The distribution of rare earth elements (REEs) in paddy soil and rice seeds from Kočani Field (eastern Macedonia)

Razporeditev REE (redkih zemelj) v tleh riževih polj in rižu na območju Kočanskega polja (vzhodna Makedonija)

Nastja Rogan[1], Todor Serafimovski[2], Matej Dolenec[1], Goran Tasev[2], Tadej Dolenec[1,3*]

[1] Faculty of Natural Sciences and Engineering, University of Ljubljana,
Department of Geology, Aškerčeva 12, 1000 Ljubljana (Slovenia),
E-mail: tadej.dolenec@ntfgeo.uni-lj.si
*****Corresponding author: Tadej Dolenec, Tel.: 00386-1-4704-620
[2] Faculty of Mining and Geology, Goce Delčev 89, Štip (Macedonia)
[3] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana (Slovenia)

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Abstract: The concentrations of rare-earth elements (REEs) were analysed in paddy soil and rice grains collected from Kočani Field in eastern Macedonia. The results showed that the paddy soil originated from composite material mostly derived from igneous, volcanic, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression. The elevated concentrations of heavy REEs (HREE) could be explained by the contribution of the mafic and ultramafic lithologies to the soil formation. The concentrations of REEs in unpolished rice from Kočani Field exhibited a similarly elevated HREE pattern, like paddy soils, with up to $6.6x10^3$ times lower values compared to those in the soil. The very similar accumulation coefficients (La - Sm) indicated no preferential fractionation of La-Sm in the rice-paddy soil system of Kočani Field.

Povzetek: V članku so podani izsledki geokemičnih raziskav vsebnosti redkih zemelj (REE) v tleh riževih polj in v oluščenem rižu z območja Kočanskega polja v vzhodni Makedoniji. Rezultati kažejo, da predstavljajo izvorne kamnine, ki so dale material za tamkajšnja tla v glavnem magmatske, metamorfne in sedimentne kamnine, katerih preperino so odložili v Kočansko depresijo reka Bregalnica in njeni pritoki. Povišane vsebnosti HREE kažejo tudi na prisotnost mafične in ultramafične komponente v materialu iz katerega so nastala tla. Vsebnost REE v neoluščenem rižu kaže podobno obogatitev s HREE kot tla, le da so njihove koncentacije do $6{,}6x10^3$ manjše kot v tleh. Na podlagi zelo podobnih koeficientov akumulacije za La-Sm sklepamo, da v sistemu tla - riž ni prišlo do bistvene frakcionacije omenjenih prvin.

Key words: Rare-earth elements (REEs), paddy soil, unpolished rice, Kočani Field, Macedonia

Ključne besede: Redke zemlje (REE), tla, nepoliran riž, Kočansko polje, Makedonija

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INTRODUCTION

The rare-earth elements (REEs) are a group of 15 elements, of which one, promethium (Pm), does not occur naturally in the earth's crust, while the others occur in all rocks (KABATA-PENDIAS & PENDIAS, 2001). They are fractionated during the crystallization of minerals from magma and during the regional metamorphism of volcano-sedimentary rocks (LIPIN & MCKAY, 1989). REEs have very similar chemical properties and tend to be present naturally as a group rather than existing alone, which makes them very useful tracers in geochemical studies (HENDERSON, 1984). REE data, however, might also be useful in the provenance determination of coarse and fine-grained sedimentary rocks or even in soil genesis (CULLERS ET AL., 1987; EGASHIRA ET AL., 1997; YOSHIDA ET AL., 1998). However the application of REEs to these problems has been hampered by the lack of a complete understanding of how they behave in aqueous solutions and size-fractions during weathering, transportation, deposition and soil-forming processes. The potential for chemical fractionation of the REEs in solution in natural waters is the energies of the formation of the common ionic species, which may cause certain elements of this series to be removed from solution by preferential sorption to colloidal particles (FAURE, 1998). For example, the chemical fractionation of trace elements, including REEs by sorption to ferric hydroxide particles was reported by CENTENO et al. (2004). YOSHIDA et al. (1998) found that REEs were rather resistant during soil-formation processes, because their concentrations and the chondrite-normalized patterns are not so far from those of the possible parent material. Therefore, a knowledge of REE concentrations in soils is required as background data for estimating soil contamination due to anthropogenic sources. Elevated concentrations of some REEs, such as La, Ce, Sm, Eu and Tb, have been found in the environments of industrial and urban areas (YOSHIDA, et al., 1998). These elements are likely to be released into the environment, mainly from coal-burning and nuclear energy material processing (KABATA-PENDIAS & PENDIAS, 2001). Phosphatic fertilizers added to agricultural soils can also be sources of REEs (TSUMURA & YAMASAKI, 1993). Brown et al. (1990) have demonstrated that the REEs could stimulate the plant growth of cereals, vegetables, fruits and tea. Inorganic compounds of REEs, such as $REE(NO_3)_2$, which act as microelement fertilizer, have been entered the environment and accumulated in the ecosystem (DING, et al., 2006). Special attention should thus be paid to the concentrations of trace elements such as REEs in agricultural soils, because of their potential to transfer to plants and the resultant internal exposure through ingestion, which could endanger public health (CHUA, 1998; VOLOKH, et al., 1990).

The objective of the present study was:

1. to estimate the contents and distribution patterns of REEs in the paddy soil of Kočani Field and unpolished rice grown on this area,
2. to reveal the possible fractionation of REE in the paddy-soil rice-grain system.

Materials and methods

Study area

The study area of the Kočani paddy fields is located in eastern Macedonia, about 32 km from the city of Štip. It is situated in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (1). Its average length is 35 km and its width is about 5 km. Previous investigations revealed the heavy metal contamination of the paddy soil, especially those areas from the western part of Kočani Field, due to the irrigation with riverine water impacted by heavy metals originating from mining activities and acid mine drainage from the Zletovo-Kratovo and Sasa-Toranica base-metal ore districts (Dolenec, et al., 2006).

Soil sampling and preparation

The objective of the field sampling programme performed in 2004-2005 was also to provide a characterization of the REEs in the paddy soil and the rice of Kočani Field. For this purpose paddy soil samples, as previously reported (Dolenec, et al., 2006), were collected at 38 locations from 7 profiles across Kočani Field, as shown in Figure 2. Near-surface paddy soils (0-20 cm in depth) were sampled using aplastic spade to avoid any heavy metal contamination. Each soil

Figure 1. Map of the study area showing the drainage system of the Bregalnica River and its tributaries

Slika 1. Geografska karta Kočanskega polja z drenažnom sistemom Bregalnice in njenih pritokov

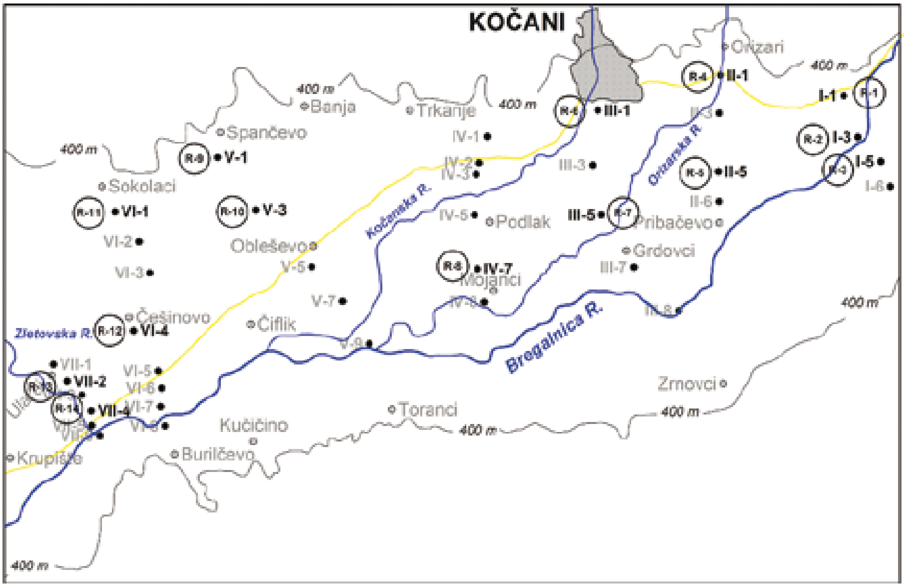

Figure 2. Sampling location map of the study area: (I - VII) soil samples®, unpolished rice samples

Slika 2. Geografski položaj vzorčnih točk (I - VII vzorčne točke tal®, vzorčne točke riža)

sample comprised a composite of 5 sub-samples taken within a 1×1 square. The soil samples were air dried at 20 °C for one week and sieved through a 2 mm polyethylene sieve to remove the plant debris, the pebbles and the stones. They were ground in a mechanical agate grinder to a fine powder for a subsequent geochemical analyses.

Rice sampling and preparation

Rice grain samples with a hull were collected in October 2005 at physiological maturity from 14 sampling sites over Kočani Field (Figure 2). At each sampling site, rice grains were taken over an area of 10x10 m to get a final composite sample of about 1 kg. Each composite rice sample was collected from approximately the same location as the corresponding soil samples for further studies of heavy metal mobility and bioavailability.

All the samples were collected and stored in polythene and brought to the laboratory for further preparation and treatment. In the laboratory, rice grains with a hull were thoroughly washed three times with deionised water to remove the soil particles and dust, and after that they were oven dried to a constant weight at 75 °C for 72 hours. The rice was de-hulled with a ceramic pestle and mortar and the de-hulled rice grains were ground in an agate mortar to a fine powder. The powdered samples were packed in clean, dry, stoppered-glass containers and stored in a refrigerator before being analyzed.

Determination of the REEs

All the paddy soil and rice samples were analyzed for their REE concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd) using different analytical methods. According to the reports, the REEs in the soil samples were determined after fusion with a mixture of lithium/tetraborate and dissolution in nitric acid by ICP-MS. The rice samples were dissolved in environmental-grade nitric acid and then also analysed by ICP-MS. The accuracy and precision of the REE soil analyses were assessed by using international reference material such as USGS G-1 (granite) and CCRMP SO-1 (soil). Quality checks of the rice analyses included analyses of certified reference material (rice flour SRM 1568) from the National Bureau of Standards (NBS). The analytical precision and accuracy were better than ± 8 %. This was indicated by the results of duplicate measurements on 10 soil and 3 rice samples as well as duplicate measurements of the G-1, SO-1 and SRM 1568 standards.

Statistical analyses

The calculations for mean, medium, minimum and maximum concentration values for analyzed elements in the soil and rice samples together with the variance and standard deviation (S. D.) data were obtained with the statistical package Statistica version 6.

RESULTS AND DISCUSSION

The REE concentrations in paddy soil

The concentrations of REEs in the paddy soil from Kočani Field are presented in Table 1 together with the concentrations of REEs in the upper continental crust (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995) and the mean concentrations of the lanthanides in soils, given by URE AND BACON (1979) and YOSHIDA et al. (1998) used for a comparison with REE contents in the Kočani paddy soil. Table 2 shows a synthesis of the main statistical parameters (mean, median, range and standard deviation - S. D.).

The mean REE levels in the paddy soil were slightly higher than those reported for the mean concentrations of the average upper crust and for the soils. Their content also exceeded the values reported by YOSHIDA et al. (1998) for the Japanese soils; however, the median content of Ce and the light rare earth elements (LREEs) were also elevated in comparision with the mean concentrations of lanthanides in the soil (Table 1 and Table 2). The sum of REEs in the paddy soil measured during this study ranged from 106.4 to 244.4 µg/g, with a median of 171.7 µg/g (Table 1). The relatively high amounts of REEs could be attributed to the predominantly granitic lithologies exposed in the drainage area of the Bregalnica and Zletovska Rivers as well as in the surroundings of Kočani Field. It is well known that granitic rocks contain a larger amount of light rare-earth elements (LREE: La-Sm) compared to other igneous rocks, such as basalts and andesites (HERMAN, 1970; REIMAN & CARITAT, 1998 and references therin). Among the essential minerals, salic minerals preferentially concentrate the LREE and the femic minerals concentrate the heavy rare-earth elements (HREE: Gd-Lu). The REEs in the paddy soil seem to be realised mainly from parent material during the weathering and soil formation. Due to their low solubility and relative immobility in the upper crust the REEs are very useful for studying sedimentary environments, because sediments inherit the REE composition of their source rocks and, therefore, carry information about the origin of those

Table 1. Total REE concentrations in the paddy soil of Kočani Field. 1) upper continental crust (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995); 2) URE and BACON (1979) and 3) YOSHIDA et al. (1998)
Tabela 1. Vsebnosti REE v tleh riževih polj Kočanskega polja. 1) zemeljska skorja - zgornji del (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995); 2) URE and BACON (1979) and 3) YOSHIDA et al. (1998)

Element		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Units		μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
Location	Sample															
I-1	1	31.6	65.4	7.6	30.1	6.0	1.14	5.80	0.98	5.93	1.16	3.44	0.53	3.32	0.51	163.51
I-3	2	48.3	99.2	11.3	45.6	8.7	1.77	7.84	1.47	7.86	1.52	4.30	0.69	4.20	0.65	243.40
I-5	3	32.7	67.6	7.8	30.6	6.1	1.29	5.44	0.94	5.30	1.03	3.03	0.48	3.11	0.44	165.86
I-6	4	20.9	47.0	5.3	23.7	5.3	1.29	5.09	0.93	5.21	1.10	3.16	0.50	3.02	0.49	122.99
II-1	5	39.6	84.9	9.3	39.3	7.9	1.50	6.58	1.13	5.97	1.24	3.32	0.53	3.41	0.53	205.21
II-3	6	38.9	84.3	8.9	37.6	7.1	1.46	5.85	1.03	5.62	1.21	3.27	0.49	3.12	0.50	199.35
II-5	7	35.3	74.9	8.4	35.7	6.7	1.31	5.21	0.98	5.05	1.13	3.04	0.49	3.05	0.46	181.72
II-6	8	38.1	83.6	9.3	40.2	7.9	1.58	6.78	1.24	6.66	1.36	3.94	0.65	4.10	0.59	206.00
III-1	9	31.9	70.2	8.1	35.0	7.0	1.49	6.99	1.25	6.95	1.42	4.24	0.65	4.00	0.62	179.81
III-3	10	34.9	74.1	8.5	37.2	6.9	1.46	6.76	1.17	6.52	1.33	3.80	0.57	3.78	0.59	187.58
III-5	11	49.8	103.1	11.5	45.9	8.6	1.63	7.00	1.26	6.45	1.26	3.51	0.56	3.33	0.49	244.39
III-7	12	30.6	64.3	7.3	30.1	5.5	1.27	5.23	0.90	5.25	1.03	3.11	0.52	3.27	0.52	158.90
III-8	13	18.4	41.2	4.8	21.0	4.3	1.00	4.04	0.67	4.28	0.83	2.45	0.40	2.64	0.39	106.40
IV-1	14	29.7	65.7	7.6	34.3	7.0	1.91	7.44	1.22	7.13	1.40	4.16	0.63	3.90	0.58	172.67
IV-2	15	28.3	63.6	7.4	34.1	7.0	1.77	7.34	1.23	6.84	1.39	3.95	0.60	3.60	0.57	167.69
IV-3	16	30.2	67.3	7.9	33.6	6.7	1.73	7.23	1.28	7.34	1.35	4.02	0.60	3.68	0.56	173.49
IV-5	17	32.3	71.0	7.6	32.3	6.1	1.31	5.63	1.01	5.91	1.06	3.28	0.51	3.29	0.50	171.80
IV-7	18	36.5	86.7	8.7	37.1	7.0	1.37	6.34	1.08	6.12	1.11	3.48	0.51	3.37	0.54	199.92
IV-8	19	42.0	87.0	10.1	41.6	7.4	1.43	6.78	1.10	6.28	1.19	3.45	0.52	3.37	0.51	212.73
V-1	20	39.2	79.1	8.7	35.0	6.2	1.39	4.84	0.81	4.48	0.85	2.43	0.37	2.51	0.34	186.22
V-3	21	39.6	83.6	9.1	37.2	6.4	1.45	5.32	0.81	4.47	0.87	2.61	0.38	2.45	0.36	194.62
V-5	22	31.6	65.8	7.3	31.0	5.8	1.26	5.46	0.95	5.25	0.98	2.92	0.47	2.98	0.44	162.21
V-7	23	26.4	56.9	6.7	28.6	5.6	1.25	5.31	0.94	5.48	1.11	3.26	0.49	3.24	0.55	145.83
V-9	24	27.1	58.7	6.7	28.4	5.6	1.20	5.09	0.87	5.19	1.05	3.01	0.49	3.06	0.47	146.93
VI-1	25	36.4	76.7	8.5	33.5	6.0	1.34	4.89	0.81	3.97	0.76	2.25	0.38	2.22	0.32	178.04
VI-2	26	40.5	88.0	9.1	36.7	6.8	1.62	5.35	0.91	4.67	0.90	2.68	0.41	2.34	0.43	200.41
VI-3	27	36.1	73.5	8.5	34.1	6.4	1.38	5.55	0.91	5.01	0.92	2.77	0.43	2.58	0.42	178.57
VI-4	28	31.5	69.0	8.0	33.4	6.4	1.35	5.98	1.02	5.84	1.15	3.46	0.52	3.52	0.50	171.64
VI-5	29	30.8	65.7	7.5	30.8	6.0	1.43	5.70	1.04	5.70	1.16	3.28	0.55	3.31	0.52	163.49
VI-6	30	30.8	67.0	7.7	32.4	6.3	1.34	5.80	0.98	5.66	1.15	3.35	0.52	3.30	0.47	166.77
VI-7	31	22.4	50.2	5.7	23.8	4.9	1.17	4.70	0.88	4.90	0.98	2.98	0.52	3.16	0.49	126.78
VI-8	32	28.6	61.3	7.0	29.7	6.0	1.38	5.65	1.00	5.66	1.07	3.25	0.50	2.99	0.48	154.58
VII-1	33	27.1	56.9	6.3	25.6	4.7	1.16	4.53	0.76	4.02	0.80	2.31	0.40	2.50	0.39	137.47
VII-2	34	31.9	66.1	7.3	31.5	5.7	1.34	5.02	0.77	4.73	0.85	2.58	0.40	2.48	0.40	161.07
VII-3	35	33.2	70.2	7.6	30.6	5.5	1.42	5.01	0.84	4.66	0.90	2.66	0.39	2.65	0.38	166.01
VII-4	36	30.7	65.5	7.1	28.2	5.4	1.33	4.76	0.86	4.66	0.88	2.60	0.41	2.56	0.38	155.34
VII-5	37	29.4	60.7	6.7	27.6	4.8	1.20	4.70	0.76	4.18	0.80	2.35	0.39	2.34	0.37	146.29
VII-6	38	35.7	75.9	8.7	36.7	6.9	1.55	6.57	1.07	6.38	1.22	3.64	0.55	3.43	0.58	188.89
	1	32.3/30	65.7/64	6.3/7.1	25.9/26	4.7/4.5	0.95/0.9	2.8/3.8	0.5/0.44	2.9/3.5	0.62/0.8	-/2.3	-/0.33	1.5/2.2	0.27/0.3	
	2	33.5	48.5	7.7	33.0	6.1	1.9	3.0	0.63	3.8	0.38	2.0	0.16	2.3	0.34	
	3	18.0	40	4.5	18.0	3.7	0.96	3.7	0.56	3.3	0.68	2.0	0.29	2.0	0.39	

Table 2. Descriptive basic statistic of the REE contents in the paddy soil of Kočani Field
Tabela 2. Osnovna statistika za vsebnosti REE v tleh riževih polj Kočanskega polja

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Units	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
Mean	33	71	7.93	33.2	6.33	1.40	5.78	1.00
Median	32	68	7.71	33.5	6.25	1.38	5.59	0.98
Minimum	18	41	4.75	21.0	4.30	1.00	4.04	0.67
Maximum	50	103	11.50	45.9	8.70	1.91	7.84	1.47
S.D.	7	13	1.40	5.5	1.00	0.19	0.94	0.18

Element	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Units	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
Mean	5.57	1.09	3.19	0.50	3.14	0.48	173.542
Median	5.55	1.11	3.26	0.51	3.20	0.49	171.720
Minimum	3.97	0.76	2.25	0.37	2.22	0.32	106.400
Maximum	7.86	1.52	4.30	0.69	4.20	0.65	244.390
S.D.	0.97	0.20	0.56	0.08	0.52	0.08	29.006

rocks (Ross, et al., 1995). The fraction and mobilization of the REEs during weathering could be related to geochemical reactions that involve changes in the pH values in the soil and waters (DUDDY, 1980; Ross, et al., 1995).

Chondrite normalized patterns of the paddy soil and those of selected granitic rocks from the Osogovo Mountains did not differ appreciably from each other and are similar to that of the mean REE concentrations for the average upper crust (Figure 3). The REE normalised patterns of paddy soil are characterized by a similar concentration of LREEs, a prominent Eu anomaly and a higher HREE content relative to the original material of the soil. The elevated levels of HREEs could be explained by the contribution of the mafic and ultramafic lithologies to the soil formation. The preferential decomposition of femic minerals and calcic plagioclases relative to the more resistant sodic and potassium feldspars during weathering of the exposed lithologies in the drainage area of the Bregalnica River and its tributaries seems to result in HREE enrichment of the paddy soil. This could be related to the irrigation of the paddy fields with water from the Bregalnica River. Another source of HREE is thought to be the amphiboles and pyroxenes present in the paddy soil (DOLENEC, et al., 2006).

A study of lateritic soils has shown that there is a preferential retention of LREEs in the solid phases and a preferential transport of the HREEs in the solution phase (SHOLKOWITZ, 1992). REEs can also be enriched during the soil-formation processes, even if the source material is not granitic rock (YOSHIDA, et al., 1998). In addition, REEs are used as fertilizer additives for the stimulation of the plant growth of cereals, vegetables, fruits and tea (BROWN, et al., 1990; YUAN, et al., 2001). Phosphatic fertilizer added to agricultural soils could thus be a source of REE as well as U and Th (TSUMURA & YAMASAKI, 1993; YOSHIDA, et al., 1998). Although the data for REE concentrations in soils are limited, compared with those in rocks and meteorites (YOSHIDA,

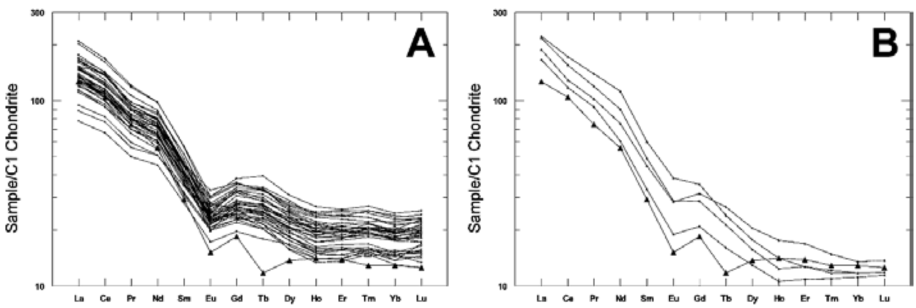

Figure 3. Rare-earth element patterns normalized to C1 chondrite for the paddy soil of Kočani Field (A) and granitic rocks (dacites, trahidacites) (B) from the Osogovo Mountains (REE content of volcanites is taken from Serafimovski et al., (2005). ▲ - Upper crust (TAYLOR & MCLENNAN, 1995)

Slika 3. Vzorec redkih zemelj (REE) za tla riževih polj Kočanskega polja normaliziran na C1 hondrit (A) in normalizirane vrednosti REE za granitoide (daciti, trahidaciti) Osogovskih planin (B) - vsebnosti REE v vulkanitih so po Serafimovskem et al. (2005), ▲ zemeljska skorja - zgornji del (TAYLOR & MCLENNAN, 1995) et al., 1998), we suppose that the observed concentrations of REEs in the paddy soil are generally attributed to the concentrations of these elements in predominantly acidic and intermediate igneous rocks, which are the main source materials for the paddy soil of Kočani Field. The possible contribution of REEs due to the application of phosphate fertilizers seems to be negligible.

The REE concentrations in unpolished rice

The concentrations of the REE in unpolished rice from Kočani Field are presented in Table 3, while Table 4 shows the synthesis of the main statistical parameters (mean, median, range and standard deviation - S. D.). Table 5 lists the accumulation coefficients for La, Ce, Pr, Nd and Sm. A synthesis of the main statistical parameters for the accumulation coefficients (mean, median, range and standard deviation-S.D.) is shown in Table 6. The contents of Eu, Gd, Tb, Ho, Er, Tm, Yb, and Lu were lower than the detection limit of the ICP-MS. Therefore, these elements were not taken into consideration during this study.

The concentrations of REEs in plants vary within a broad range from below 0.001 to above 15µg/g (KABATA-PENDIAS & PENDIAS, 2001). In rice the sum of the REEs was found to be 0.6 µg/g (LIU, 1988). The sum of the REEs in unpolished rice found during this study ranged from 0.037 to 0.155 µg/g, with a median of 0.066 µg/g, which is about nine times lower than the value reported by LIU (1988). This could be explained by the different REE content of the paddy soils. Plants grown on REE enriched soils showed very high concentrations of these elements (MIEKELEY, et al., 1994), although the concentrations of the individual REEs were not a function either of their total content or their soluble forms in soils (WYTTENBACH, et al., 1997). The concentrations of REEs

Table 3. Total REE (La - Sm) concentrations in the unpolished rice of Kočani Field
Tabela 3. Vsebnosti REE (La - Sm) v oluščenem (nepoliranem) rižu iz Kočanskega polja

Sample ID:		La	Ce	Pr	Nd	Sm	ΣREE
Units		µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I-1	R-1	0.0141	0.0286	0.0036	0.0117	0.0023	0.060
I-3	R-2	0.0141	0.0329	0.0035	0.0110	0.0023	0.064
I-5	R-3	0.0155	0.0330	0.0037	0.0131	0.0031	0.068
II-1	R-4	0.0255	0.0546	0.0059	0.0235	0.0047	0.114
II-5	R-5	0.0129	0.0273	0.0032	0.0111	0.0025	0.057
III-1	R-6	0.0115	0.0240	0.0028	0.0096	0.0018	0.050
III-5	R-7	0.0173	0.0383	0.0041	0.0152	0.0036	0.079
IV-7	R-8	0.0119	0.0270	0.0031	0.0108	0.0022	0.055
V-1	R-9	0.0145	0.0326	0.0033	0.0141	0.0031	0.068
V-3	R-10	0.0089	0.0173	0.0015	0.0079	0.0016	0.037
VI-1	R-11	0.0348	0.0778	0.0081	0.0287	0.0056	0.155
VI-4	R-12	0.0157	0.0326	0.0041	0.0137	0.0025	0.069
VII-2	R-13	0.0092	0.0197	0.0025	0.0081	0.0019	0.041
VII-4	R-14	0.0263	0.0587	0.0063	0.0232	0.0057	0.120

Table 4. Descriptive basic statistic of the REE contents in the unpolished rice of Kočani Field
Table 4. Osnovna statistika za vsebnosti REE v oluščenem rižu iz Kočanskega polja

	La	Ce	Pr	Nd	Sm	ΣREE
Units	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
Mean	0.016586	0.036029	0.003979	0.014407	0.003064	0.074
Median	0.014300	0.032600	0.003550	0.012400	0.002500	0.066
Minimum	0.008900	0.017300	0.001500	0.007900	0.001600	0.037
Maximum	0.034800	0.077800	0.008100	0.028700	0.005700	0.155
Std.Dev.	0.007337	0.016702	0.001712	0.006296	0.001359	0.033

Table 5. The accumulation coefficients (La - Sm)$\times 10^{-4}$ for unpolished rice from Kočani Field
Tabela 5. Koeficient akumulacije za (La - Sm)$\times 10^{-4}$ za oluščen riž iz Kočanskega polja

Section	Sample	La2/La1	Ce2/Ce1	Pr2/Pr1	Nd2/Nd1	Sm2/Sm1
I-1	**R-1**	4.46	4.37	4.74	3.89	3.83
I-3	**R-2**	2.92	3.32	3.1	2.41	2.64
I-5	**R-3**	4.74	4.88	4.74	4.28	5.08
II-1	**R-4**	6.44	6.43	6.34	5.98	5.95
II-5	**R-5**	3.65	3.64	3.81	3.11	3.73
III-1	**R-6**	3.61	3.42	3.46	2.74	2.57
III-5	**R-7**	3.47	3.71	3.57	3.31	4.19
IV-7	**R-8**	3.26	3.11	3.56	2.91	3.14
V-1	**R-9**	3.7	4.12	3.79	4.03	5
V-3	**R-10**	2.25	2.07	1.65	2.12	2.5
VI-1	**R-11**	9.56	10.14	9.53	8.57	9.33
VI-4	**R-12**	4.98	4.72	5.13	4.1	3.91
VII-2	**R-13**	2.88	2.98	3.42	2.57	3.33
VII-4	**R-14**	8.57	8.96	8.87	8.23	10.56

Table 6. Descriptive basic statistic of the accumulation coefficients (La - Sm)$\times 10^{-4}$ for unpolished rice from the Kočani Field
Tabela 6. Osnovna statistika za koeficient akumulacije z (La - Sm)$\times 10^{-4}$ za oluščen riž iz Kočanskega polja

	La2/La1	Ce2/Ce1	Pr2/Pr1	Nd2/Nd1	Sm2/Sm1
Mean	4.61	4.71	4.69	4.16	4.7
Median	3.68	3.92	3.8	3.6	3.87
Minimum	2.25	2.07	1.65	2.12	2.5
Maximum	9.56	10.14	9.53	8.57	10.56
Std.Dev.	2.17	2.31	2.2	2.05	2.45

in plants seem to be extremely variable and dependent on the various species of plant and their corresponding habitat (Ichihashi, et al., 1992; Wyttenbach, et al., 1998). The REE content of different parts of the plants followed the order root > leaf > stem > grain (Li, et al., 1998; Xu, et al., 2002). In addition, enrichment with the HREEs relative to the LREEs in rice grains was also observed. This suggested that the rice grains had a greater ability to absorb the HREEs compared to the LREEs. Shi-Ming et al. (2006) also reported similar HREE enrichment for wheat grains.

To visualize REE abundance variations, accumulation coefficients, the soil normalized REE contents of rice grains were calculated according to Shi-Ming et al. (2006) by dividing the content of each REE in the rice grains by the content of the same REE in the soil. The accumulation coefficients (La - Sm) are shown in Table 5. From Table 5 it is clear that the accumulation coefficients for La, Ce, Pr, Nd, and Sm are very similar. Their median values were 3.7×10^{-4} (La2/la1), 3.9×10^{-4} (Ce2/Ce1), 3.8×10^{-4} (Pr2/Pr1), 3.8×10^{-4} (Nd2/Nd1), and 3.9×10^{-4} (Sm2/Sm1). Such values indicated a similar fractionation event of these elements in the paddy soil-rice system of Kočani Field. This is also suggested by the chondrite normalised pattern (La - Sm) (Figure 4), which is similar to that of the paddy soils.

CONCLUSIONS

The relatively high REE concentrations of the paddy soil from Kočani Field could be attributed predominantly to the granitic lithologies exposed in the drainage area of the Bregalnica River and its tributaries. This was confirmed by the REE normalised patterns of selected granitic rocks from the Osogovo Mountains, which did not differ appreciably from each other and are similar to those of the Kočani paddy soil. The elevated concentrations of HREEs could be explained by the contribution of the mafic and ultramafic lithologies, also exposed in the broader area of Kočani Field to the soil formation.

The concentrations of REEs in unpolished rice from Kočani Field exhibited a similarly elevated HREE pattern like the paddy soil, although their absolute values were up to

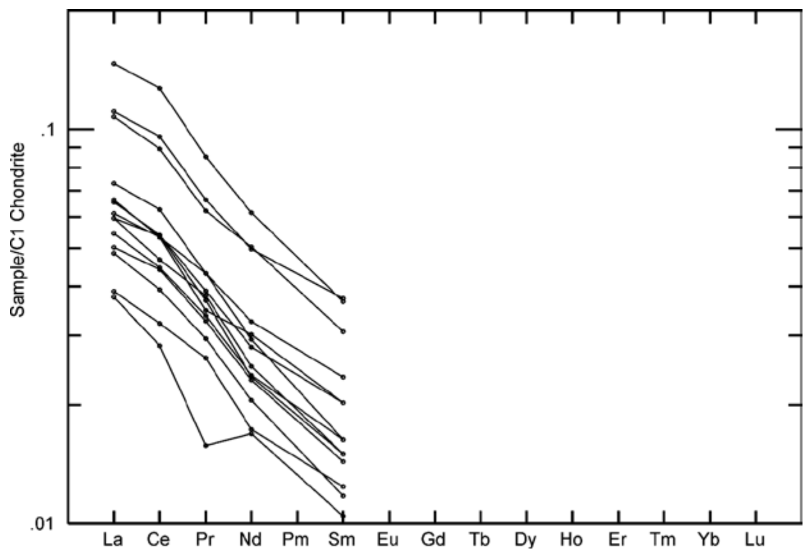

Figure 4. Rare-earth element patterns normalized to C1 chondrite for the unpolished rice from Kočani Field

Slika 4. Vzorec redkih zemelj (REE) za oluščen riž iz Kočanskega polja normaliziran na C1 hondrit

6.6 x 10^3 times lower than those in the soils. The very similar accumulation coefficients (La - Sm) indicated no preferential fractionation of La - Sm during their uptake by the rice plant.

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