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CHROMIUM AND NICKEL IN SOIL IN THE WIDER MAGLAJ AREA – CONCENTRATION AND GENESIS

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ABSTRACT

Research on potentially toxic elements chromium and nickel and laboratory testing of their concentrations was carried out in the wider area of Maglaj, with the aim to detect and determine their quantities, which gave basis for discussion about origins of these pollutants in soil. Field and laboratory observations included 45 soil samples, taken by the network, which is dictated by geomorphological conditions. The most frequently sampled type of soil are fluvisol and humofluvisol. Concentration of chromium (Cr) and nickel (Ni) are obtained by the most sophisticated laboratory method (ICP-MS), with a highly sensitive detection threshold (0.1 to 10,000 ppm).

Evaluation of test results showed that concentrations of Cr (max. 954 ppm, min 154 ppm, average 457.5 pmm) and Ni (max 504.5 ppm, min 103.5 ppm; average 275.57 pmm) are significantly increased compared to the concentrations prescribed in the Regulations on determination of allowed amounts of harmful and hazardous substances in soil (Cr max = 100 ppm and Ni max = 50 ppm). Considering geological settings of surrounding area (the dominant presence of igneous ultramafic and mafic rocks) it can be concluded that high concentrations of Cr and Ni have geogenic origins, what is mean that they originate from source rocks from which they are separated through the long-term decomposition and disintegration processes.

Key words: *potentially toxic elements, Cr and Ni, soil, Maglaj, concentration, genesis, geogenic origin*

INTRODUCTION

Term geologic base implies surface of rock from which under the influence of numerous factors can be created and developed soil. Forming material can be given by any rock, which is located on the surface and thus exposed to physical, chemical and biological influences that lead to decomposition of its surface layer [1].

Recently, awareness of connection between environmental pollution and human health has increased, which has led to the intensification of geochemical research in urban areas. In this way, within environmental geochemistry has been developed new subdiscipline - urban geochemistry. Task of urban geochemistry is to study urban ecosystems in urban areas and to detect contaminated areas. Recently, the city area and the wider area of Maglaj are characterized by the processes of urbanization and deruralization, industrialization and deagrarization (flooding in 2014), which contributed mostly in pollution, degradation and soil devastation. Maglaj is interesting for urban geohemical research because it is overlaid with various natural and anthropogenic impacts on the ground.

Main goal of the research was to determine to what extent the area of Maglaj is contaminated with potentially toxic elements, and what is their origin in the soil. Taking into consideration defined goal, comprenhensivly soil testing was performed, with the purpose to determine presence and quantity of a numerous potentially toxic elements. Based on the presence and the quantity of defined elements, it was observed that the concentrations of Cr and Ni much higher than allowed in the entire research area. This paper gives an overview of the origins of these two scientifically proven and highly toxic elements. Potentially toxic elements are very dangerous for humans, flora and fauna, depending on their concentration, bioavailability and bioaccumulation.

GEOLOGICAL SETTINGS

Maglaj is situated in the valley of Bosna River, next to the highway that connects Doboj and Sarajevo. In geological composition of the wider Maglaj area predominante are igneous and sedimentary rocks. Igneous rocks, which are part of ophiolite complexe, are presented with ultramafic (peridotite) and mafic (gabbro-peridotite, micro gabbro, dolerite and spilite) varieties. Products of the youngest volcanism are presented with dacites. Sedimentary rocks are composed of conglomerate, sandstone, breccia, marl and massive limestone.

Ophiolite mélange presents a "chaotic" lithological unit in which are found all the above mentioned types of rocks. The youngest rocks are Quaternary age and represent alluvial deposits of sand and gravel along banks of the river Bosna. Due to disintegration and decomposition over them, such as over the surrounding rocks, there is formed a soil cover. From this soil cover samples were taken for analysis of the heavy metal content, Figure 1, [2,3].

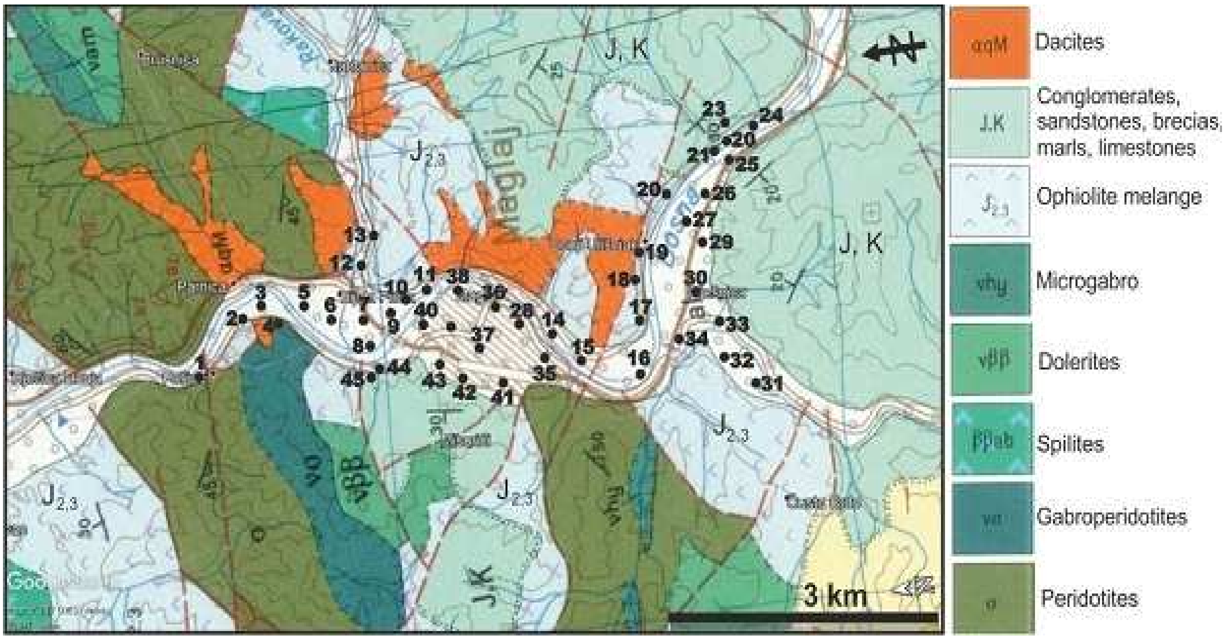

Figure 1. Geological map of the wider Maglaj area with soil samples position (BGM sheet Zavidovići, R – 1 : 100 000)

PEDOLOGICAL STRUCTURE

The most common soil categories subjected to sampling are: recent riverbanks - alluvial soil (fluvisol) and fluvial meadow soil (humofluvisol), while to a lesser extent are present acid-brown soil (distric cambisol), eutric brown soil (eutric cambisol) and ilimerisated- lesivated soil (luvisol) (Figure 2), [4].

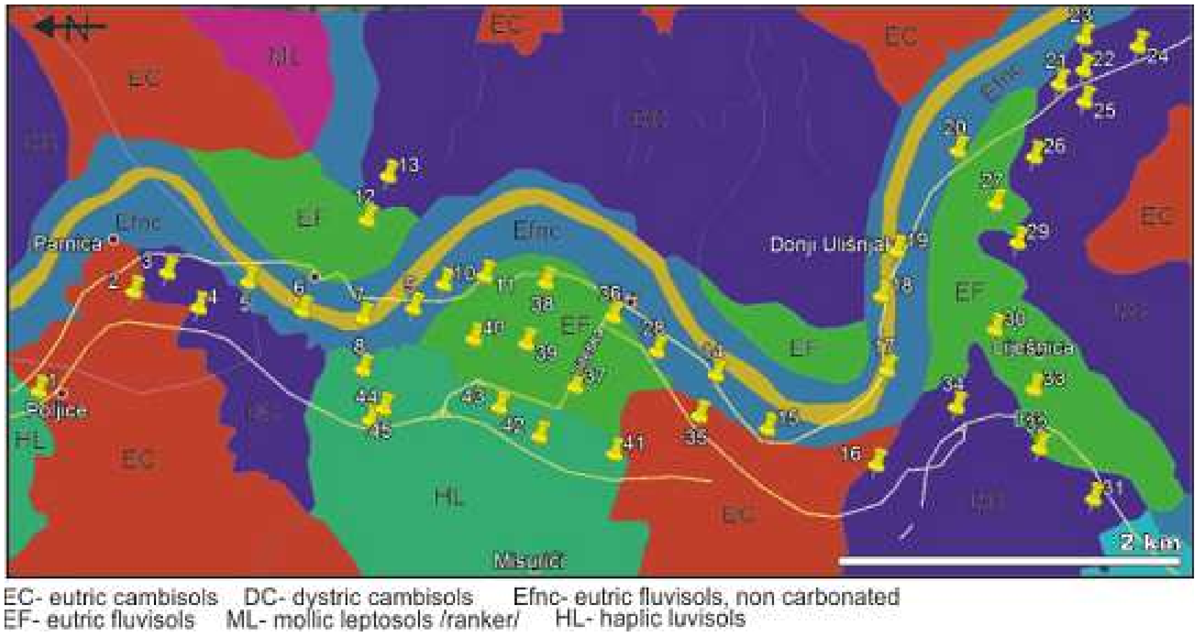

Figure 2. Pedological map of the wider Maglaj area with sampling positions and soil chategories

RESEARCH AND TEST METHODS

Field methods included collection of soil samples according to the Geo-Experimental Expertise Group (URGE - Euro Geo Survays) [5]. It is sampled by a network which is dictated by geomorphological structure of the terrain. Composite sample consisted of five sub-samples: 4 marginal and one central sample, taken in the square of 2 m. Sampling depth was 15 - 30 cm. Samples are stored in PVC bags with the specified ordinal number, locality, coordinates and lithological descriptions.

Preparation of soil samples for laboratory analysis (sieving, drying, milling, weighing) is carried on Faculty of Mining, Geology and Civil Engineering of the Tuzla University. Laboratory analyzes were performed at Bureau Veritas Commodities Canada Ltd. Laboratory in Vancouver - Canada, by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Detection limit of this method for chromium is from 1 – 10.000 ppm, and for nickel is 0.1 – 10.000 ppm. Graphical processing of the results was done using software package Golden software Surfer 12.

TEST RESULTES

Concentrations of chromium and nickel were analyzed on 45 samples, which are collected in the wider Maglaj area. Samples were taken by network that is formed in relation to the geomorphological structure of the terrain. Research covered also and flat part of the terrain, prone to flooding. Sampling was carried out in the regions of Poljice, Bijela Ploča, Omerdino Polje, Ulišnjak, Natron, city area and Liješnica. The area covered by the sampling is approximately 5 km^2. Results of heavy metals Cr and Ni content in the collected soil samples are shown in Table 1a and 1b.

Table 1a. Concrentations of Cr and Ni in soil of the wider Maglaj area

locality	sample	Ni (ppm)	Cr (ppm)
Poljice	1	310,4	585
	2	348,1	607
	3	215,0	411
	4	504,5	766

Table 1b. Concrentations of Cr and Ni in soil of the wider Maglaj area

locality	sample	Ni (ppm)	Cr (ppm)	locality	sample	Ni (ppm)	Cr (ppm)
B. Ploča	5	265,5	457	Grad	28	246,0	409
	6	214,2	385		35	411,5	508
	7	173,4	356		36	268,7	486
	8	452,6	954		37	277,9	294
	9	199,3	357		38	198,2	314
	10	103,5	154		39	219,7	328
	11	211,0	284		40	275,7	348
	12	368,7	597		41	317,0	408
	13	387,2	595		42	258,4	339
O. Polje	14	284,2	524		43	250,0	363
	15	233,6	438		44	290,3	459
	16	268,4	490		45	230,1	305
	17	350,1	691	Natron	25	284,9	467
Ulišnjak	18	176,6	285		26	364,6	464
	19	203,6	353		27	221,6	378
	20	315,4	578		29	287,0	482
	21	351,4	664		30	195,8	445
	22	246,9	433		34	253,9	455
	23	226,2	364	Liješnica	31	238,5	484
	24	222,5	370		32	301,1	452
					33	320,6	492

DISCUSSION

Chromium is a lithophile element. Geohemically associates with Fe and Mn, and it is an indicator for ultramafic and to a lesser extent mafic igneous rocks. Average content of chromium in rocks is shown in Table 2.

Concentration of chromium in soils depends on the parent rock. Concentration range is wide (5 ppm - 1%). The average value is about 40 ppm. It can be reduced, oxidized, left in solution or adsorbed on mineral and organic complexes. Most of chromium is found in parent minerals: chromite - $FeCr_2O_4$ (up to 46.5% Cr), magnetite - Fe_3O_4 and ilmenite - $FeTiO_3$. His mobility is low. Chromium appears in pyroxene, amphibole, mica, chlorite, spinel [6,7,8,9]. During magmatic crystallisation is fractionated in the first stages. Hydrolyse at pH 5.5. By alteration of source rocks, chromium is fixed in clay minerals, as the final products of rocks decomposition. Higher concentrations of chromium are related to fine grained (pelite) products of decomposition. In normal conditions chromium is not toxic, unless in the above mentioned ultramafic rocks and their derivatives - serpentinites. Toxicity depends on the valence state: Cr^{3+} is untreated, Cr^{2+} and Cr^{6+} are highly poisonous. Chromium is an essential micronutrient for energy metabolism of organisms (plants, animals and humans) [9,10,11].

Table 2. Concrencatitons of Cr and Ni in rocks

stijene								
igneous	Cr	Ni	sedimentary	Cr	Ni	metamorphic	Cr	Ni
ultramafic	3000	2000	sandstone	35	2	shale	90	68
toleite basalt	300	-	carbonates	≤ 10	10			
basalt	170	130						
granodiorite	20	15						
granite	4	5						

According to geohemical properties nickel is siderophile element, but also can be halkophil and lithophile. It belongs to the feric group and associate with Mg, Fe, Co, Cr and V. The most important isotope is Ni^{2+}, because it is associated within largest number of minerals (sulfides, arsenides, silicates). Average nickel content in rocks is shown in Table 2.

Nickel is distinguished in the first stages of magma crystallization in peridotite-gabroid rocks. In exogenous conditions, nickel is transferred by surface waters and deposited in weathering crust at a pH of 6.5. For the behavior of nickel in exogenous conditions it is a significant character of the geochemical environment (alkalinity and oxidation -reduction potential). It is poorly movable due to strong adsorption on clay minerals and Fe-Mn oxides and hydroxides [8,10,11]. Concentrations of nickel in the most common types of soil ranges from 5 to 500 pmm, an average concentration is about 40 ppm. In soils formed over the ultramafic rocks, concentrations of nickel ranges from 100 pmm to 0.5%.

In magmatic crystallization, nickel usually enters in the olivine structure, but also can be incorporated in pyroxene and amphibole. Nickel concentrates in a sulfide mineralization together with Co, Cu and As. In deposited sediments nickel is related to the fine-grained fraction. It is poisonous for plants in concentration > 50 ppm. Increased nickel concentrations may have genotoxic, neurological, reproductive, allergic and cancerous effects [6,7,12,13].

Concentrations of Cr in soil samples ranges from 154 to 954 mm (average 457.15 ppm). Maximal (954 ppm) and minimal (154 ppm) values were recorded in the area of Bijela Ploča. The highest average concentrations of Cr were recorded in Poljice (592 ppm) and the lowest in the urban city area (380 ppm), table 3.

Concentrations of Ni in soil samples ranges from 103.5 to 504.5 mm (average 275.57 ppm). Maximal value (504.5 ppm) was registrated in the Poljice area and minimal (103.5) in the area of Bijela Ploča. The highest average concentrations of Ni were detected in Poljice (344.5 ppm) and the lowest in the other regions (248.9 – 286.7 ppm), Table 3.

Table 3. Concrenctations of average values of Cr and Ni in soil of the wider Maglaj area

Locality	Ni (ppm)	Cr (ppm)
Poljice	344,5	592,0
Bijela Ploča	263,9	460,0
Omerdino Polje	284,1	536,0
Ulišnjak	248,9	435,3
Natron	268,0	449,0
Liješnica	286,7	476,0
Grad	270,3	380,1

General conclusion is that the concentrations of Cr and Ni are related to surrounding terrains of Maglaj (Table 3, Figure 3a and 3b). This conclusion can be connected to the geological structure of terrain. The most abundant source rocks are ultramafites, which are genetically related to Cr and Ni, what is the main reason why concentration of chromium and nickel in general are increased. Intensity of recent exogenous processes, as well as anthropogenic activity, is less evident in suburban regions. These conditions caused preservation "source" soil "in-situ".

Based on the curves of average Cr and Ni values, there is observed a strong correlation between these two elements: high concentrations of chromium in most samples match with high concentrations of nickel (Figures 3 and 4). Oleates of chromium and nickel distributions are shown in Figures 4a and 4b.

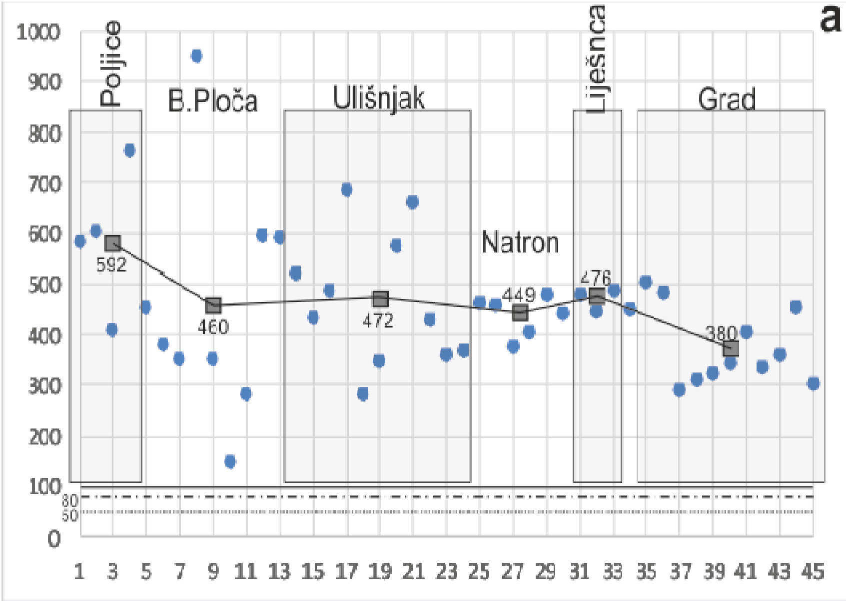

Figure 3a. Diagrams of Cr distribution with average values

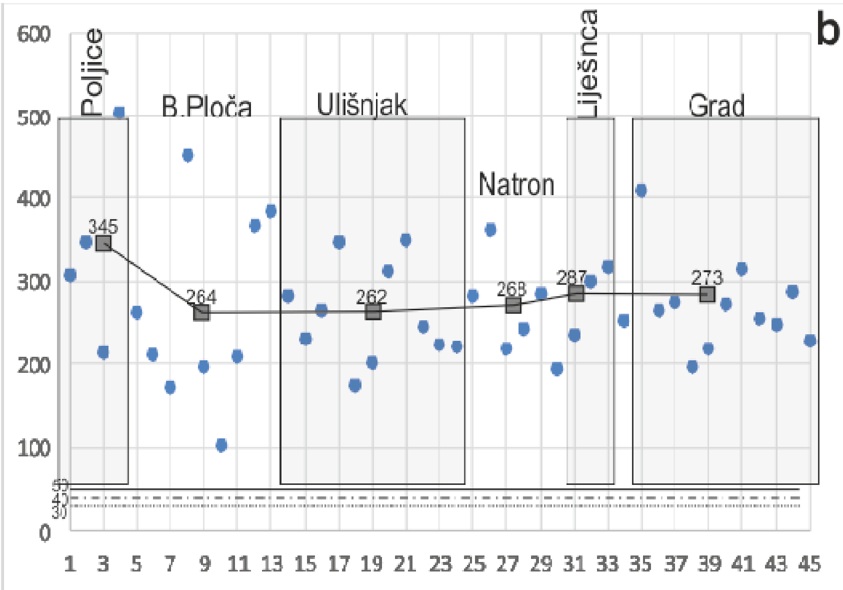

Figure 3b. Diagrams of Ni distribution with average values

According to the regulations on determination of permissible quantities of harmful and hazardous substances in the ground and methods of their examination (Official Gazette FBiH, No. 72/09), permitted chromium and nickel concentrations depending on soil structure are, Table 4, [14].

Table 4. Maximaly allowed concentrations of Cr and Ni in soil

heavy metal	sandy soil (ppm)	silty - loam soil (ppm)	clayey soil (ppm)
Cr	50	80	100
Ni	30	40	50

In regards to concentrations allowed by the regulations, it is noticeable that the lowest nickel concentration is greater than maximum permissible for more than 100%. Nickel average value is about

500% higher than the maximum permissible. The lowest chromium concentration is about 50% higher than the maximum permissible concentration and the average value is about 250% higher.

From the evaluation of the previous conclusions follows that pollution of soil in the area predominantly has geogenic character. This conclusion is also indicated by differences in concentrations from the narrow urban area and the peripheral parts of Maglaj.

In the case of anthropogenic source of pollution, higher concentrations would be in the narrow urban area.

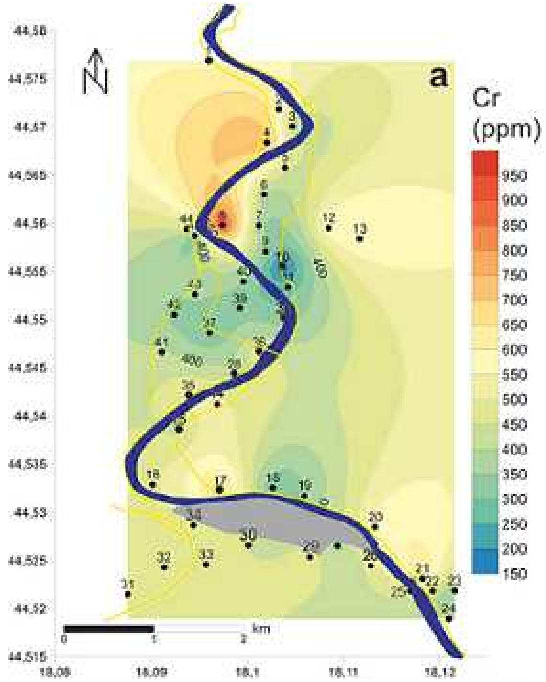

Figure 4a. Oleates of Cr distribution in soil of the wider Maglaj area

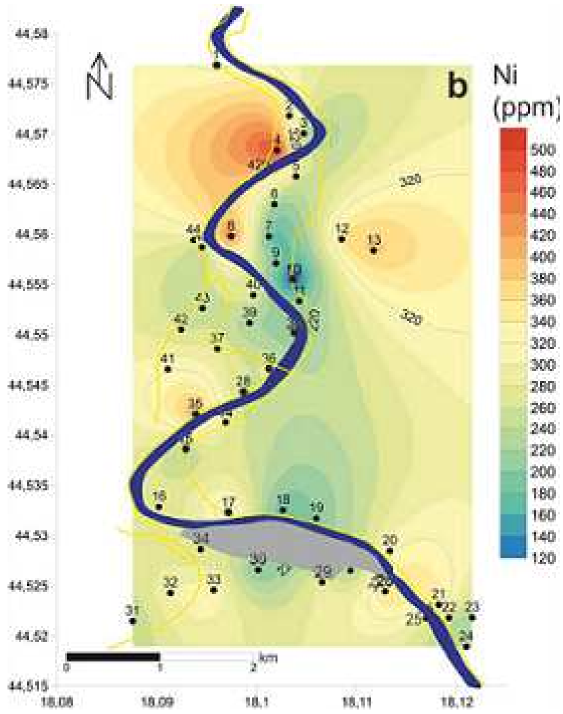

Figure 4b. Oleates of Ni distribution in soil of the wider Maglaj area

CONCLUSION

Potentially toxic metals Cr and Ni are genetically related to the most frequent rock type in the wider area of Maglaj - ultramafic rocks. Chromium and nickel are genetically related to feromagnesium minerals (olivine and pyroxene), which are the main petrogenous minerals in ultramafic rocks and are subjected to alteration processes in exogenous conditions. During the uprise and placement of ultramafic rocks through spreading, subduction and obduction processes, parent rocks pass through intense disintegration and decomposition processes. Alteration processes potentiate separation of chromium and nickel and their distribution in the weathering crust, such as in the soil. Spatial distrubution of Cr and Ni concentrations in the wider Maglaj area differs: the narrow urban area has lower concentrations than the marginal parts of Maglaj. From the previous follows that origin of chromium and nickel in soil of the wider Maglaj area is geogenic.

GRATITUDE

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