Geochemical Distribution of Selected Elements in Serpentinite Deposit in Ginigalpelessa, Sri Lanka

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Abstract

Serpentinite deposits are well known for their natural enrichments of heavy metals (Ni, Cr, Co) and depletions of macro nutrients (Ca, Mg), which have caused different ecological and health impacts in the surrounding areas. In addition, they are considered as potential sources for rare earth elements (REEs). While Ginigalpelessa, the largest serpentinite deposit in Sri Lanka, has been the focus of several toxicological studies, to date, there have been no significant studies related to geochemical distribution of heavy metals, macro nutrients, and REEs in the deposit. Therefore, the present study is focused on the assessment of geochemical distribution of selected elements (Ni, Cr, Co, Ca, Mg, and REEs) in the deposit. Accordingly, concentrations of these elements in 30 rock and soil samples were analyzed and their geochemical distributions were studied using the results of the present study and literature. Ni (6629 ppm) and Cr (35875 ppm) showed the highest enrichments in the deposit, whereas all the studied heavy metals have exceeded the permissible levels of the World Health Organization. In addition, a low Ca/Mg ratio was observed in the deposit, which explains the inhibition of plant growth in the deposit. Moreover, the identified areas with high enrichments of Ni, Cr, and Co using the prepared geochemical distribution maps will be useful in the spot remediation for toxicity in the deposit. Since serpentine soil is recognized as a low-grade source for Ni, low-grade extraction techniques such as phytomining and bioleaching are recommended to extract valuable metals from the Ginigalpelessa deposit.

Keywords: Heavy metals, Plant-essential nutrients, REEs, Serpentine soil, Toxicity

1. Introduction

Serpentinite rock is formed by hydrothermal alteration of olivine-rich ultramafic rocks at relatively low temperature (300-600 ^{0}C). They mainly consist of serpentine group minerals, including magnetite and brucite, and secondary minerals such as talc, calcite, and magnesite [1]. Serpentine soil is derived from the weathering of serpentinite rocks or ultramafic rocks [2].

Serpentine soil has been a major concern of the world because of the naturally enriched content of heavy metals (Ni, Cr, Co), low concentration of plant essential nutrients (Mg, Ca), and significant potential of trace metals, including rare earth elements (REEs) [3]. In addition, serpentine soil is used as a raw material for a variety of applications such as a source of Ni, agriculture, geopolymer, catalysts, and lubricating oil additives [4]. Even though there is a low occurrence of serpentinite in the earth's crust (approximately 1% of total terrestrial land), it has a wide distribution over the globe [5].

In Sri Lanka, there are six serpentinite outcrops – Ussangoda, Katupotha, Ginigalpelessa, Rupaha, Indikolapelessa, and Yudhaganawa, all of which locate along the boundary between the Highland Complex and the Vijayan Complex. Among these six outcrops, Ginigalpelessa is the largest serpentinite outcrop in Sri Lanka that expands approximately 1 km^2 [5].

Although some studies carried out on the perspective of geochemical, mineralogical, and toxicological characteristics of Ginigalpelessa serpentinite body, no geochemical distribution maps of heavy metals (Ni, Cr, and Co) for the identification of highly enriched areas, and plant-essential nutrients (Mg and Ca) for the investigation of areas with nutrient deficiencies are available [6]. These spatial distribution maps can be highly applicable for the identification of the concentrated areas of the above elements in the serpentinite body, which in turn is useful to find potential areas of interest for exploration, mining, and remedial approaches for the prevention of toxicity.

Moreover, the current supply of REEs is at a high risk due to rapid increment of REE demand and the monopolistic behaviour of China [7]. Therefore, it is important to explore new and alternative sources of REEs worldwide to secure the global supply chain of REEs. Serpentinite deposits have also been identified as potential sources of REEs [8]. In this context, Ginigalpelessa serpentinite outcrop can be investigated.

Therefore, this research is mainly focused on the assessment of geochemical distribution of heavy metals (Ni, Cr, Co), macro-nutrients (Mg and Ca), and REEs in the Ginigalpelessa serpentinite body.

2. Methodology

2.1 Study Area

Ginigalpelessa serpentinite outcrop is located 14 km away from the Embilipitiya Sri Lanka in the southern part of the litho-tectonic boundary between the Highland Complex and the Vijayan Complexes. It is surrounded by the rocks, such as charnockites, calc-gneisses, and migmatites. In addition, varieties of serpentinites, including fibrous serpentinites, mesh-like serpentinites, and micaceous serpentinites are found in the deposit [8].

2.2 Sample and Data Collection

A total of 30 samples including 15 soil samples and 15 rock samples were collected from the Ginigalpelessa serpentinite outcrop. In addition to that, already available data on concentrations of Ni, Cr, Co, Ca, and Mg from 18 soil samples and 18 rock samples in the Ginigalpelessa serpentinite outcrop were used [9]. Thus, concentration data on a total of 64 samples were used for the analysis of geochemical distribution of heavy metals (Ni, Cr, and Co) as well as plant-essential nutrients (Ca and Mg) in the Ginigalpelessa serpentinite outcrop (Figure 1).

2.3 Sample Preparation and Analysis

Samples were oven dried until the moisture is completely removed (105 0C for 8 h). Rock samples were initially crushed into small pieces using a laboratory jaw crusher. All the samples were then powdered via the laboratory Tema mill and sieved through 63 µm sieve to obtain the undersize fraction. After, representative samples were prepared via coning and quartering method and stored in airtight polythene bags.

A 0.5 g of each prepared representative sample was weighed prior to digestion, and each weighed sample was digested using aqua regia (Conc. HCl and Conc. HNO_3 (1:3 volume ratio)) with 1 ml of H_2O_2 for 2 hours. Then, 1 ml of each digested sample was filtered using 0.45 µm syringe filters and diluted up to 100 ml using distilled water. The diluted samples were then subjected to Atomic Absorption Spectroscopy (AAS) for Ni analysis and Inductive Coupled Plasma Mass Spectrometry (ICP-MS) for Cr, Co, and REE analyses.

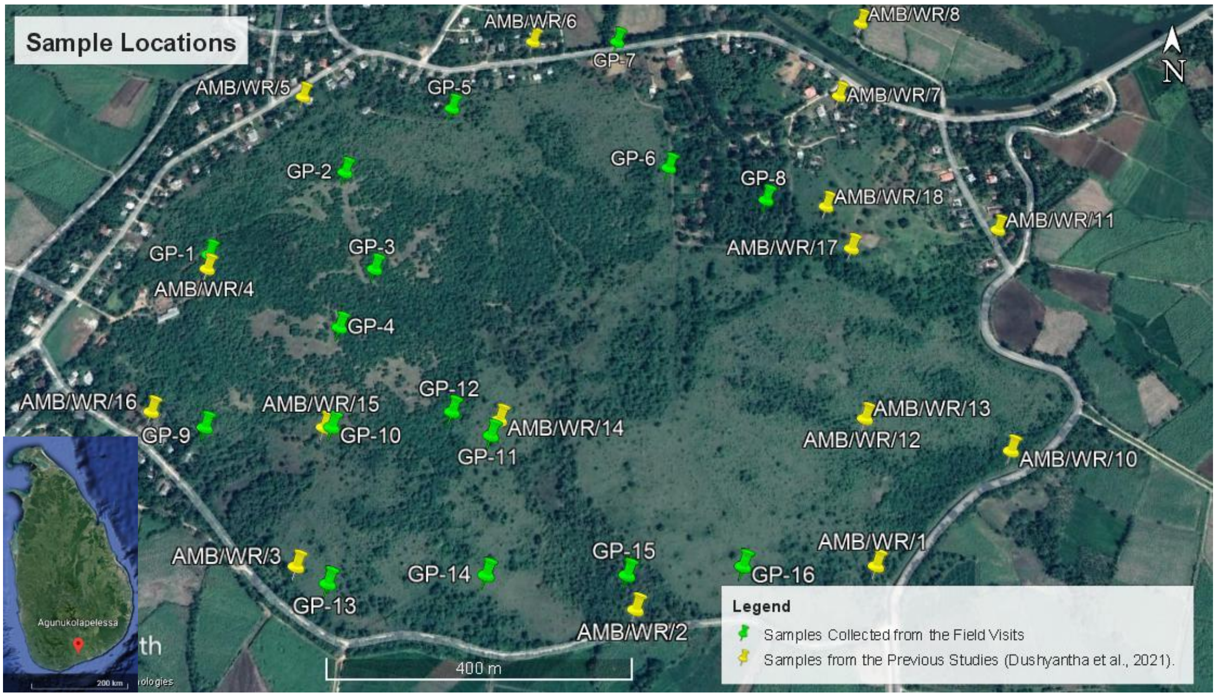


Figure. 1: Study Area - Ginigalpelessa

Heavy metals (Ni, Cr, Co), Mg and Ca concentrations of the serpentinite outcrop were investigated as the macro-nutrient elements in the outcrop (Table 2) while REE concentration in serpentinite rock and soil was investigated to identify the potential of valuable metals in the outcrop (Table 3).

2.4 Data Interpolation and Mapping

Results from AAS and ICP-MS analysis was interpolated using Inverse Distance Weighted (IDW) interpolation technique for the identification of the geochemical distribution of the heavy metals and plant-essential nutrients in the study area. This method is specifically used for the interpolation due to the simplicity and it is an efficient method for the data interpretation at unknown locations [10]. Accordingly, geochemical distribution maps for Ni, Cr, Co, Mg, and Ca were created by using ArcGIS 10.4.1.

3. Results

Results of the AAS analysis carried out in this study for 30 samples and the previous data of 36 samples [9] indicated a significant variation of the concentration of heavy metals (Ni, Cr, and Co) in serpentinite rocks and soil (Table 1).

Ni had the highest concentration in serpentinite rocks with an average of 5,311 ppm compared to Cr and Co. In contrast to the rock, soil was more enriched in Cr, Ni, and Co metals and Cr was identified as the highest concentrated metal (average = 35875 ppm) in the soil.

Geochemical distribution of Ni and Co were high in serpentinite rocks at the west side of the area while an increased

Table 1: Heavy Meta Concentration in Soil and Rock Samples

Element	Minimum Value (ppm)	Maximum Value (ppm)	Average (ppm)
Rock Samples			
Ni	1895.0	12600.0	5311.0
Cr	27.0	1196.0	448.0
Co	92.0	136.0	112.0
Soil Samples			
Ni	1420.0	12400.0	6629.0
Cr	7342.0	109787.0	35875.0
Co	105.0	455.0	318.0

distribution of Cr was observed at the northeast side of the area. Furthermore, a uniform distribution of Co in serpentine soil was observed in the Ginigalpelessa outcrop while Cr and Ni were observed more towards the westside of the area (Figure 2).

Furthermore, Mg concentration in the soil and rock was significantly higher than Cr concentration (Table 02). Geochemical distribution maps for Mg and Ca indicated a low distribution of plant-essential nutrient elements on the eastern side of the Ginigalpelessa area (Figure 6).

Table 2: Plant-Essential Nutrient Metal Concentration in Soil and Rock Samples

Element	Minimum Value (w%)	Maximum Value (w%)	Average (w%)
Rock Samples			
Mg	20.1	21.5	20.9
Ca	0.04	0.57	0.22
Soil Samples			
Mg	3.02	4.22	3.62
Ca	0.62	0.74	0.69

The concentrations of REEs in the Ginigalpelessa serpentinite outcrop indicated a considerable enrichment of REEs in serpentine soil. Among all the REEs, Ce had the highest concentration in the serpentinite rock while Tb had the lowest concentration (Table 03).

Higher chondrite-normalized values for REEs in soil can be observed in the Chondrite-Normalized REE pattern (Figure 7) and it also highlights the high enrichment of REEs in serpentine soil compared to serpentinite rock.

Table 3: REE Concentration in Soil and Rock Samples

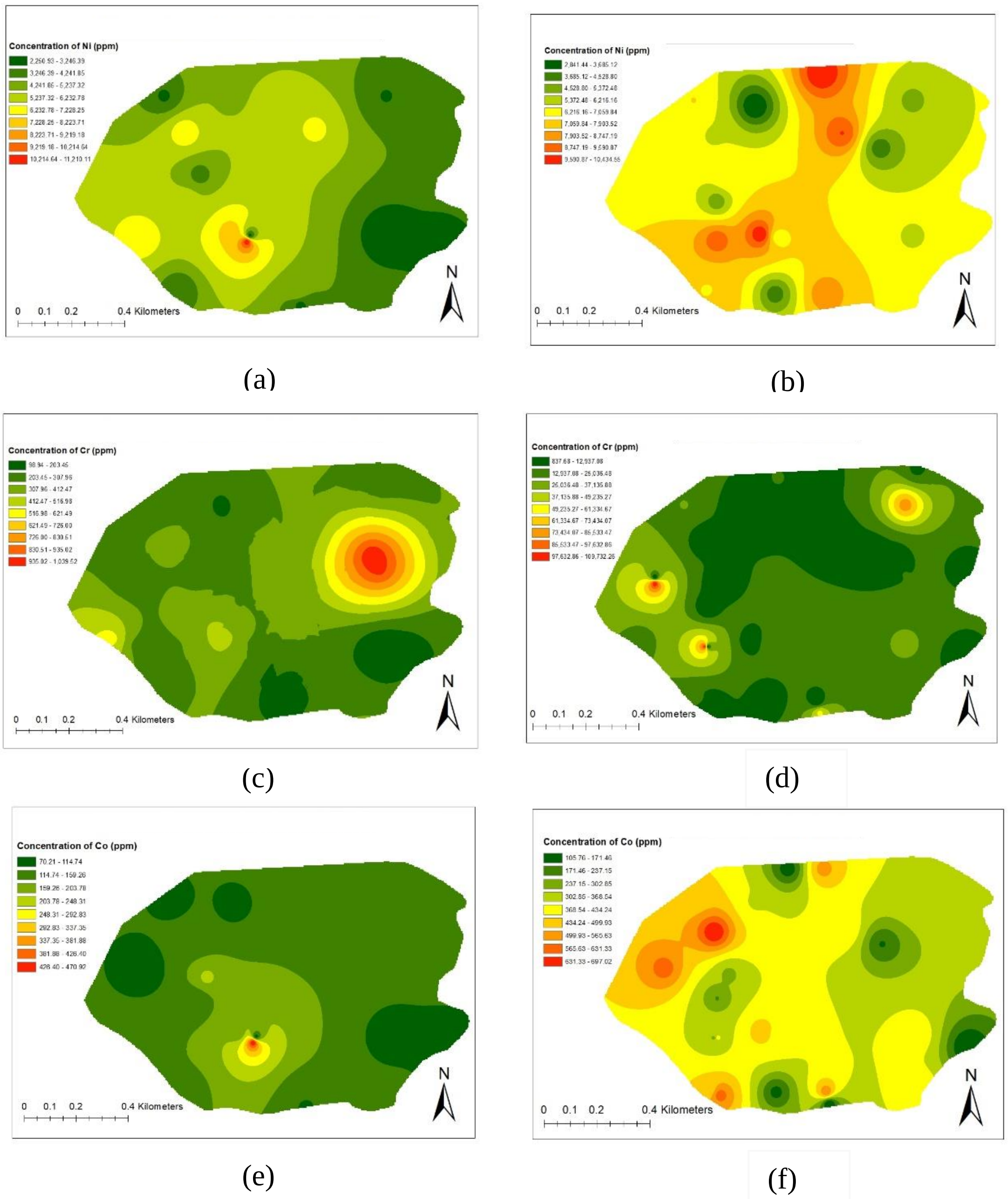
Element	Minimum Value (ppm)	Maximum Value (ppm)	Average (ppm)
Rock Samples			
TREEs	0.6	31.6	5.56
LREEs	0.052	26.12	4.59
HREEs	0.003	1.9	0.33
Soil Samples			
TREEs	15.39	150.12	65.74
LREEs	12.33	118.13	52.45
HREEs	0.82	10.18	4.18

4. Discussion

Low concentration values for Co in both serpentinite rock and soil were observed in the outcrop which may be due to the controlling of Co content by reacting with Mn-oxide [11].

However, heavy metal concentrations obtained in this study are comparatively similar to the reported heavy metal contents in the other serpentinite outcrops in Sri Lanka [12].

In addition, concentrations of heavy metals in the Ginigalpelessa serpentine soil are higher than the permissible levels (Table 4) issued by the World Health Organization (WHO), specifically Ni and Cr. Such high concentrations of heavy metals can be toxic and cause health related issues [6] to people living around the Ginigalpelessa area.



(a) (b)

(c) (d)

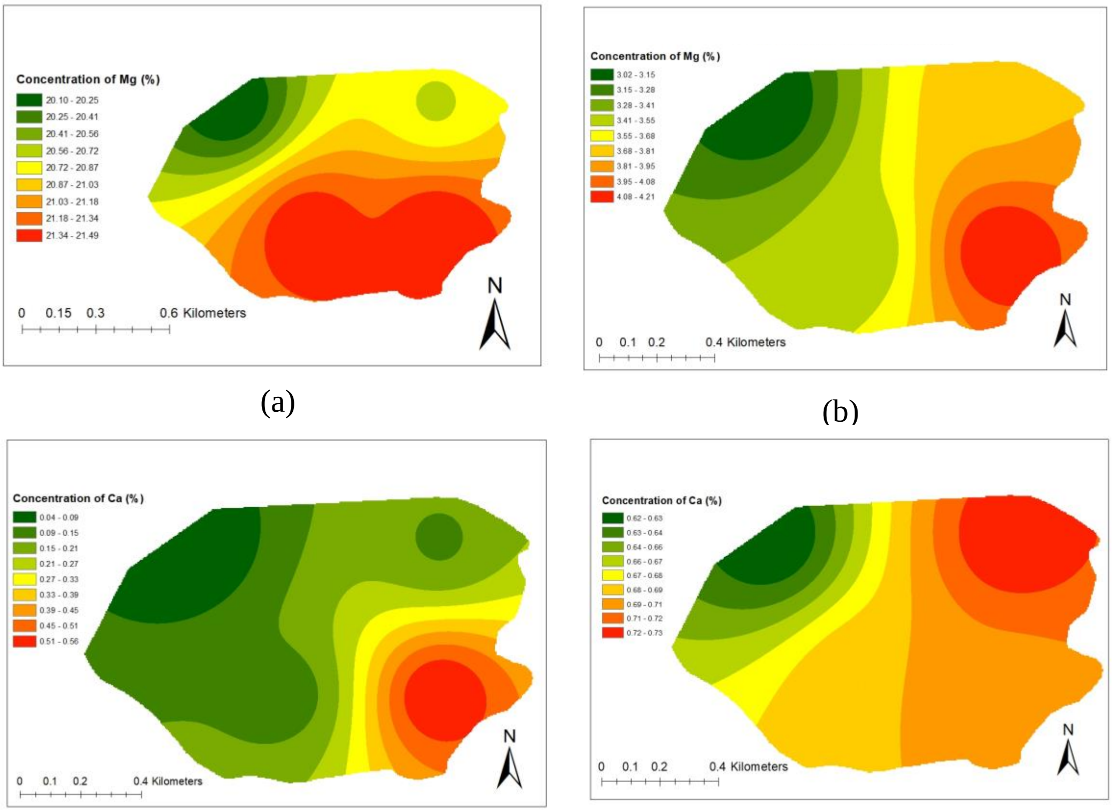
(e) (f)

Figure. 2: Geochemical Distribution of Heavy Metals. (a) Ni in Serpentinite Rock. (b) Ni in Serpentine Soil. (c) Cr in Serpentinite Rock. (d) Cr in Serpentine Soil. (e) Co in Serpentinite Rock. (f) Co in Serpentine Soil.

In this regard, geochemical distribution maps created in this study will be helpful in identifying heavy metal concentrated areas within the Ginigalpelessa outcrop. Accordingly, remedial measures such as Phyto-remediation can be effectively applied for the prevention of health-related problems.

In this study, the availability of Mg and Ca as plant-essential nutrient metals in serpentine soil was also taken into account, since the low Ca/Mg ratio inhibits the plant growth [14]. Observations carried out in this study revealed that both serpentinite rock and soil had comparatively low Ca/Mg ratio which is a common characteristic for the serpentinite outcrops located in Ussangoda and Indikolapelessa as well [12].

Apart from that, average concentrations of both Mg and Ca in the area were lower in soil than rock which might be the reason to the nutrient deficiency in soil [15].



(a) (b)

(c) (d)

Figure. 3: Geochemical Distribution of Plant-Essential Nutrient Metals (a) Mg in Serpentinite Rock. (b) Mg in Serpentine Soil. (c) Ca in Serpentinite Rock. (d) Ca in Serpentine Soil.

When perceiving the geographical map of the area and field observations, it was clearly identified that the density of residences and vegetation on the eastern side were low. This is further proved by the results of the soil sample analysis as well.

In addition, LREEs content in the serpentinite outcrop was higher compared to the HREEs content and the LREE/HREE ratio was higher in soil. Even though the concentration of REEs is comparatively low in the serpentinite outcrop than other sources in the world, it may have an economic significance as a potential low-grade source of REEs in the future owing to their surging demand and the expected supply risk [16].

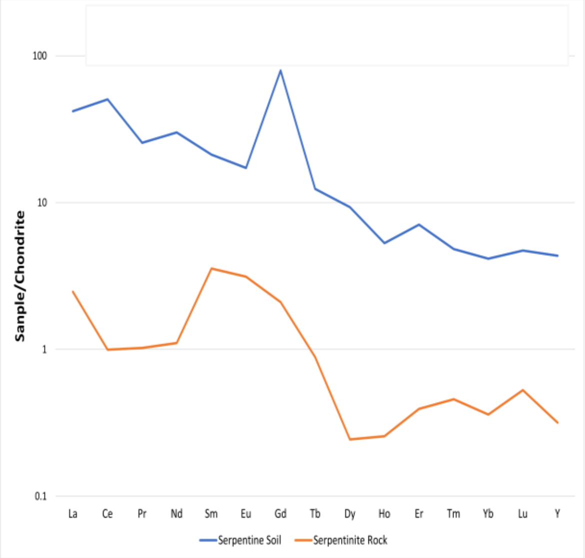


Figure. 4: Chondrite-Normalized Pattern of REE

5. Conclusion

According to the results, it was clearly observed that the heavy metal concentration in serpentine soil was higher than rock. Co had the lowest potential in this outcrop compared to Ni and Cr, however, Co and Ni in soil had a higher and uniform distribution over the area. In contrast, plant-essential nutrients, specifically Mg and Ca had low concentrations in serpentine soil compared to the rock and the light vegetation cover was observed in the area which may indicates the nutrient deficiency of the serpentinite soil. Low Ca/Mg ratio was also observed in the Ginigalpelessa outcrop which is a characteristic behavior for other serpentinite outcrops as well. Observations carried out in this study also indicate a low potential of REEs in the outcrop with a higher enrichment in soil than the rock. However, further investigations are needed to identify the potential of this deposit for economic extraction of REEs. Generally, concentration of Ni was higher than the maximum permissible levels of heavy metals in unpolluted soil which can be toxic and have the potential for causing health issues for the residents of the area. Therefore, geochemical distribution maps prepared in this study can be applied for the determination of such areas and economic extraction of Ni using low-grade techniques, which in turn becomes a remedial approach are suggested.

Table 4: WHO Permissible Limits for Heavy Metals in Plant and Soil [13]

Elements	Target value of soil (mg/kg)	Permissible value of plant (mg/kg)
Cd	0.8	0.02
Zn	50	0.60
Cu	36	10
Cr	100	1.30
Pb	85	2
Ni	35	10
Co	0.5	0.2

Acknowledgements

The authors wish to acknowledge the financial supports provided by the Accelerating Higher Education and Development (AHEAD) Operation of the Ministry of Higher Education of Sri Lanka funded by the World Bank (AHEAD/DOR/6026-LK/8743-LK). In addition, all academic and non-academic staff in the Department of Earth Resources Engineering, University of Moratuwa are acknowledged.

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