

Introduction

Fresh-water, coarse-grained and detritus-dominated Mura Formation in North-Eastern Slovenia includes pyroclastic and volcanoclastic deposits originating from Upper Pliocene volcanic activity of basaltic geochemical character. Although localized in occurrence at the hamlet Grad, these pyroclastic and volcanoclastic sediments form a distinctive depositional unit, for which the term "Grad Member" is proposed and introduced in this paper.

Upper Pliocene Grad Member consists of pyroclastic, syn-eruptive resedimented volcanoclastic and mixed volcanoclastic-fluvial deposits. Their formation is closely related to continental alkali basaltic volcanism which

was active about 3 million years ago in the area of the present medieval castle and the surrounding hamlet Grad in Goričko, North-Eastern Slovenia. The volcanism forms a part of a broader volcanic province encompassing South Styrian Basin (Pöschl, 1991; Winkler, 1927; Poulditis, 1981; Poulditis & Scharbert, 1986) and Little Hungarian Plain (Martin & Németh, 2004), and developed as a consequence of post-collisional extension of the south-western realm of the Pannonian Basin.

At the present, no lavas are preserved in the Grad area, but only their fragmented remains (Plate 1 – Fig. 1) in volcanoclastic debris flow deposits. For this reason, doubts have been posed again recently about the existence of local volcanic centre in the

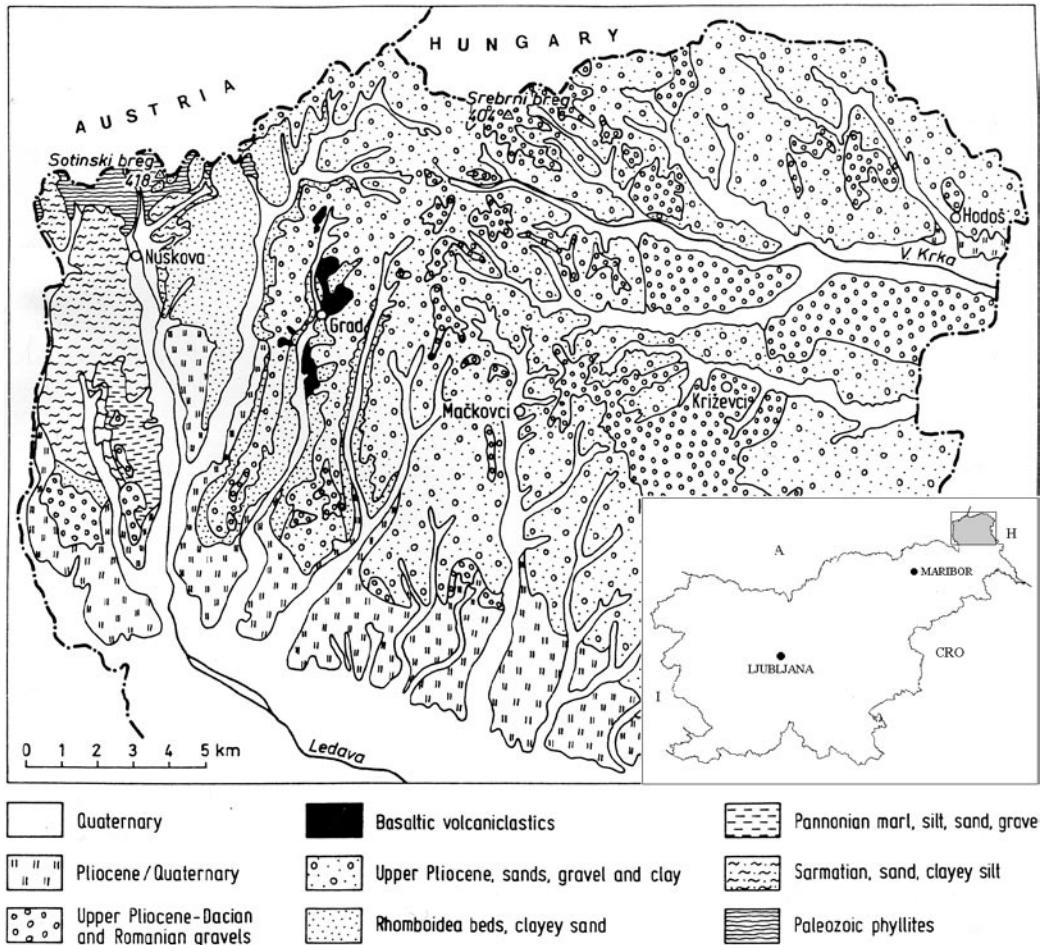


Figure 1. Simplified geological map of Goričko (after Pleničar, 1970)

Slika 1. Poenostavljena geološka karta Goričkega (po Pleničarju, 1970)

Grad area (Martin & Németh, 2004). Close proximity – about 10 km – of large lava flows on the crest of the South Burgenland Swell and in the neighboring Styrian Basin in Austria – at Stradner Kogel, Klöch, Kindsberg, Dölling and Neuhaus, supported a possibility that some of them might have been an additional source of volcanoclastic debris at Grad. The present contribution deals with detailed chemical composition of potential rock occurrences in Austria, and lava fragments in the Grad Member volcanoclastic rocks in order to characterize the source and consider possible paleotransport directions for volcanoclastic rock fragments of the Grad Member.

Geological setting outline

North-easternmost Slovenian territory (Fig. 1) is a hilly country that forms a part of the Mura Basin – the south-easternmost extending of the Pannonian Basin. The Mura Basin is filled with clastic, and to minor extent carbonate sediments, that range in age from Neogene to Quaternary. The Mura Basin consists of two depressions – northerly positioned southwest – northeast trending Radgona depression, and nearly west-east trending Ljutomer depression. They are separated by the Murska Sobota Swell (Kisovar, 1979). The Radgona depression is separated from the neighboring Styrian Basin in the north by the South Burgenland Swell (Tollmann, 1986; Oberhauser, 1980).

The basement of the Mura Basin mainly consists of Paleozoic metamorphic and clastic sedimentary formations; only in the deepest parts of depressions, Mesozoic carbonates are preserved. Tertiary sediments were deposited in a marine environment during Karpatian, Badenian and Sarmatian stage (Rijavec et al., 1985). Except for Badenian, they are developed as clastics – clays, marls, silts and sands.

During Pannonian, brackish conditions prevailed. Lower Pannonian sediments are silts and marls characterised by the occurrence of ostracods. They are overlain by the beds with *Paradaena* abichi molluscs, termed the »Abichi beds« (Pleničar, 1968). Overlying Lower Pliocene – Pontian sediments are mainly limnic, and consist of quartz sands, sandy silts and clayey silts. These deposits are regarded as »the freshwater equivalent of the Rhomboidea beds« (Pleničar, 1968). Middle Pliocene deposits

overlie discordantly Pontian beds and are developed as sands and gravels. Fluvial sedimentation that started with Middle Pliocene persisted during Upper Pliocene and Quaternary.

Sarmatian sediments are united in the Murska Sobota Formation, Pannonian and Lower Pontian in the Lendava Formation, and Upper Pontian and Quaternary in the Mura Formation (Šimon, 1966).

During Pliocene, volcanic activity of basaltic composition occurred in the Styrian Basin and in the northern margins of the Radgona depression. On the crest of the South Burgenland Swell large lava flows occur (Fig. 2). Towards the north, maars, tuff rings and tuff cones are more common in occurrence. Strongly differentiated and alkalies-rich varieties include nephelinites, basanites, nepheline basanites, thrachybasalts and alkali basalts. Peridotite and/or lherzolite xenoliths are common and indicate the origin of magmas and their rapid ascend towards the surface (Embey-Isztin & Kurat, 1996).

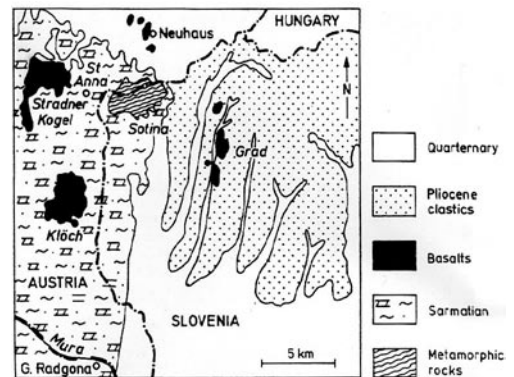


Figure 2. Simplified geological map of the Grad area with the neighbouring outcroppings of basaltic rocks in Austria (after Pleničar, 1968 & Winkler, 1927)

Slika 2. Poenostavljena geološka karta območja Grada z bližnjimi izdanki bazaltnih kamnin v Avstriji (po Pleničarju, 1968 in Winklerju, 1927)

Volcanic activity at Grad occurred in an active continental sedimentary environment characterized by alluvial fan and braided river systems (Kralj, 2000 b). Rapid deposition of coarse-grain dominated detritus was closely related to the rise of the South Burgenland Swell and the subsidence of the Radgona depression. During Early Pliocene, a system of alluvial fans formed along the

south-eastern slopes of the South Burgenland Swell, and towards the south, east and south-east it continued as a system of braided rivers, although the main transport direction was from north-west to south-east. The present maximum thickness of clastic deposits in the Radgona depression amounts to about 2000 m. Lavas and pyroclastic deposits occurring in such active depositional environment had little preservation potential and rapidly underwent redistribution by fluvial currents. Magmas ascending towards the surface reached water-bearing strata and consequently, and with the time, the style of eruptions became essentially influenced by hydrovolcanic processes. Their violent explosions additionally contributed to destruction of primary volcanic edifices and lavas (Plate 1 – Figure 1) which already had little preservation potential in such dynamic fluvial sedimentary environment (Kralj, 1995; 2000a, b).

Chemical composition of alkali basaltic rocks

Chemical composition of alkali basaltic rocks in Styria and Burgenland is extensively treated by Poulditis (1981) and Poulditis & Scharbert (1986). Their absolute age was determined by Balogh et al. (1994). At Stradner Kogel, the most differentiated varieties - nephelinites occur in the form of lava massive. At Klöch and Kindsberg, lavas of nephelinite basanite composition outcrop. At Neuhaus, alkali basalts occur. They penetrated soft sands, probably soaked with water, and consequently, they underwent extensive autobrecciation (Plate 1 – Fig. 2). In such form, they could be easily eroded and transported by water currents.

In order to minimize analytical errors related to procedures in different laboratories, rock samples from potential locations in Austria were analyzed in the same laboratory and under the same analytical conditions as the samples from Grad. The analyses were performed in X-RAL Activation Services Inc. in Ann Arbor, Michigan and Don Mills, Ontario, and it encompasses determination of 73 elements by combined wet chemical method, atomic absorption spectroscopy, and inductively coupled plasma source and mass spectroscopy.

The rocks from Klöch, Kindsberg, Dölling and Neuhaus were determined as potential sources with respect to the general pa-

leotransport direction. Stradner Kogel was eliminated in the first place since the composition of nephelinite lavas is too declined from the composition of lava clasts from of the Grad Member volcanoclastics as evidenced from preliminary petrographic studies. Chemical composition of the studied rocks is shown in Table 1 and Table 2.

General overview of chemical analyses indicates that among major oxides silica and K_2O do not differ significantly in the studied samples. The rocks from Austria have higher abundance of TiO_2 , CaO , MgO and Na_2O , and are lower in P_2O_5 . Rock fragments from the Grad Member volcanoclastics tend to be enriched in almost all trace elements – Rb, Be, Sr, Ba, Ag, Zn, Th, U, Zr, Hf, Ta, W, Y, REEs, As and Sb, and depleted in Cu, V, Ni and Sc. The magma(s) producing rock fragments from the Grad Member volcanoclastics seem to be more differentiated than those from Austria. Depleted CaO , MgO , TiO_2 , Cu, V, Ni and Sc might be related to the removal of pyroxenes from the melt by crystal fractionation.

Discussion

The studied basaltic rock samples occupy mainly the fields of trachybasalt and basalt (Fig. 3) in the $Na_2O + K_2O$ vs. SiO_2 diagram after LeBas et al. (1986). Only one sample from Klöch falls in the field of tephrite and basanite. Based on the content of alkali oxides and silica, the samples from Austria and the Grad Member volcanoclastics do not vary significantly, although the samples from the Grad Member tend to be more rich in silica at a given $Na_2O + K_2O$ content. Similar trend can be observed in the Al_2O_3 vs. SiO_2 variation diagram (Fig. 4). In the diagram MgO vs. SiO_2 , the samples from Klöch, Kindsberg and Dölling are clearly separate from the others. One of the samples from Neuhaus is positioned close to the Grad Member population, while the other shows extremely low abundance of MgO , possibly owing to alteration processes. In the diagram TiO_2 vs. SiO_2 the samples from Austria clearly separate from the Grad Member rock fragments. This trend is even more obvious in the diagrams of SiO_2 vs. Zr, Sc vs. Zr and TiO_2 vs. Zr (Fig. 5); herein, a further distinction between the samples from Klöch, Kindsberg and Dölling, and Neuhaus can be seen.

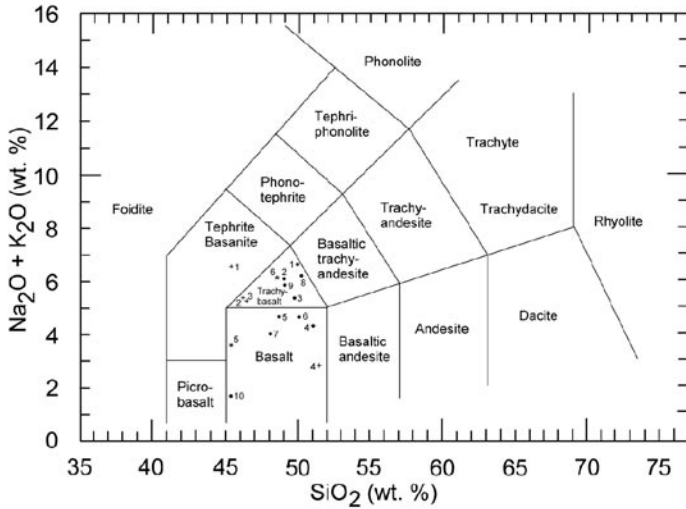


Figure 3. $\text{Na}_2\text{O} + \text{K}_2\text{O}$ vs. SiO_2 (after LeBas et al., 1986) for the studied basaltic rocks. Closed circles (1-10) are for the samples from the Grad Member, crosses (1-4) for the samples from Klöch, Kindsberg and Dölling, and asterisks for the samples from Neuhaus

Slika 3. Diagram $\text{Na}_2\text{O} + \text{K}_2\text{O}$ vs. SiO_2 (po LeBas-u et al., 1986) za preiskane vzorce bazaltnih kamnin. Polni krogi (1-10) predstavljajo vzorce iz Graškega člena, križi (1-4) vzorce iz Klöcha, Kindsberga in Döllinga, ter zvezdice vzorce iz Neuhausa

Conclusions

Geochemical characteristics of basaltic rocks from Klöch, Kindsberg, Dölling, and Neuhaus and basaltic rock fragments from the Grad Member volcanoclastics based on the abundance of major oxides and trace elements have shown the following:

- Chemical composition of the Grad Member rock fragments and basaltic rocks from potential source locations in Austria is different. It is not likely that the lava fragments from the Grad Member are eroded and redistributed detritus from the occurrences in Austria.
- Rock fragments from the Grad Member volcanoclastics could have two sources (volcanoes), or one, from which the magmas underwent differentiation during volcanic activity.
- Late-stage hydrovolcanic explosions produced proclastic surges, large lahars and volcanic debris flows that destroyed the former volcanic edifice(s) including lava flows and cinder cones.

In spite of numerous works (Hinterlechner-Ravnik & Mišič, 1986; Kralj, 1995; 2000a, b; Lugović & Kralj, 2006), the study of the Grad Member is far from completed and will continue in the future.

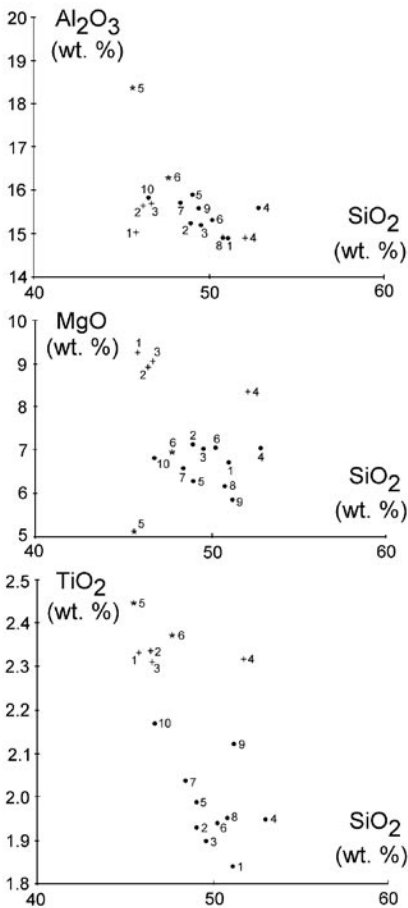


Figure 4. Variation diagrams Al_2O_3 vs. SiO_2 , MgO vs. SiO_2 , and TiO_2 vs. SiO_2 for the studied basaltic rock samples. Closed circles (1-10) are for the samples from the Grad Member, crosses (1-4) for the samples from Klöch, Kindsberg and Dölling, and asterisks for the samples from Neuhaus

Slika 4. Variacijski diagrami Al_2O_3 napram SiO_2 , MgO napram SiO_2 in TiO_2 napram SiO_2 za analizirane vzorce bazaltnih kamnin. Polni krogi (1-10) predstavljajo vzorce iz Graškega člena, križi (1-4) vzorce iz Klöcha, Kindsberga in Döllinga, ter zvezdice vzorce iz Neuhausa

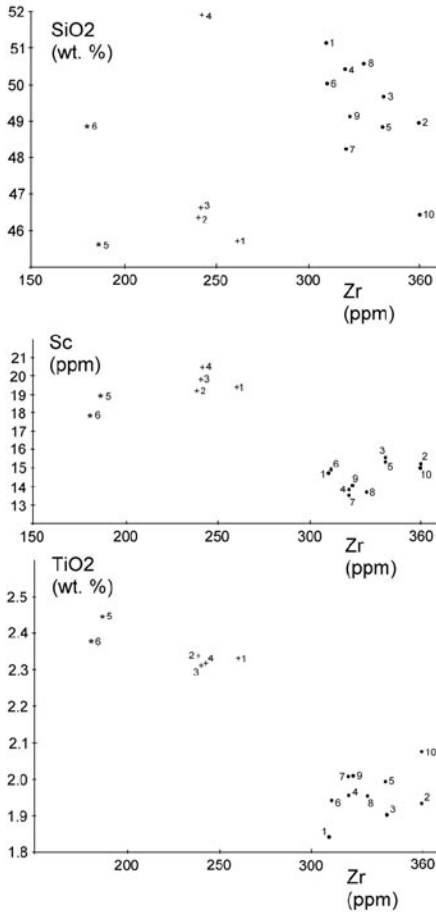


Figure 5. Variation diagrams SiO₂ vs. Zr, Sc vs. Zr, and TiO₂ vs. Zr for the studied basaltic rock samples. Closed circles (1-10) are for the samples from the Grad Member, crosses (1-4) for the samples from Klöch, Kindsberg and Dölling, and asterisks for the samples from Neuhaus

Slika 5. Variacijski diagrami SiO₂ napram Zr, Sc napram Zr in TiO₂ napram Zr za analizirane vzorce bazaltnih kamnin. Polni krogi (1-10) predstavljajo vzorce iz Graškega člena, križi (1-4) vzorce iz Klöcha, Kindsberga in Döllinga, ter zvezdice vzorce iz Neuhausa

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A.

Sample Oxide (wt.%)	1 Klöch 7	2 Klöch 9	3 Kindsberg	4 Dölling	5 Neuhaus 3	6 Neuhaus 4
SiO ₂	44,5	43,9	44,3	48,1	41,1	46,4
TiO ₂	2,27	2,22	2,19	2,15	2,21	2,25
Al ₂ O ₃	14,6	14,8	14,9	13,8	16,6	15,9
Fe ₂ O ₃	3,54	3,75	6,63	4,66	5,20	3,51
FeO	5,9	5,3	2,8	4,0	3,1	5,2
MnO	0,18	0,17	0,17	0,15	0,25	0,14
MgO	8,98	8,40	8,58	7,73	4,61	6,61
CaO	10,3	9,28	9,63	8,90	13,3	8,73
Na ₂ O	4,07	4,09	3,70	1,45	1,90	3,60
K ₂ O	2,15	1,47	1,30	1,11	1,26	2,22
P ₂ O ₅	0,74	0,75	0,74	0,50	0,51	0,49
H ₂ O ⁺	0,9	2,2	2,5	4,3	3,2	3,2
H ₂ O ⁻	0,5	0,9	1,0	2,1	2,0	1,0
CO ₂	0,28	0,02	0,02	<0,01	4,34	0,50
Sum	99,48	98,30	98,75	99,55	100,2	100,3

B.

Element (ppm)	1 Klöch 7	2 Klöch 9	3 Kindsberg	4 Dölling	5 Neuhaus 3	6 Neuhaus 4
Be	3	4	5	4	2	3
B	31	10	29	30	<10	26
Sc	19,4	19,2	19,8	20,5	18,9	17,9
V	220	230	230	200	197	207
Cr	140	120	110	120	137	178
Co	46	43	45	48	43	56
Ni	180	180	160	170	90	77
Cu	37,4	40,3	39,4	37,0	36,8	41,7
Zn	99,1	99,9	110,1	87,1	92,2	94,8
Rb	71	59	31	51	32	67
Sr	939	991	1000	681	613	607
Y	30	20	20	<10	37	<10
Zr	260	240	241	239	186	179
Nb	101	111	131	99	57	59
Cd	2	2	<1	1	1	2
Sb	<0,2	<0,2	<0,2	0,4	0,2	0,3
Cs	<1	2	1	1	1	2
Ba	682	851	954	902	789	608
La	56,3	62,2	65,5	49,8	36,9	35,6
Ce	105	114	110	98	72	72
Nd	39	42	46	36	31	29
Sm	6,4	6,8	7,3	6,7	5,8	5,5
Eu	2,0	2,2	2,9	2,2	2,1	2,2
Tb	0,6	0,7	0,8	0,9	0,7	0,6
Yb	1,6	1,8	1,9	1,4	1,5	1,4
Lu	0,25	0,25	0,26	0,20	0,21	0,19
Hf	4,1	5,2	4,9	5,1	4,5	4,4
Ta	5	6	5	5	3	3
W	75	48	43	67	25	120
Th	7,6	8,6	9,6	8,1	5,7	5,2
U	2,6	3,1	3,2	1,1	2,4	1,6

Table 1. Chemical composition of alkali basaltic rocks from Klöch, Kindsberg, Dölling and Neuhaus. A, major oxides (in wt. %); B, trace elements (in ppm).

Tabela 1. Kemična sestava alkalnih bazaltov iz Klöcha, Kindsberga, Döllinga in Neuhaus. A, glavni oksidi (v mas. %); B, sledne prvine (v ppm).

A.

Sample Oxide (wt.%)	1 B 1	2 B2	3 B 3	4 BB	5 GGo4	6 KaW	7 P 53	8 KuKIA	9 KuSc4	10 KuSc6
SiO ₂	48,9	46,3	47,0	46,8	45,4	47,7	43,6	47,9	46,9	41,6
TiO ₂	1,76	1,83	1,80	1,81	1,85	1,85	1,84	1,85	1,93	2,43
Al ₂ O ₃	14,3	14,4	14,4	14,5	14,8	14,6	14,2	14,1	14,9	14,2
Fe ₂ O ₃	3,47	3,63	3,58	4,15	5,08	4,57	5,18	4,89	5,08	7,28
FeO	5,2	5,3	5,2	4,7	4,4	4,6	4,2	4,3	4,6	3,7
MnO	0,18	0,19	0,19	0,19	0,20	0,19	0,22	0,19	0,52	0,21
MgO	6,34	6,76	6,66	6,60	5,93	6,80	5,93	5,88	5,55	6,10
CaO	8,49	9,28	9,02	8,78	9,20	9,08	9,83	8,88	9,58	11,6
Na ₂ O	3,90	3,89	3,97	2,20	2,63	3,16	1,61	3,86	2,96	0,41
K ₂ O	2,27	2,11	2,01	2,20	2,15	1,79	1,89	1,99	2,45	1,15
P ₂ O ₅	0,88	0,94	0,92	0,97	1,28	0,99	1,78	0,93	1,02	1,00
H ₂ O ⁺	2,0	2,2	1,9	3,0	2,9	3,3	5,6	2,9	3,4	5,8
H ₂ O ⁻	0,5	1,1	1,0	1,7	1,5	1,8	2,6	1,1	0,7	3,3
CO ₂	0,32	0,51	0,44	0,04	0,04	0,05	0,14	0,16	0,04	0,01
Sum	98,87	99,00	98,51	99,35	98,96	100,5	99,37	99,40	100,3	100,3

B.

Element (ppm)	1 B 1	2 B2	3 B 3	4 BB	5 GGo4	6 KaW	7 P 53	8 KuKIA	9 KuSc4	10 KuSc6
Be	6	4	3	6	5	4	5	4	5	4
B	30	10	20	30	20	20	10	20	27	10
Sc	14,7	14,2	14,5	13,8	14,4	14,8	14,5	13,6	14,1	16,1
V	191	171	162	161	182	169	179	161	184	191
Cr	120	130	120	110	130	120	92	100	140	180
Co	25	37	43	39	51	25	28	52	42	38
Ni	81	110	110	110	110	85	100	124	128	145
Cu	29,4	36,0	37,2	36,9	37,5	29,4	21,9	34,1	24,7	29,9
Zn	110	110	140	110	130	110	110	120	134	157
Rb	68	60	50	70	70	48	54	70	81	35
Sr	1060	1160	1120	1200	1310	1150	1280	975	909	706
Y	26	10	40	30	30	41	30	20	32	29
Zr	310	360	340	320	340	310	320	330	322	361
Cd	<0,2	2	1	1	2	<0,2	<0,2	2	2	2
Sb	0,7	0,5	0,6	0,7	0,7	0,5	0,6	0,3	n.d.	n.d.
Cs	2	1	2	1	2	1	1	1	3	1
Ba	920	900	920	1300	1400	1000	1100	970	1080	800
La	73,4	77,8	74,6	74,5	80,3	78,3	90,5	73,8	81,3	71,8
Ce	138	143	133	133	146	133	155	137	145	140
Nd	57,2	54	50	52	54	62,1	63,6	50	51	59
Sm	9,5	8,9	8,3	8,2	8,8	9,8	10,5	8,2	7,8	10,4
Eu	2,8	2,6	2,6	2,4	2,7	3,3	3,2	2,5	3,7	3,2
Tb	1,0	1,1	1,0	1,0	1,2	1,1	1,1	0,9	0,9	1,3
Yb	2,3	2,1	2,3	2,1	2,6	2,5	2,8	2,0	2,2	2,8
Lu	0,38	0,28	0,31	0,28	0,34	0,41	0,40	0,27	0,39	0,27
Hf	8,0	7,1	7,2	6,1	7,1	8,4	7,6	6,2	6,5	8,4
Ta	6	6	6	5	6	6	7	6	6	6
W	150	110	120	130	160	110	97	370	170	14
Th	12	11	11	11	11	11	12	11	11	13
U	4,1	3,4	3,1	3,7	3,2	3,7	5,6	3,4	4,3	1,1

Explanation:

n.d. – not defined

Table 2. Chemical composition of volcanic rock fragments from the Grad Member volcanoclastics. A, major oxides (in wt. %); B, trace elements (in ppm).

T vine (v ppm).

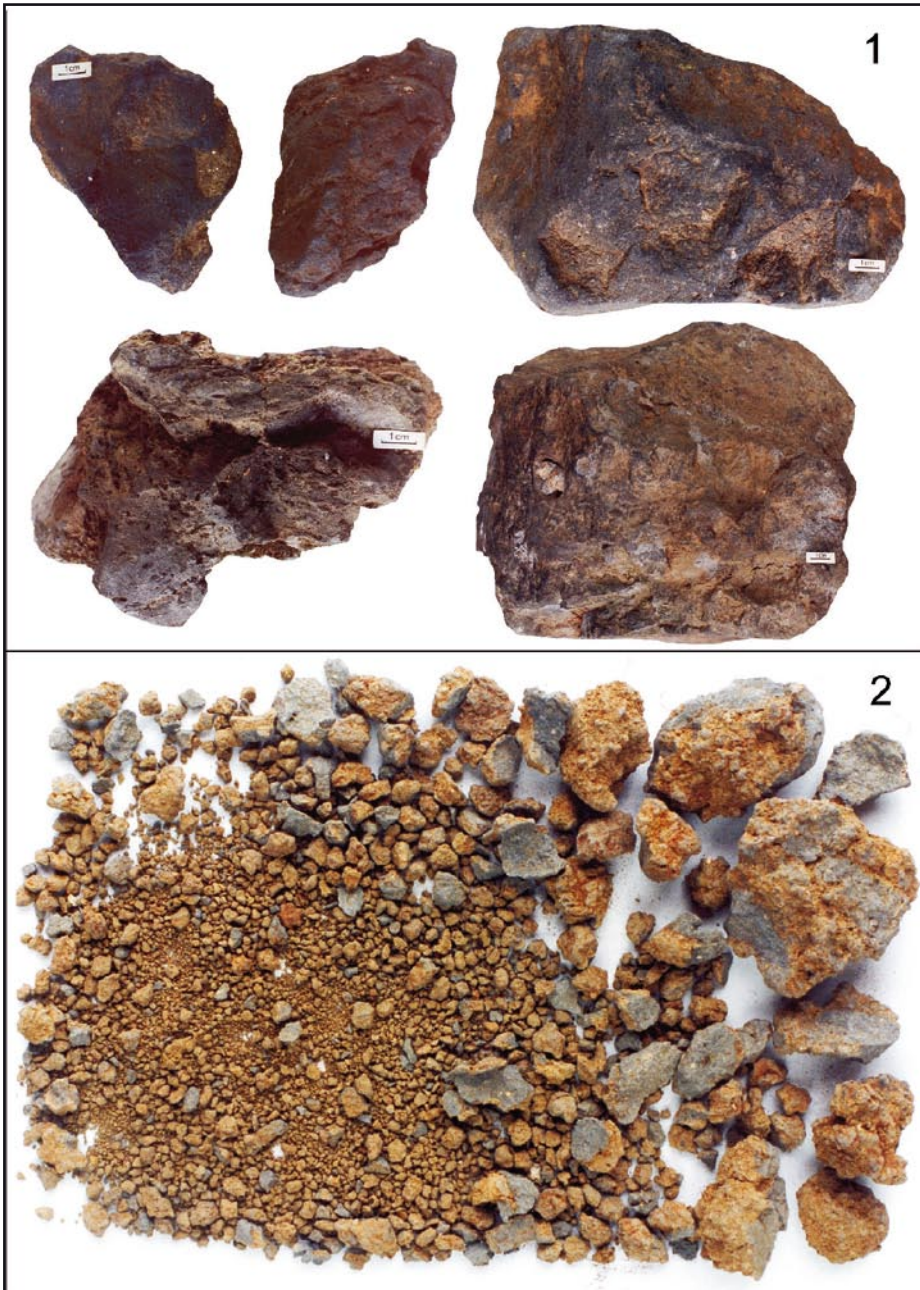


Plate 1 – Tabla 1

- 1 Basaltic rock fragments from the Grad Member volcanoclastics.
Odlomki bazaltnih kamnin iz vulkanoklastitov Graškega člena
- 2 A lava sample from Neuhaus which underwent disintegration into hyaloclasts after being frozen in a solution of hydrogen peroxide. The largest clast is about 3,5 cm long.
Vzorec lave iz Neuhaus, ki je po zmrzovanju v raztopini vodikovega peroksida razpadel v številne hialoklaste. Največji hialoklast meri približno 3,5 cm v dolžino

