The possibility of using soil instead of rock samples for a petrological interpretation

Možnost uporabe tal namesto kamnin za petrološko interpretacijo

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Abstract: In the area of the Pohorje Mts. (NE Slovenia, Eastern Alps) igneous complex we tried to test whether the sampling of soil instead of fresh rock yields adequate results for a petrological interpretation. In 22 locations granodiorite, dacite, gabbro and lamprophyre with corresponding soil were sampled. Whole rock and trace element analysis was performed using ICP – MS and – ES. A statistical t-test showed that the major element content as well as Ba, Nb, Rb, and Sr are generally significantly different in both media. On the petrological diagrams based on these elements soil and rock samples from the same location plot in different fields. In the case of major elements the use of soil samples instead of rock is not advisable. However for diagrams constructed with immobile elements – such as diagrams for tectonic setting and REE patterns – a soil sample might possibly be used quite safely in place of fresh rock.

Izvleček: Na področju pohorskega magmatskega masiva (SV Slovenija, Vzhodne Alpe) smo skušali preveriti, ali vzorčenje tal na mestu vzorcev kamnin daje enakovredne rezultate za petrološko interpretacijo. Na 22 lokacijah smo vzorčili granodiorit, dacit, gabbro in lamprofir ter tla nastala na teh kamninah. Vsebnost glavnih in slednih prvin smo določili z ICP – MS in – ES. Statistični t-test je pokazal, da se vzorci značilno razlikujejo po vsebnosti glavnih prvin ter Ba, Nb, Rb in Sr. Na petroloških diagramih, ki so zasnovani na teh prvinah, se vzorci kamnin in tal uvrščajo na različna področja. Uporaba vzorcev tal v diagramih, ki vključujejo glavne prvine, zato ni primerna. V diagramih, zasnovanih z nemobilnimi prvinami – kot na primer diagrami tektonskega okolja ter vzorci REE – pa lahko vzorci tal dokaj dobro nadomestijo vzorce kamnin.

Key words: geochemistry, weathering, petrological diagrams, soil, granodiorite, Eastern Alps

Ključne besede: geokemija, preperevanje, petrološki diagrami, tla, granodiorit, Vzhodne Alpe

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Introduction

The Pohorje Mts. (NE Slovenia, Europe) consist of prevailing granodiorite pluton with a small satellite gabbro body, a minor dacite stock and several lamprophyre veins. In previous years studies on these igneous rocks have been performed to establish their origin and genesis (Zupančič, 1997a, b). During field work it has become obvious that in a temperate climate at altitudes of below 2000 m fresh rock samples are quite difficult to obtain due to the rapid weathering and formation of soil. Silicate rocks are often covered by deep soil and vegetation. Sampling is limited to outcrops which are not uniformly distributed. That is why the reliability of petrological and statistical studies may often be in question.

In this study we tried to test weather it is possible to use soil samples instead of fresh rock and still obtain authentic data for a petrological interpretation. The applicability of the different classification and discrimination diagrams constructed with data from the soil samples is discussed.

Materials and methods

Five kilogram samples of different igneous rocks and the corresponding two kilograms of soil (the upper 20 cm) were collected. Altogether, there were 22 sampling localities distributed throughout the massive in accordance with the volume of different rock types. Both media were collected as close as possible to ensure that the soil was truly a weathering product of the treated rock. In randomly chosen locations replicate samples were obtained to control the sampling quality. To control the quality of analytics some duplications were added. The chemical composition of three gabbro and two corresponding soils, three lamprophyres and their soils, five dacites with appropriate soils and 16 granodiorites with 19 soils were analyzed at the ACME Laboratories in Vancouver, Canada. For an analysis of major elements a 2 g sample was digested in 5 % HNO_3 after a $LiBO_2$ fusion. The contents were determined by inductively coupled plasma – emission spectroscopy (ICP – ES). For the trace elements analysis, a 0.5 g sample was leached with 3 mL of an HCl – HNO_3 – H_2O (2 : 2 : 2) mixture at 95 °C for one hour, then diluted to 10 mL and analyzed using an inductively coupled plasma – mass spectroscopy (ICP – MS). According to the added replicates and AGV-1 and RGM-1 standards the analytical error is below 10 % for the elements used in the proceeding study (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, CaO, Na_2O, K_2O, P_2O_5, MnO, LOI, Ba, Nb, Rb, Sc, Sr, Th, V, Zr, Y and REE). For REE chondrite the normalization values suggested by Nakamura (1977) were used.

Results and discussion

Generally in more basic rock types (gabbro and lamprophyre) the mean values (Table 1) of the majority of analyzed elements are higher in soils than in rock, while the opposite is true for more acid rocks (granodiorite and dacite). The situation is reverse concerning data scattering i.e. standard deviations (Table 2). These are higher in soils formed on acid rock types and lower in soils weathered from basic rocks. But it should be noted that for both basic rock types the number of observations is ex-

Table 1. Mean values of major (%) and trace (µg/g) values in rock and soil samples from Pohorje Mts. Number of observations: gabbro soil = 2, rock = 3, dacite soil = 5, rock = 5, lamprophyre soil = 3, rock = 3, granodiorite soil = 19, rock = 16.
Tabela 1. Srednje vrednosti glavnih (%) in slednih (µg/g) prvin v pohorskih vzorcih kamnin in tal. Število opazovanj: gabbro (tla) = 2, kamnina = 3, dacit (tla) = 5, kamnina = 5, lamprofir (tla) = 3, kamnina = 3, granodiorit (tla) = 19, kamnina = 16.

	Gabbbro soil	Gabbro rock	Dacite soil	Dacite rock	Lamprophyre soil	Lamprophyre rock	Granodiorite soil	Granodiorite rock
SiO_2	57.95	54.57	54.31	67.99	52.93	56.82	58.53	68.59
TiO_2	0.61	0.41	0.45	0.34	0.97	0.85	0.44	0.30
Al_2O_3	11.50	8.01	13.61	15.58	16.91	16.99	13.89	15.97
Fe_2O_3	2.55	2.75	1.79	1.67	4.04	2.63	1.70	1.29
FeO	2.08	2.24	1.46	1.44	3.30	3.42	1.33	1.41
MnO	0.11	0.15	0.06	0.06	0.14	0.11	0.04	0.07
MgO	6.49	12.27	0.66	1.03	2.62	4.74	0.64	0.96
CaO	6.51	14.01	1.79	3.10	1.80	6.04	1.91	3.23
Na_2O	2.22	2.20	2.42	3.93	1.14	3.74	2.51	4.01
K_2O	1.27	0.19	2.17	3.02	2.27	1.94	2.10	2.84
P_2O_5	0.21	0.13	0.14	0.16	0.16	0.29	0.12	0.13
LOI	8.42	3.04	21.06	1.53	13.99	2.41	16.73	1.04
Ba	907.5	81.66	780.80	1124.60	611.66	1197.66	994.84	1246.81
Nb	9.25	11.56	14.16	2.80	14.83	6.93	13.38	7.66
Rb	37.40	9.90	82.10	110.00	120.56	62.85	73.57	103.67
Sc	39.50	69.33	4.60	5.28	16.66	20.33	4.36	4.31
Sr	440.45	417.33	326.92	509.60	206.96	822.80	426.79	666.84
Th	12.20	9.56	13.34	13.20	15.76	11.16	15.80	16.28
V	141.50	143.33	40.40	36.40	138.00	106.33	41.15	32.31
Zr	89.65	64.36	156.64	164.60	181.83	150.30	162.53	156.52
Y	16.50	16.43	13.46	15.80	28.00	19.53	14.04	16.07
La	34.75	25.13	34.98	33.40	46.43	41.40	40.71	37.06
Ce	66.75	46.96	69.36	67.92	97.86	84.83	75.88	70.57
Pr	7.14	5.28	6.33	6.10	10.34	8.29	7.45	6.68
Nd	26.15	19.70	21.72	21.42	38.06	21.70	25.42	23.33
Sm	5.25	4.30	3.58	3.72	7.63	5.50	4.16	3.98
Eu	1.23	1.07	0.79	0.99	1.59	1.51	0.87	1.04
Gd	4.05	3.73	2.62	3.24	6.36	4.70	2.96	3.22
Tb	0.53	0.49	0.38	0.42	0.88	0.59	0.41	0.43
Dy	3.09	2.93	2.36	2.28	5.36	3.47	2.45	2.54
Ho	0.58	0.55	0.46	0.41	1.02	0.63	0.46	0.46
Er	1.74	1.67	1.44	1.12	3.05	1.75	1.46	1.37
Tm	0.23	0.23	0.21	0.18	0.38	0.23	0.20	0.20
Yb	1.52	1.53	1.49	1.12	2.82	1.64	1.48	1.39
Lu	0.24	0.24	0.24	0.33	0.42	0.41	0.24	0.29

Table 2. Standard deviations of major (%) and trace (μg/g) values in rock and soil samples from Pohorje Mts. Number of observations is the same as in Table 1.
Tabela 2. Standardni odkloni glavnih (%) in slednih (μg/g) prvin v pohorskih vzorcih kamnin in tal. Število opazovanj je enako kot v tabeli 1.

	Gabbbro soil	Gabbro rock	Dacite soil	Dacite rock	Lamprophyre soil	Lamprophyre rock	Granodiorite soil	Granodiorite rock
SiO_2	0.452	0.618	5.064	2.828	0.856	0.631	3.727	1.632
TiO_2	0.021	0.015	0.071	0.068	0.070	0.201	0.186	0.076
Al_2O_3	0.063	0.170	1.427	0.549	0.258	0.639	1.607	0.469
Fe_2O_3	0.007	0.015	0.313	0.723	0.297	0.573	0.916	0.559
FeO	0.007	0.011	0.254	0.296	0.245	0.646	0.540	0.311
MnO	0.000	0.000	0.048	0.021	0.020	0.010	0.034	0.017
MgO	0.014	0.125	0.271	0.237	0.157	0.421	0.545	0.245
CaO	0.035	0.820	1.102	0.681	0.086	0.260	0.402	0.648
Na_2O	0.042	0.057	0.295	0.235	0.257	0.226	0.544	0.208
K_2O	0.021	0.141	0.273	0.253	0.100	0.302	0.275	0.570
P_2O_5	0.106	0.010	0.087	0.040	0.030	0.041	0.040	0.037
LOI	0.282	0.001	5.968	1.350	0.669	0.200	4.861	0.371
Ba	0.707	22.030	78.017	101.455	137.128	138.896	165.891	510.820
Nb	0.494	0.472	1.789	0.836	0.378	7.695	2.269	5.769
Rb	0.141	0.435	12.399	14.142	9.176	4.030	14.201	24.739
Sc	0.707	2.081	1.516	1.517	1.527	2.300	3.531	1.339
Sr	5.727	16.510	41.609	46.516	25.364	109.393	105.749	138.180
Th	1.555	3.629	1.289	2.387	1.501	2.020	3.975	3.469
V	4.949	1.527	13.630	11.653	19.000	60.467	33.258	10.150
Zr	1.060	3.957	11.866	36.390	19.062	21.035	23.852	28.336
Y	1.131	0.650	3.870	1.643	3.593	1.858	4.713	4.845
La	7.283	4.880	6.460	7.893	5.750	8.190	10.431	9.294
Ce	12.515	6.815	5.073	11.646	12.444	4.916	18.904	14.415
Pr	1.195	0.528	1.140	0.913	1.401	1.118	2.120	1.611
Nd	4.596	0.818	4.470	2.751	4.735	16.674	7.696	5.266
Sm	0.212	0.360	0.858	0.593	1.457	0.700	1.554	0.878
Eu	0.091	0.017	0.224	0.120	0.183	0.026	0.314	0.169
Gd	0.254	0.393	0.788	0.427	1.000	0.300	1.153	0.696
Tb	0.028	0.025	0.115	0.044	0.117	0.085	0.177	0.108
Dy	0.325	0.201	0.558	0.238	0.729	0.654	0.909	0.748
Ho	0.042	0.043	0.127	0.040	0.134	0.136	0.181	0.147
Er	0.091	0.142	0.351	0.130	0.376	0.444	0.491	0.484
Tm	0.028	0.015	0.047	0.044	0.064	0.063	0.066	0.065
Yb	0.084	0.051	0.297	0.178	0.215	0.338	0.400	0.425
Lu	0.007	0.037	0.019	0.232	0.043	0.253	0.047	0.123

Table 3. t-values of comparison of soil and rock samples from Pohorje Mts. Number of observations is the same as in Table 1. * - value is statistically significant at 95 % probability level.
Tabela 3. t-vrednosti primerjave pohorskih vzorcev kamnin in tal. Število opazovanj je enako kot v tabeli 1. * - vrednost je statistično značilna na 95 % stopnji verjetnosti.

	Gabbro	Dacite	Lamprophyre	Granodiorite
SiO_2	6.50*	–5.27*	–6.32*	–9.99*
TiO_2	12.63*	2.61*	0.94	2.76*
Al_2O_3	26.49*	–2.86*	–0.18	–4.98*
Fe_2O_3	–16.55*	0.35	3.79*	1.55
FeO	–17.23*	0.12	–0.30	–0.48
MnO		0.08	2.75	–3.52*
MgO	–61.69*	–2.33*	–8.17*	–2.15*
CaO	–12.25*	–2.26	–26.74*	–7.35*
Na_2O	0.34	–8.96*	–13.13*	–10.35*
K_2O	10.19*	–5.10*	1.79	–4.98*
P_2O_5	1.50	–0.51	–4.47*	–1.23
LOI	36.20*	7.13*	28.71*	12.85*
Ba	50.28*	–6.00*	–5.20*	–2.03
Nb	–5.28*	12.85*	1.77	3.98*
Rb	82.50*	–2.61*	8.05*	–4.50*
Sc	–18.69*	–0.70	–2.29	0.059
Sr	1.82	–6.54*	–9.49*	–5.81*
Th	0.93	0.11	3.16*	–0.37
V	–0.64	0.49	0.86	1.02
Zr	8.42*	–0.46	1.92	0.68
Y	0.08	–1.24	3.62*	–1.25
La	1.81	0.34	0.87	1.08
Ce	2.37	0.25	1.68	0.92
Pr	2.51	0.35	1.98	1.19
Nd	2.58	0.12	1.63	0.91
Sm	3.26*	–0.29	2.28	0.41
Eu	3.29*	–1.73	0.74	–1.97
Gd	0.98	–1.53	2.75	–0.78
Tb	1.53	–0.68	3.44*	–0.26
Dy	0.67	0.30	3.33*	–0.28
Ho	0.76	0.83	3.52*	0.11
Er	0.61	1.90	3.85*	0.51
Tm	–0.35	1.16	2.81*	–0.20
Yb	–0.22	2.42*	5.09*	0.67
Lu	0.05	–0.82	0.04	–1.76

tremely low so the data are not very trustworthy, and the results rather on the level of indications.

The statistical significance of the differences has been checked by the t-test (Table 3). Mainly the differences are statistically significant for all major elements except for Fe, Mn and P, and for the most part for Ba, Nb, Rb and Sr. REE seem to be unaffected by weathering except for HREE in the case of lamprophyre (where the observation number is low and so the conclusion is not so indicative). Between the soil and rock in all four rock types the largest differences are observed for the loss of ignition (LOI). This is normal, since weathering includes hydratation. What was less expected was the statistically significant change in SiO_2, MgO and Rb in all four rock types. These observations are well expressed on the standard petrological plots.

Diagrams using major elements

In igneous petrology major elements are used for different types of rock classification. In recent times (Wilson, 1989) a TAS (total alkalis/silica) diagram (Cox et al., 1979) has also been used for plutonic rocks. It is obvious in Figure 1 that the rock samples plot in the appropriate fields – granodiorite and dacite in the field of granite and granodiorite, gabbro in the area between gabbro and diorite and lamprophyre in the field of diorite. Yet the soil samples show quite a different classification. The majority of samples indicate a far more basic character with less silica and alkalis i.e. they all plot in the fields of diorite, the fields between diorite and gabbro and some soils from dacites and granodiorite even in the field of gabbro.

According to the silica saturation index (Thornton & Tuttle, 1960), all rock samples are described as silica oversaturated, which is supported by free quartz observed in hand specimen and under the microscope. On the contrary, soils from granodiorites and dacites seemed to be predominantly silica saturated or even under saturated, which is not in accordance with the true situation in the igneous body.

Saturation with aluminia is expressed with the A/CNK (Al_2O_3/(CaO+Na_2O+K_2O)) and A/NK (Al_2O_3/Na_2O+K_2O)) index (Shand, 1947). In the diagram (Figure 2) granodiorites and dacites are in the field of peraluminous rocks, close or even partly in the field of metaluminous rocks. Gabbro and lamprophyre of a more pronounced mantle source are, as expected, in the metaluminous field. Again, the soil samples behave differently. They showed a much more pronounced peraluminous character. Only soil derived from gabbro is metaluminous. The same diagram enables a distinction between I- and S-type granites as proposed by Chapell & White (1974). In this case, the allocation of soil samples far from their rock counterparts is crucial. Instead of the I-type, the soils are prevailingly classified as the S-type, with the exception of soil from gabbro and one soil sample from dacite.

The interpretation of trends and magma evolution is performed with the use of Harker diagrams (Rollinson, 1993). In those diagrams the major and trace elements are plotted versus SiO_2. Figure 3 indicates that normally there is much more data scatter when using soil samples in place of fresh rock samples. The low silica content in the soil samples in comparison to adequate rock samples is one of the main characteristics.

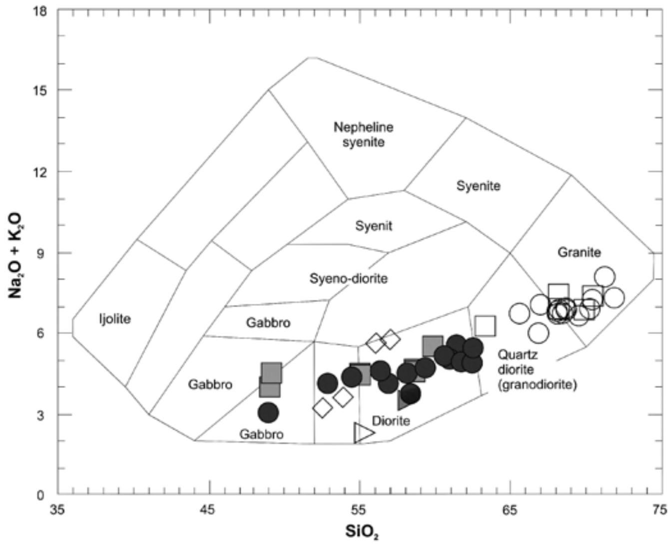

Figure 1. TAS classification of rock (empty symbols) and soil samples (full symbols) from the Pohorje Mts. ■ - gabbro, ▶ - dacite, ◆ - lamprophyre, ● - granodiorite.

Slika 1. TAS-klasifikacija vzorcev kamnin (prazni znaki) in tal (polni znaki) s Pohorja. ■ - gabbro, ▶ - dacit, ◆ - lamprofir, ● - granodiorit.

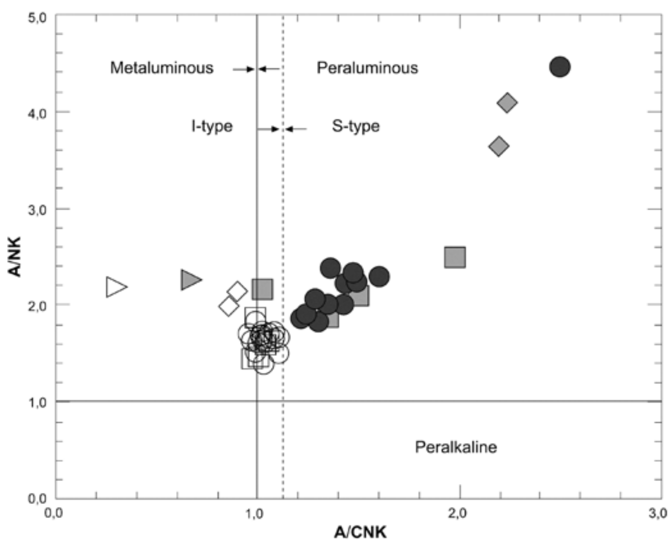

Figure 2. Aluminia saturation index and the I- and S-type division of Pohorje rock (empty symbols) and soil samples (full symbols). Legend: see Figure 1.

Slika 2. Indeks nasičenja z glinico ter razdelitev pohorskih kamnin (prazni znaki) in tal (polni znaki) v I- in S-tip. Legenda: glej sliko 1.

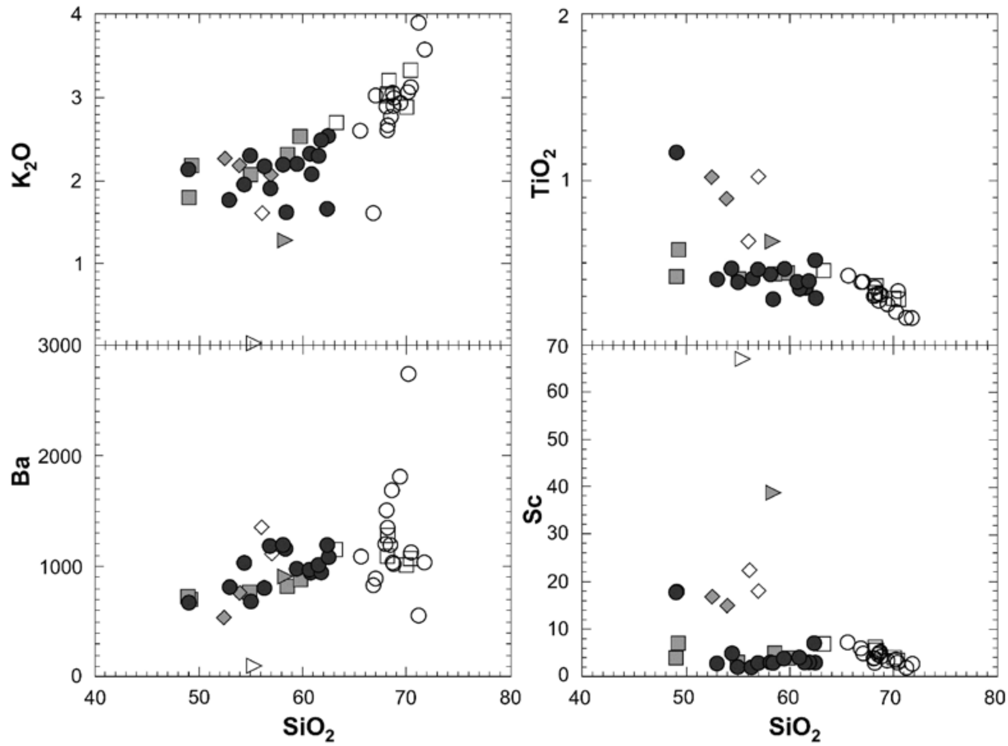

Figure 3. Harker diagrams of Pohorje rock (empty symbols) and soil samples (full symbols). Major elements in *w*(%), trace in *w*(μg/g). Legend: see Figure 1.
Slika 3. Harkerjevi diagrami vzorcev kamnin (prazni znaki) in tal (polni znaki) s Pohorja. Glavne prvine so izražene z *w*(%), sledne pa z *w*(μg/g). Legenda: glej sliko 1.

In some instances (i.e. TiO_2 in Figure 3) we can still trace the same trend as if using rocks, but in others (i.e. K_2O in Figure 3) this information is completely missing. In the soil samples with some trace elements (i.e. Ba in Figure 3) we even observed trends not shown by the rock samples. The petrogenetic interpretation of such a trend is, of course, misleading.

Trace elements

Although the statistical t-test indicates that the Ba, Rb and Sr content in soils does not reflect the amount of the mentioned elements in the rock, Figure 4 makes it obvious that in the ternary diagram of El Bouseily & El Sokkary (1975) all the samples fall within the same area.

Pearce et al. (1984) started with use of geochemical parameters to distinguish between the different tectonic settings of basalts and granites. One of the conditions for constructing such diagrams was that the elements involved should not be subject to mobilization during weathering or other alteration processes. The appropriate selection of elements in tectonic setting diagram proposed by Pearce et al. (1984) is

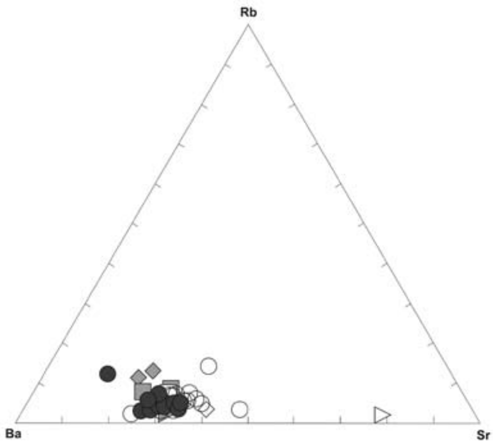

Figure 4. Ternary diagram Rb-Ba-Sr of Pohorje rock (empty symbols) and soil samples (full symbols). Legend: see Figure 1.

Slika 4. Trikotni diagram Rb-Ba-Sr pohorskih kamnin (prazni znaki) in tal (polni znaki). Legenda: glej sliko 1.

clearly demonstrated in the Figure 5 where the soil and rock samples overlap in the field of volcanic arc granites.

REE patterns

REE show various degrees of mobility during weathering or metamorphic alteration (HUMPHRIES, 1984; PRICE et al., 1991). They could be even mobilized inside the soil profile (NESBITT, 1979; SHARMA & RAJAMANI, 2000; PANAHI et al., 2000; AUBERT et al., 2001). HREE are reported to be more mobile than LREE (NESBITT, 1979; BRAUN et al., 1998; MINAŘIK, 1998; AUBERT et al. 2001,). Figure 6 indicates that during weathering and soil formation the REE patterns of each rock type preserved their form as well as their REE content, which is consistent with the work of certain authors (SHARMA & RAJAMANI, 2000; MUCHANGOS, 2006). There are some isolated

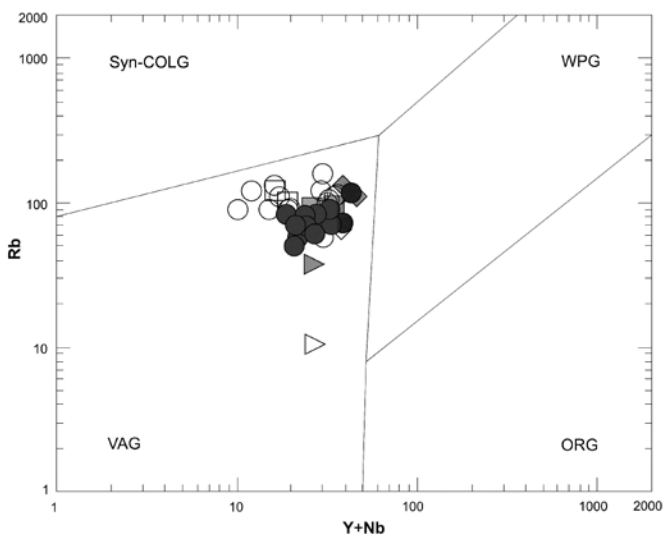

Figure 5. Tectonic setting diagram of Pohorje rock (empty symbols) and soil samples (full symbols). Values in w(μg/g). Legend: see Figure 1.

Slika 5. Diagram tektonskega okolja Sr pohorskih kamnin (prazni znaki) in tal (polni znaki). Vrednosti so izražene z w(μg/g). Legenda: glej sliko 1.

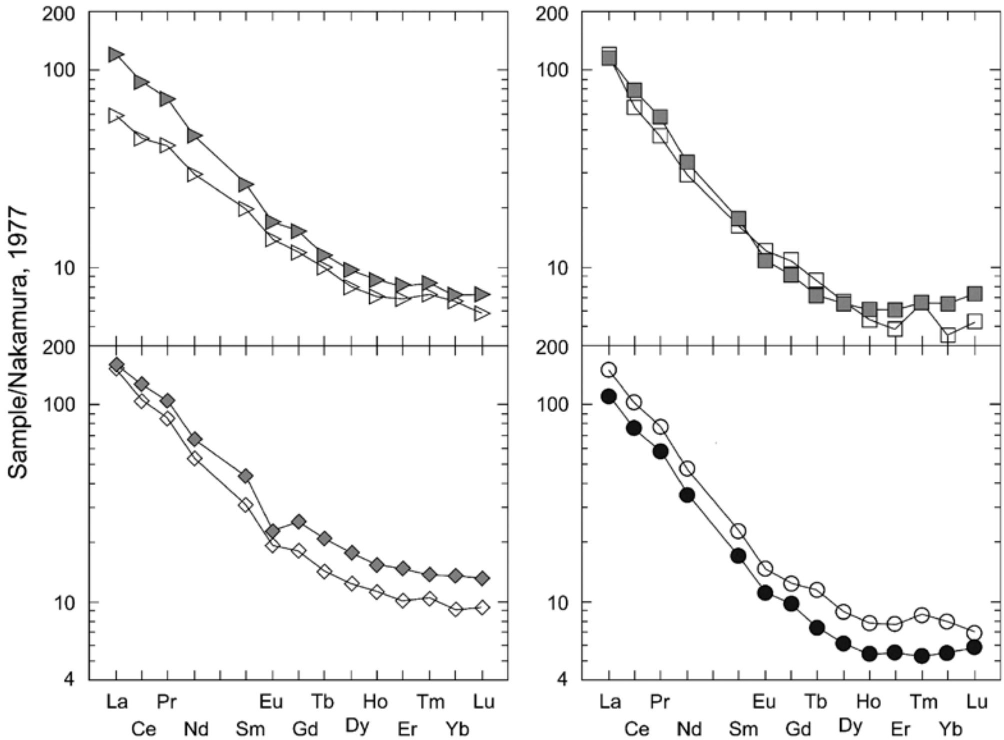

Figure 6. REE patterns of selected Pohorje rock (empty symbols) and soil samples (full symbols). Legend: see Figure 1.
Slika 6. Vzorec REE izbranih pohorskih kamnin (prazni znaki) in tal (polni znaki). Legenda: glej sliko 1.

cases with a deviation from the original rock pattern. In particular, there was one lamprophyre sample with a pronounced negative Eu anomaly and a higher HREE fractionation, which caused significant differences in the t-test results (Table 3). In spite of low number of samples for significant results, generally with some precaution the REE data from the soil samples can be used in the same manner as rock samples.

Conclusions

During weathering and soil formation major and some trace element (Ba, Nb, Rb and Sr) content becomes more or less changed. In basic rock types (gabbro and lamprophyre) we noticed their increase, while in more acid rocks (granodiorite and dacite) we observed their decrease. Only Fe, Mn, and P seemed to be an exception.

Consequently it appears inappropriate to use soil samples instead of fresh rocks for the majority of petrological classifications – i.e. TAS diagram, silica and aluminia saturation indexes, and the division between I- and S-type granites. The use of Harker diagrams based on soil samples is also highly unreliable.

More promising appears to be the application of soil samples in the construction of variation diagrams with less mobile elements. Diagrams such as Ba-Rb-Sr, or Rb/(Y+Nb) for the tectonic setting and REE patterns do not show discrepancies between the soil and rock samples.

POVZETEK

Zaradi preperevanja in nastajanja tal se bolj ali manj spremeni vsebnost glavnih in nekaterih slednih prvin (Ba, Nb, Rb in Sr). V bazičnih kamninah (gabbro, lamprofir) je njihova količina narasla, v bolj kislih (granodiorit in dacit) pa padla. Izjeme so le Fe, Mn in P.

Zato je uporaba vzorcev tal namesto svežih kamnin za večino petroloških klasfikacij (TAS–diagram, indeks nasičenja s kremenico in glinico, ločevanje I- in S-tipa granitov) neustrezna. Tudi uporaba Harkerjevih diagramov je pri talnih vzorcih skrajno nezanesljiva.

Bolj ustrezna je videti uporaba talnih vzorcev v primeru variacijskih diagramov, ki temeljijo na manj mobilnih prvinah. Diagrami, kot so Ba-Rb-Sr ali Rb/(Y+Nb), za tektonska okolja ter vzorci REE ne kažejo razlik med kamninskimi in talnimi vzorci.

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