Slovak Geol. Mag., 8, 2 (2002), 171 – 176

Distribution of Si in Stream Sediments of Slovakia – an Amendment to the Geochemical Atlas of the Slovak Republic

STANISLAV RAPANT[1], DUŠAN BODIŠ[1], DANIELA MACKOVÝCH[2], & SILVESTER PRAMUKA[2]

[1]Geological Survey of the Slovak Republic, Mlynská dolina 1, 817 04 Bratislava
[2]Geological Survey of the Slovak Republic, Regional Centre Spišská Nová Ves

Abstract. Distribution and geochemical characteristics of silicon in stream sediments of Slovakia are presented in this paper. Si contents have been evaluated additionally from laboratory records, archived from the samples from the Geochemical Atlas of the Slovak Republic, part VI. – Stream Sediments. It was possible to credibly additionally evaluate and determine Si contents in 22 920 samples from the original 24 432 samples of stream sediments. Si contents in stream sediments range from 0.37 % to 46.13 %. Average content is 29.02 % (arithmetic mean), or 29.95 % (median), respectively. Si content in stream sediments is controlled mainly by its concentration in rock substrate of their source areas and by geochemical processes during weathering and migration. Si is the most abundant element in rock environments as well as in stream sediments. Particularly thanks to the high resistance of Si minerals during weathering and migration the average Si contents in stream sediments in source areas of various rock types differ between each other significantly less than in primary rocks of the source areas. The lowest average values of Si contents have been documented in the source areas of Mesozoic limestones and dolomites (23.48 %) and the highest in the rock environment of sandstones and siltstones of the Outer Carpathians (32.07 %).

Key words: silicon, stream sediment, Geochemical Atlas, Slovak Republic

Introduction

During geochemical mapping of stream sediments in the framework of Geochemical Atlases of Slovakia programs (Vrana et al., 1997) 24 432 samples have been collected, that were analysed for total contents of 35 elements. Possibly due to conventional reasons, one of the most important main elements – **silicon** has not been determined, similarly to nearly all other national geochemical atlases (apart from Finland– Koljonen, T. (ed.) 1992), published at the end of 20th century. By the laboratory processing of the Geochemical Atlas of River Sediments of Slovakia (Bodiš – Rapant, eds. 1999) a fraction of each sample has been archived, so as it would be able to use it for consecutive laboratory works (e.g. to apply an analytical technique with more sensitive detection limits or to analyse elements not originally determined). In the same way, all laboratory analytical records, which contain also element records that were not originally evaluated, are archived.

As Si represents a very significant major element, important especially for interpretation of genesis of river sediments and rock weathering, its concentrations have been evaluated additionally from archived laboratory records. It was possible to additionally evaluate and determine Si contents in 22 920 samples from the original 24 432 samples of stream sediments, representing nearly 94 % of the total number of sample materials of the Geochemical Atlas of Slovakia. Below, a concise geochemical characteristics and distribution of Si in stream sediments of Slovakia is reported, as it was presented at other elements in the framework of the Geochemical Atlas (Bodiš – Rapant, eds. 1999).

Sampling, processing of samples and chemical analyses

Stream sediments have been sampled in the statistical density 1 sample per 2 km^2 and after drying they have been sieved to the fraction below 0.125 mm. For the quantitative analyses of silicon in stream sediments, atomic emission spectrometry with inductively coupled plasma (AES-ICP) method has been used after preliminary decomposition of samples by sintering with hydrogen peroxide.

Stream sediment samples were decomposed by sintering with Na_2O_2 in a Pt crucible at the temperature 490 °C for the duration of 30 minutes. After termination of sintering and cooling, the content of the Pt crucible has been dissolved in HCl (1+1) and a deposit solution has been prepared. Chemicals with pure p.a. have been used. Simultaneously, with every sample series a blank experiment has been prepared for the used chemicals. Silicon was analysed on the simultaneous spectrometer of the firm ARL 34 000. In order to remove physical influences, related to the atomisation of samples with high content of dissolved components, to the transport of samples, etc.,

Slovak Geol. Mag., 8, 2 (2002), 171 – 176

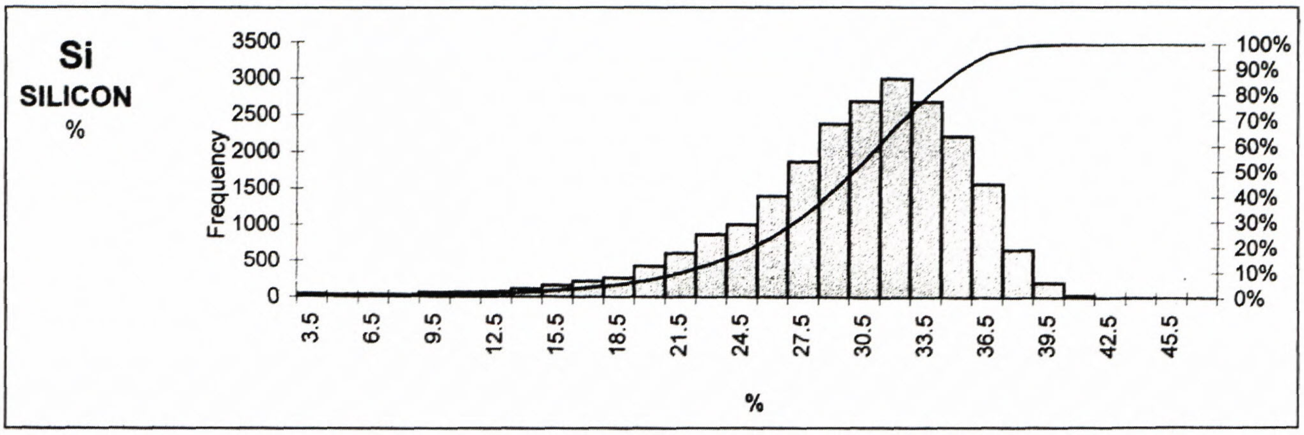

Table 1 Basis statistical characteristics of Si in stream sediments of Slovakia

Statistical Parameters		*Classes*	*Frequency*	*Cumulative %*	*Classes*	*Frequency*	*Cumulative %*
Arithmetic mean	29.022	3.5	45	0.20 %	26.0	1 407	23.87 %
Standard deviation	5.656	5.0	31	0.33 %	27.5	1 881	32.08 %
Geometr. mean	28.246	6.5	34	0.48 %	29.0	2 394	42.53 %
Median	29.950	8.0	35	0.63 %	30.5	2 704	54.32 %
Minimum	0.370	9.5	63	0.91 %	32.0	3 014	67.47 %
Maximum	46.130	11.0	67	1.20 %	33.5	2 696	79.24 %
25 %-il	26.250	12.5	78	1.54 %	35.0	2 236	88.99 %
75 %-il	32.940	14.0	120	2.06 %	36.5	1 577	95.87 %
99 %-il	38.220	15.5	168	2.80 %	38.0	670	98.80 %
Confidence level (95 %)	0.073	17.0	221	3.76 %	39.5	212	99.72 %
		18.5	269	4.93 %	41.0	40	99.90 %
Detection limit	0.005	20.0	432	6.82 %	42.5	8	99.93 %
		21.5	616	9.51 %	44.0	10	99.97 %
Number of samples below	0	23.0	874	13.32 %	45.5	3	99.99 %
Detection limit		24.5	1 012	17.74 %	<45.5	3	100.00 %

Table 2 Si contents in stream sediments of Slovakia sorted according to main rock types of source areas

Rock environment	Mean	Median	St. deviation	n
Neogene sediments	29.37	30.39	5.26	7 508
Neogene volcanics	28.10	28.35	4.04	2 614
Inner Carphathian Paleogene	30.24	31.24	5.32	2 535
Cretaceous and Paleogene of Outer Carpathians	32.07	32.80	4.23	4 296
Mesozoic carbonates	23.48	24.96	7.76	2 188
Mesozoic sediments other than carbonates	26.67	27.66	6.26	632
Inner Carphatian Late Paleogene	28.14	28.82	4.47	594
Inner Carphatian Early Paleogene	29.49	29.95	3.60	491
Tatricum and Veporicum basement	27.52	27.92	4.13	734
Inner Carphathian plutonites	27.70	28.21	3.95	1 247

Note: Contents are expressed in %, n = number of samples, rock types correspond to types according to Marsina et al, (1999).

the internal reference element Cd has been used. Thereby, improved, short-time and long-time, reproducibility has been achieved. Analytical signal has been evaluated using the calibration curve technique. Detection limit was 0.005 % Si. The accuracy and correctness has been tested on certified reference materials of river sediments GBW 07309, 07310.

Properties and distribution of silicon

After oxygen, silicon is the second most wide-spread element in earth's crust from the point of view of mass. In the nature it occurs almost exclusively in the oxidation level +4. It has a sharp affinity to oxygen and its bonds with oxygen in quartz or in silicates in the form of $[SiO_4]^{4-}$ tetrahedrons have characteristic high strength in all geochemical conditions. During weathering processes the most widespread Si mineral – quartz is liable mainly to mechanical abrasion. Subject to normal PT conditions it is virtually insoluble in water (the solubility reaches 6–10 mg.kg^{-1}) and chemical decomposition virtually does not occur. During weathering, other main and rock-forming minerals of silicon, silicates as well as alumosilicates – e.g. feldspars, micas, olivines etc., are liable to partial or total hydrolysis, accompanied by the origin of hydrosilicates and hydroalumosilicates in the form of hydromicas and clay minerals. At the same time the release and removal of a part of the silicon always occur, namely in the form of soluble silicates (especially Na and K), or in a colloid form. In term of Si content in stream sediments, the high weathering resistance of silicate rocks is essential. In stream sediments, similarly to sedimentary rocks, relative enrichment in silicon occurs thanks to the high resistance of Si minerals during weathering, while the SiO_2 concentrations often reach up to 90 % (more than **40** % Si).

Average silicon content in the continental crust is 263 580 mg.kg^{-1} (Taylor, McLennan, 1985). Sandstones reach the highest concentrations (403 000 mg.kg^{-1}) and in granites and granodiorites their contents are 337 000 mg.kg^{-1}. Silicon has the lowest concentration in limestones (31 000 mg.kg^{-1}). Average silicon content in fine fraction of glacial sediments (till) in Finland is 28.8±2.3 % (Koljonen, 1992). For instance, average Si contents in river sediments are 27.34 % for Czech Republic (fraction below 0.063 mm, median of 150 samples from main rivers, Veselý, 1995) and 298 388 mg.kg^{-1} for the region of Harz, Germany – (fraction below 0.063 mm, median, in Reimann – Caritat, 1998). In natural ground and surface waters Si contents range from miligrams up to first tenths of miligrams per liter. Estimated average Si content in world ocean is 2.2 mg.l^{-1} (Reimann – Caritat, 1998).

Silicon is an essential element for many organisms. It influences the growth, as it affects the building-up of the skeleton. As a nutrient, it is important just for a few organisms (e.g. diatomites). Some sorts of grasses are able to accumulate silicon. Silicon itself is not toxic, however, some of its compounds, e.g. asbestos, are carcinogeneous. Silicon oxide is a fibroid causing silicosis.

Generally, natural sources of silicon prevail over its antropogenic sources, to which production of cement, quartz, building materials, etc., belong.

In natural conditions the environmental mobility of quartz is very low, namely in acid to neutral up to alkaline, as well as in oxidizable and reductive conditions.

The average Si content in stream sediments of Slovakia is 29.02±5.5 % and the median is 29.95 %, suggesting relatively uniform distribution of values. The maximum determined concentration is 46.13 %, while the minimum concentration is 0.37 % (table 1). In table 2 average Si contents in stream sediments, sorted according to basic types and rock substrate composition of source areas, are presented.

The distribution of silicon in stream sediments of Slovakia (fig. 1) has several typical features. The highest concentrations (over 35 %) are focused into the region of Outer Flysh Belt, crystalline core of core mountains and Neogene volcanics of Slánske Vrchy Mts. and Vihorlatské vrchy Mts. This also indicates their source areas. The lowest silicon contents are present in source areas formed by Mesozoic limestones and dolomites (3–15 %) and in aluvial Quarternary sediments of the river Danube in Podunajská Nížina lowland (10–25 %).

In the rock environments, from the point of view of source areas, sandstones (37 %) granitoids (35 %), ryolites and ryodacites (34 %), andensites (28 %) have the highest average contents of silicon and, on the contrary, limestones (0.6 %) and dolomites (0.4 %) have the lowest concentrations of silicon (Marsina et al., 1999). While Si contents in stream sediments in source areas, formed by silicite rocks (sandstones, shales, granitoids, andesites), roughly correspond to their contents in source rocks, in areas with low Si contents in primary rocks (especially limestones and dolomites) an apparent enrichment in silicon occurs in stream sediments, mainly at the expense of calcium and magnesium contents. This implies that the distribution of silicon, calcium and magnesium in stream sediments has its regularity and it is controlled not just by contents of the above elements in rock substrate but also by the character and intensity of geochemical processes during weathering, transport and sedimentation. The complicated and, from the lithological point of view, very variable geological structure of the Slovak Republic is also very significant. In stream sediments these relations have been also tested using the correlation analyse with the following correlation coefficients: Si-Ca = -0.758; Si-Mg = -0.689 and Ca-Mg = 0.642. By other words, the distribution of silicon is indirectly proportional to the distribution of calcium and magnesium, while the concentration of both of these elements decreases with increasing silicon content. The distribution of Si/Ca (fig. 2) and Si/Mg (fig. 3) ratios also document this regularity. The source areas, formed by clastic sediments of the Outer Flysh Belt, have the maximum influence on the high concentrations of silicon in the Východoslovenská Nížina lowland that, unlike the Podunaská Nížina lowland, has much higher silicon contents. The sediments of the Podunajská Nížina lowland have different source areas, which is also mirrored in Si/Ca and Si/Mg ratio values that are below 1.84 and 6.78, respectively. This is also reflected by the high content of carbonates in soil profile of the Podunajská Nížina lowland (Čurlík – Šefčík, 1999). Lower Si content is probably also influenced by the decomposition of more soluble Si minerals (feldspars) during long transport in Danube, and furthermore in the Danube sandy gravels a relative enrichment in insoluble quartz occurred. The prevailing lower silicon content in the area of Central Slovakia Neogene Volcanic Field, compared to the Eastern Slovakian Volcanic Field, is also interesting. Here probably the influence of Flysh Belt source areas has also occurred, that is best observable in the Ondava river basin.

The radius of the silicon migration from the source areas is relatively large. Silicon migrates most often in the

Slovak Geol. Mag., 8, 2 (2002), 171 – 176

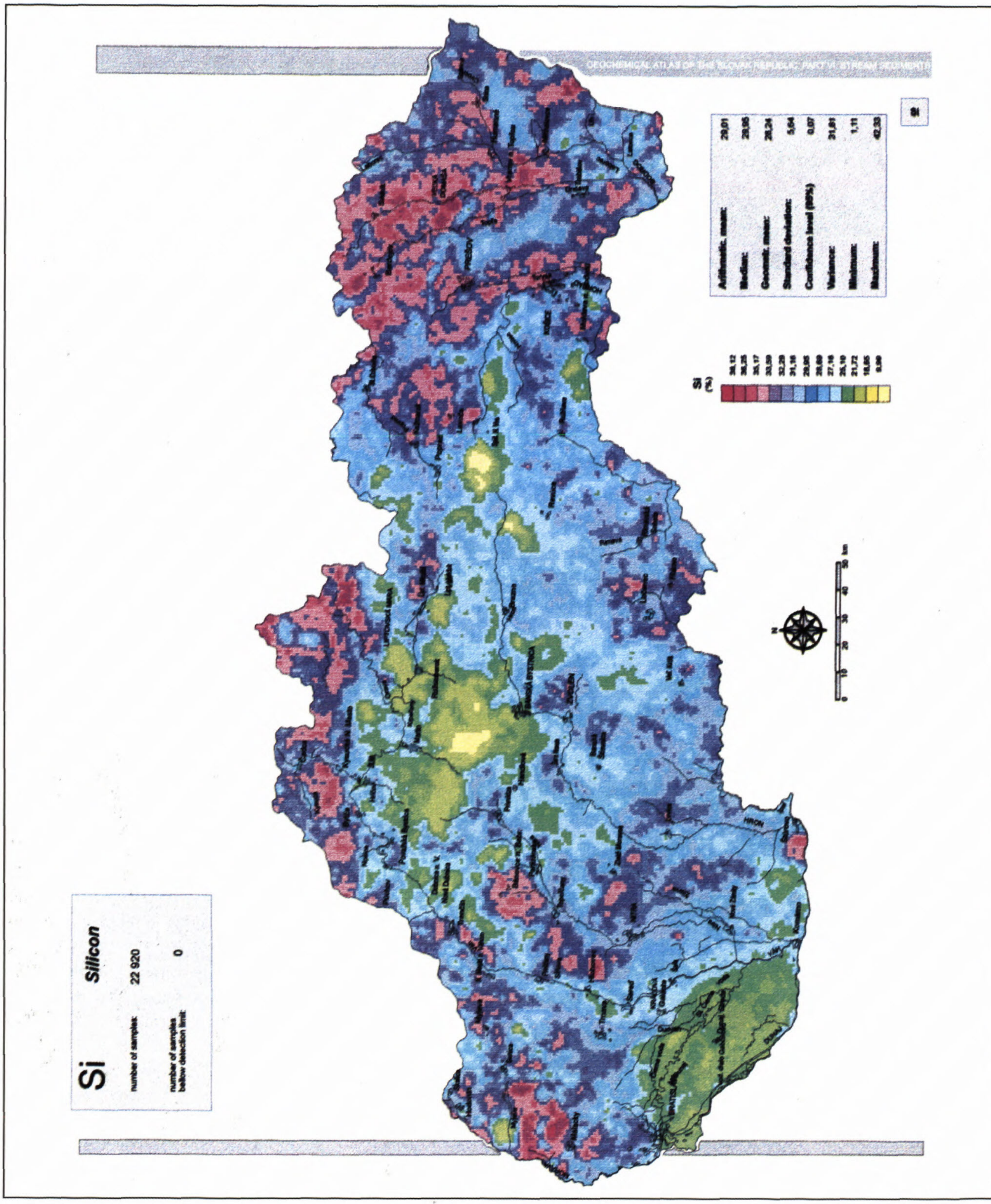

Fig. 1 Distribution of Si in stream sediments

form of quartz, that virtually does not have a geochemical barrier, and the migration is realised especially in a mechanical way. The distribution of silicon in stream sediments is proportional mainly to the distribution of calcium and magnesium. Due to different migration forms of these elements a mutual overlapping of their anomalies and thereby local, or eventually regional, variations can occur.

Conclusions

In the paper, the distribution of silicon in stream sediments of Slovakia is presented, those analyses have been evaluated additionally from samples from the Geochemical Atlas of the Slovak Republic, part VI. – River Sediments (Bodiš – Rapant, eds. 1999). From the achieved

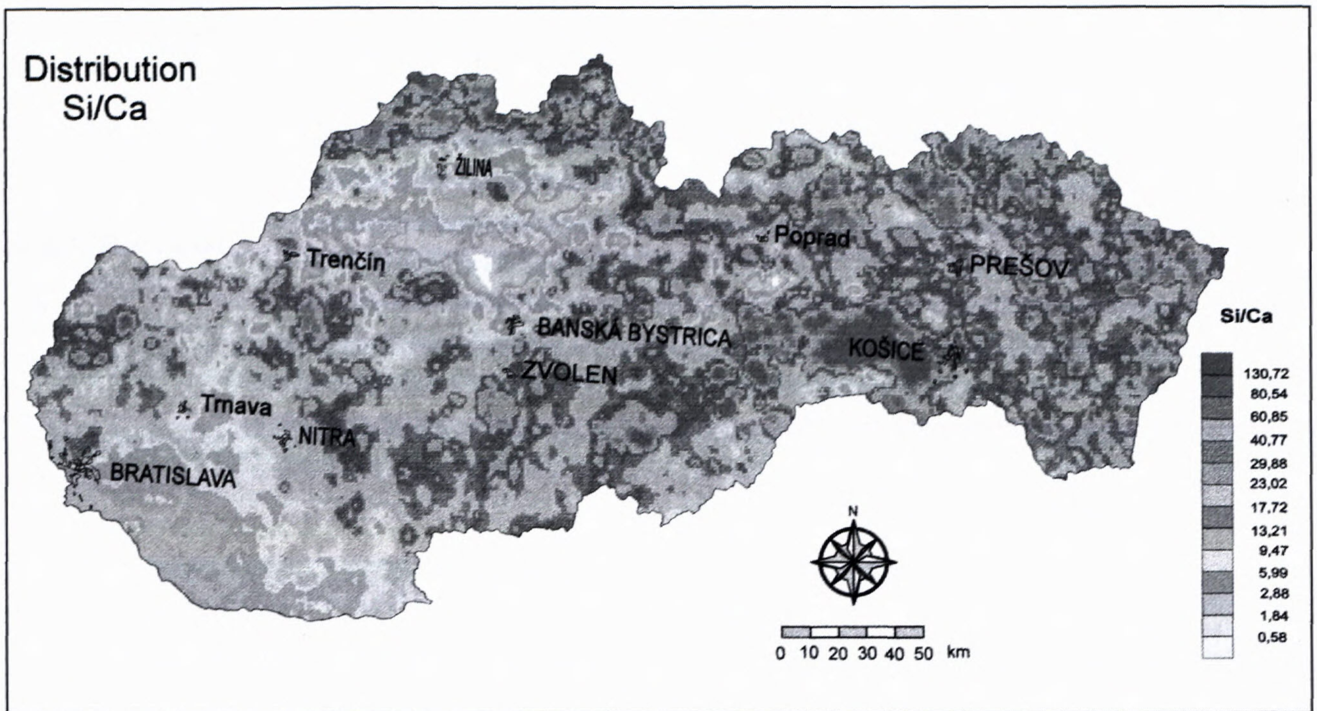

Fig. 2 Distribution of Si/Ca in stream sediments

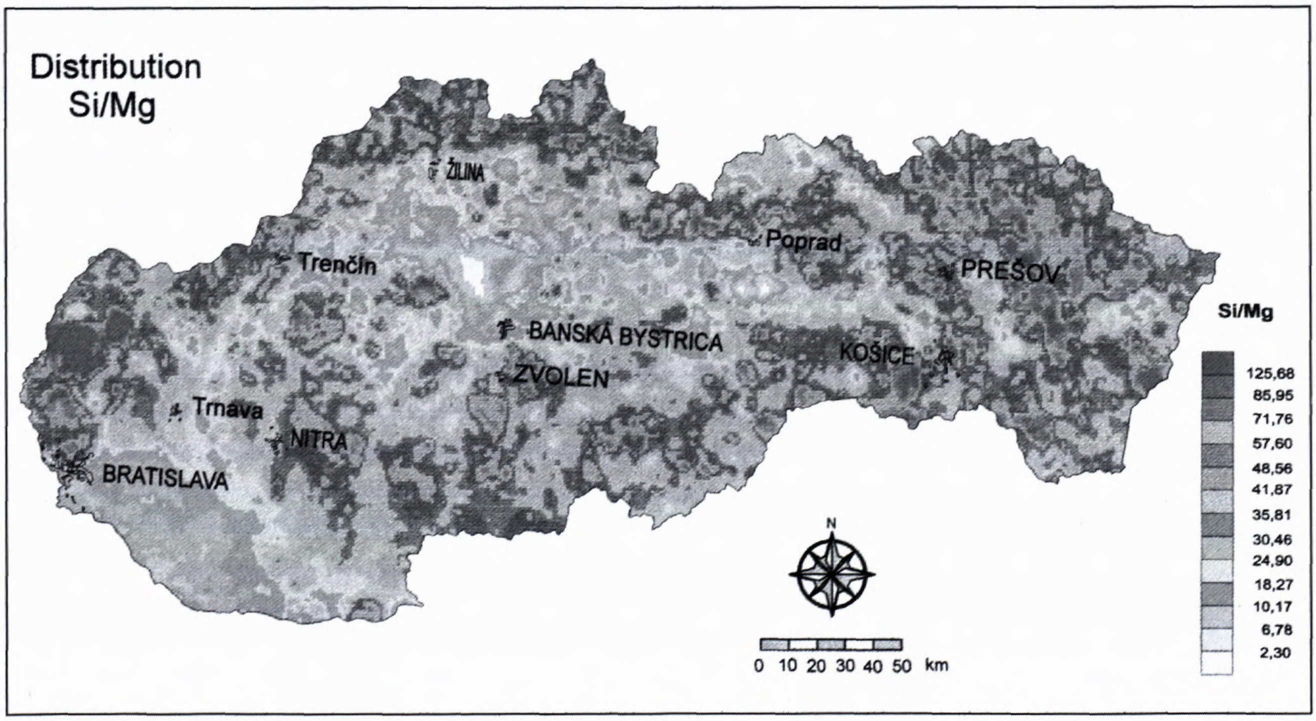

Fig. 3 Distribution of Si/Mg in stream sediments

results it is clear that Si content in stream sediments is mainly controlled by its content in rock substrate and by geochemical processes during weathering and migration. Si is the most abundant element in the rock substrate as well as in stream sediments. In stream sediments of Slovakia the radius of silicon migration from source areas is relatively large. In the conditions of the Slovak Republic it represents the order of up to tenths of kilometres.

Especially due to the high resistance of Si minerals during weathering and migration the average Si contents in stream sediments in areas of various rock types differ between each other apparently less than in primary rocks, forming source areas.

Si content is known and published for various natural environs. From the regional point of view mean Si concentrations are assessed, e.g. for different sorts of soils

Slovak Geol. Mag., 8, 2 (2002), 171 – 176

(agricultural, woodland, municipal, topsoil, etc.), natural waters (ground, surface and precipitation), stream flat sediments, etc. However, in literature in regional studies Si contents in stream sediments are published rarely only. Consequently, the presented information about contents and distribution of Si in stream sediments of Slovakia can be important from the point of view of knowledge and mapping of silicon in stream sediments not just in Slovakia but world-wide as well.

Literature

Bodiš, D., Rapant, S., Khun, M., Klukanová, A., Lexa, J., Mackových, D., Marsina, K., Pramuka, S. & Vozár, J. 1999: *Geochemical Atlas of Slovak Republic-part VI.- Stream sediments.* Monography, Geol. Survey of Slovak Republic, Bratislava, 145 p.

Čurlík, J. & Šefčík, P. 1999: *Geochemical Atlas of Slovak Republic – part V. – Soils*, Monography, VÚPOP, Bratislava. 99 p.

Koljonen, T. (ed.) 1992: *The Geochemical Atlas of Finland, part 2: Till.* Geological Survey of Finland, Espoo, 218 p.

Marsina, K., Bodiš, D., Havrila, M., Janák, M., Káčer, Š, Kohút, M., Lexa, J., Rapant, S. & Vozárová, A. 1999: *Geochemical Atlas of Slovak Republic-part III.- Rocks.* Monography, Geol. Survey of Slovak Republic, Bratislava, 134 p.

Rapant, S., Vrana, K. & Bodiš, D. 1996: *Geochemical Atlas of Slovakia-part I.-groundwater.* Monography, Geol. Survey of Slovak Republic, Bratislava, 127 p.

Reimann, C. & Caritat, P. 1998: *Chemical Elements in the Environment.* Springer, Berlín, 397 p.

Taylor, S. R. & McLennan, S. M. 1985: *The continental crust: Its composition and Evolution.* Blackwell Scientific Publications, 312 p.

Veselý, J. 1995: *Drainage sediments in environmental and exploration geochemistry.* Vestník Českého geologického ústavu 70, 3, p. 1–8.

Vrana, K., Rapant, S., Bodiš, D., Marsina, K., Lexa, J., Pramuka, S., Maňkovská, B., Čurlík, J., Šefčík, P., Vojtaš, J., Daniel, J. & Lučiviansky, L. 1997: *Geochemical Atlas of Slovak Republic at a scale 1 : 1 000 000.* Jurnal of Geochemical Exploration, 60, p. 7–37.