles is relatively constant (15-18%), nevertheless, there are, some sporadic cases when the quantity of silt increases to over 20%. The content of sand particles as a rule varies between 5-7%, and only sporadically exceeds 10%. In contrast to the insoluble residue of underlying limestones which has a clayey character, the red infillings contain also abundant admixture of silt as well as sandy grains. The silt and sand particles of the infillings could not have originated from limestones (Fig. 2).

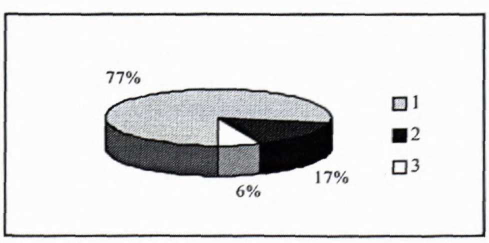

Fig. 2 Average grain size distribution of the red clays 1– clay, 2 – silt, 3– sand

Clay material of the insoluble residue of the different limestones consists generally of a monotonous mineral assmblage, for example illite and a small quantity of chlorite (cf. Lintnerová et al., 1988). There is a much wider range of clay minerals present in the red infillings, while the mineralogical composition varies relatively strongly from place to place. The infillings differ generally (mineralogy, trace elemensts) from the insoluble residues (Činčura & Šucha, 1992, Činčura & Puškelová, 1999). This finding indicates, that the infillings do not represent a product of weathering in situ. In assessing the problem of allochthony or autochthony we consider rapid changes in the mineralogical composition of clay minerals of individual samples to be significant factors of allochthony. Trace elements of the infillings differ considerably from the insoluble residues of underlying limestones.

2. The facial characteristics of the infillings. The presence of bauxite in the sedimentary traps, the relatively high contents of Al_2O_3, Fe_2O_3, TiO_2 as well as the dominance of kaolinite in many samples indicates, that the infillings are products of intensive weathering on land, in conditions of a warm climate. A warm, alternating wet and dry climate has been essential to reduce the parent material to the final aluminum hydroxides (boehmite). Boehmite is the main alumina mineral of the bauxite from Brezová pod Bradlom. The trace elements, which may reflect facial conditions (gallium, strontium), as well as source areas (vanadium, nickel, chromium, zirconium) were studied separately. The red infillings are enriched also in vanadium, nickel, chromium, zirconium, titanium and gallium. In comparing the chemical composition of bauxite and red clays, it is possible to see significant differences (Tab. 1). The most marked differences are in the contents of Al_2O_3, Fe_2O_3 and SiO_2. In contrast, areas with carbonate rocks, e. g. the superficial nappes of Hronic and Silicic are marked by low concetrations of Al_2O_3, Fe_2O_3, TiO_2. In the karst bauxite from Brezová pod Bradlom a positive correlation has been found between the Al_2O_3, Fe_2O_3, and TiO_2 contents. For facial analysis from trace elements, we can rely on gallium and stronctium. The lower content of strontium, as well as the high content of gallium in the red clays/silty clays point rather to a fresh water environment during the transport of material to karstic traps (Činčura & Puškelová, 1999). (Fig.3)

3. The characteristics of source areas. Differences in the values of contents of trace elements characterizing the source rocks, may bear wittness to different materials, which give the source for the infillings of the traps. Vanadium, nickel and chromium are ranked among trace elements whose distribution is mostly affected by the nature of parent rocks in the original source areas. The extraordinary high content of nickel 213-494 ppm, chromium 42-231 ppm, vanadium 342-630 ppm in the bauxite and the raised content of nickel 62-207 ppm, chromium 76-191 ppm, vanadium 132-276 ppm in the red clays/silty clays, indicate that the source material for the infillings was marked by a significant proportion of alkaline eruptive rocks. In relation to the geology of the Hronic, above all the basalts of Ipoltica Group of Permian age should be taken into account (cf. Vozárová & Vozár, 1988). This possibility also appears to be real, from a comparison of the trace element contents, directly with the basalts mentioned. The content trends are mutually quite compatible.

4. Age of the infillings of karstic traps. The lower boundary of the Paleoalpine karst period is age-determined by the gradual emergence and termination of the marine deposition in the main tectonic units of the Western Carpathians. As overlying rocks of the karstic traps infillings often occur: 1.Valchov Conglomerates, the

Tab. 1: Contents of some major and trace elements in bauxites and red clays, Malé Karpaty Mts.

Bauxites

		ČIN-1	ČIN-2	ČIN-3	ČIN-4	ČIN-5	BRE 101	BRE 103	BRE 105	BRE 106	BRE 107
SiO_2	%	22,89	23,02	22,41	24,67	22,39	22,62	25,63	31,84	25,62	27,30
TiO_2		1,88	1,88	2,00	1,87	1,97	2,25	2,14	1,91	2,30	2,06
Al_2O_3		41,48	40,12	40,60	38,90	39,84	42,32	39,46	37,11	38,83	38,80
Fe_2O_3-tot		15,53	16,25	16,24	15,64	16,58	16,77	15,93	12,81	17,08	14,51
Ga	ppm	26	31	31	26	25	56	42	39	65	41
Sr		134	61	61	95	40	393	248	305	500	389
V		630	562	417	354	468	506	342	440	529	380
Ni		238	218	213	234	240	393	350	358	494	389
Zr		690	793	723	707	954	211	253	326	278	354
Cr		95	42	53	66	48	124	116	116	231	123

Red clays

		V8-č2	V8-č3	V8-č4	V8-č5	V8-č6	V8-č7	BRE 102	BRE 108	BRE 112	BRE 113	MKP-1
SiO_2	%	47,05	45,97	48,72	46,25	55,09	54,20	37,37	40,09	37,98	36,23	50,07
TiO_2		0,76	0,79	0,79	0,84	1,04	0,85	1,68	1,52	1,51	1,75	0,86
Al_2O_3		22,03	22,59	21,21	21,90	18,56	17,12	33,59	30,30	33,23	33,64	23,12
Fe_2O_3-tot		8,40	9,10	9,01	8,84	8,11	9,46	10,62	9,09	9,15	10,82	8,15
Ga	ppm							28	19	33	46	20
Sr		36	48	48	41	48	64	155	153	172	233	219
V		157	173	150	132	137	132	245	183	299	261	276
Ni		84	79	84	69	63	62	182	110	207	198	78
Zr		637	298	301	223	555	428	79	68	101	128	418
Cr		133	191	154	156	124	121	76	84	101	119	93

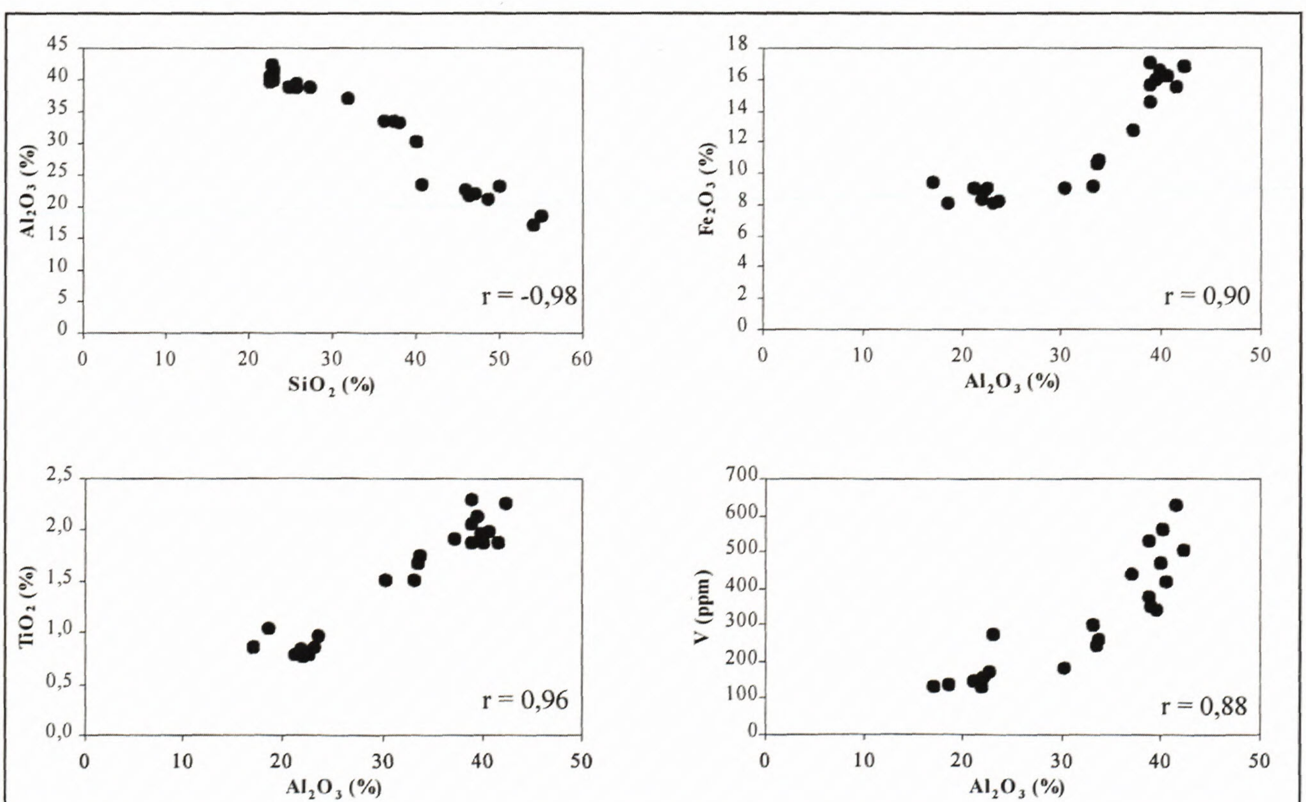

Fig. 3 Correlation between Al_2O_3 and various elements in the infillings of karstic traps, Malé Karpaty Mts.

lithostratigraphical equivalent of the basal conglomerates of the „Tiefere Gosau„ (Coniac) of the Northern Calcareous Alps in Austria. Coarse to medium grained Valchov Conglomerates pass sometimes into breccias. Their clasts (different limestones and dolomites - 60-75% of Triassic, 25-30% of Jurassic age, the rest form eruptive rocks) are unsorted or badly sorted, angular to subangular (Salaj et al., 1987). The changing matrix of the Valchov Conglomerates is formed by red ferruginous clay and/or silty clay, or fine clasts of limestone, dolomite and quarz. 2. Borové Formation, which represents the basal part of the transgressive Paleogene sequence. It consists of carbonate breccias, conglomerates and carbonatae sandstones, followed by organogene and organodetrital limestones (Gross & Köhler, 1991). The organogene and organodetrital limestones of Borové Formation are not karstified. In both cases is the infilling of the karstic traps older than the overlying rocks.

Conclusions

1. Grain-size analyses explicitly prove that silt and sand particles of the infillings could not have originated from the surrounding and underlying limestones. The results of analyses (grain-size, mineralogy, trace and major elements) speak for the allochthony of the material of the fillings of karstic traps.

2. The material of weathering crusts on non-carbonate rocks was transported during the dry season by wind, or washed onto the carbonate karst surface by areal waterflows during the wet season of the year and caught in the karstic traps.

3.. The infillings are products of a warm, alternating wet and dry climate with monsoonal features which prevailed not only during the pre-Gosau period, but probably also during the Late Cretaceous.

4. As the trace elements indicate the source material for the infillings was marked by a significant proportion of alkaline eruptive rocks. In relation to the geology of the Hronic superficial nappe, the basalts of Ipoltica Group of Permian age should be taken into account.

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