

Determining the Characteristics of the Calcite Intrusions in the Southern Part of Eppawala Deposit and its Applicability for the Industries

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Abstract

Eppawala is the only phosphate deposit that is currently being mined in Sri Lanka and is composed of mainly two parts northern and southern. The ongoing phosphate mining process in the southern part has resulted in the exposure of fresh carbonatite embedded with large apatite crystals and those intrusions need to be removed before continuing further phosphate mining in that area. Therefore, we need to address a suitable method to use those calcite intrusions properly. In this paper, we are discussing the characteristics of calcite matrix such as critical anions (fluoride, chloride), P₂O₅ content, heavy metals, oxides, and the suitability of applying those removing calcite boulders for further industries including the fertilizer industry. Ion selectivity, titration, colorimetry, and induced coupled plasma spectrophotometry were used for analyzing the characteristics respectively for fifteen samples from three different boulders in the southern part. Results from critical anions and heavy metal percentages proved the absence of toxicity in calcite matrix and oxides percentages showed that it can be applied directly in its natural form only for the fertilizer industry by a quantitative comparison whereas upgrading processes need to be implemented to meet the specifications in other industries.

Keywords: Carbonatites, Fertilizer, Magmatic origin, Phosphate

1. Introduction

The Eppawala phosphate deposit, which is the only phosphate source in Sri Lanka, has enough reserves to last nearly two centuries for utilization according to the current rate of exploitation (32000 MT/yr.) [1]. Phosphate rock mined in this deposit is directly applied to long-term crops like tea, rubber, and coconuts. The Eppawala phosphate deposit is in the Eppawala village in the north-central province of Sri Lanka that extends into an area of about 20 km² with several deeply weathered hillocks [2]. These hillocks are directed in a North-South direction and the average height is about 170m from sea level.

A weathered phosphate-rich regolith with abundant apatite crystals overlies the parent carbonatite rock in the deposit and spreads over two main localities: northern and southern areas [3]. Carbonatites are a magmatic rock type enriched in mostly carbonate minerals (>50%) and have low silica content [4] compared to limestone and marble. While calcite, dolomite, and olivine occur as major minerals, apatite, spinel, ilmenite, magnetite, amphibole, and mica exist as minor minerals in the Eppawala phosphate deposit. Further, it is enriched in F,

Nb, Sr, U, Th, rare earth elements, and different isotopes of carbon and oxygen [5].

Unlike the northern part of the deposit, the southern part contains carbonatite intrusions scattered in the mined area as a hummocky topography. They mainly consist of calcite minerals [5]. During the apatite mining process, these exposed carbonatite outcrops are left behind as waste, and they cover an area of over 80,000m² [4].

Calcite is used in many industries such as paint, cement, lime, ceramic, textile, rubber, and plastic depending on the purity of calcite in their mineralogy and the chemical composition [4],[6]. Based on previous literature Eppawala carbonatites can be used for making synthesized precipitated calcium carbonate (PCC) which is in turn applicable as a raw material for the above-mentioned industries. However, the purity of PCC making from Eppawala carbonatite is not enough for biomedical and pharmaceutical applications [4],[5].

Even though there are studies carried out for analyzing the economic potential of Eppawala carbonatites for further industrial applications, there have been no significant attempts made to

compare the characteristics of Eppawala calcite with the specifications mentioned by the calcite industries. Therefore, we focus this study on determining the characteristics of calcite intrusions (chloride and fluoride ion content, P_2O_5 , heavy metal, and oxides percentages) and applicability for the industries as raw materials through a comparison with their specifications.

2. Methodology

2.1 Geological setting of the study site

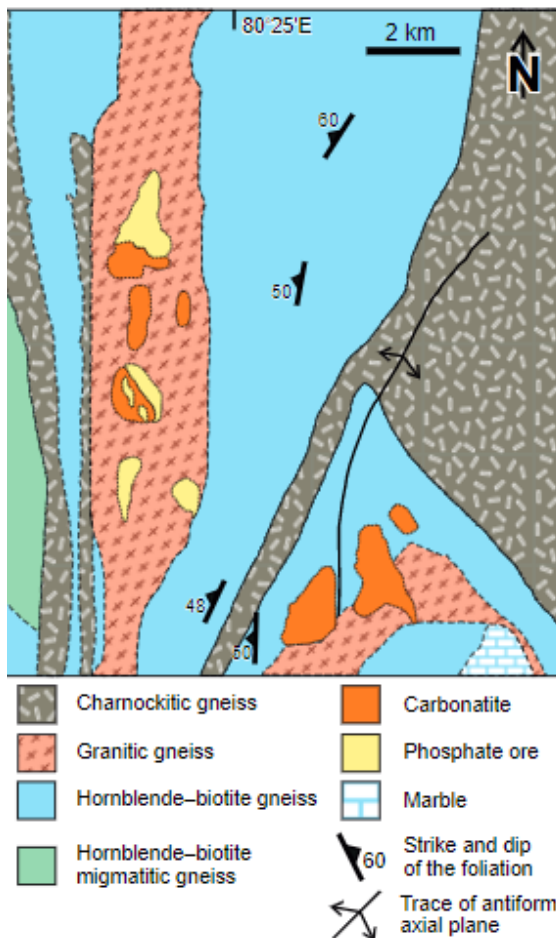


Figure 1 - Simplified geological map of Eppawala and the surrounding [7]

Out of the main two parts of the deposit divided by the “Jaya Ganga”, the Southern part was selected as the study area. The study area is over 4 km² and the deposit is extending to a larger area over the mining site (Figure 1).

2.2 Determination of apatite mineral phase percentage in the calcite matrix

The apatite percentages in calcite boulders were determined approximately by counting the area

governed by the apatite crystals on the surface as in Figure 2.

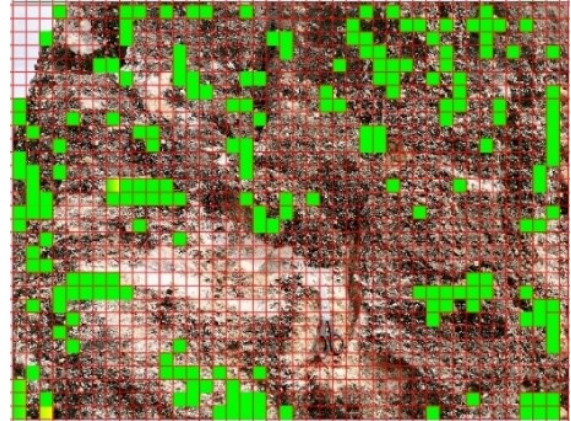


Figure 3 - Marked Apatite grains in a 2D image of boulder 1 using AutoCAD

A 2D image of a selected calcite boulder (boulder 1) was divided into squares with 1-inch (0.0254 m) squares, counted the number of squares with apatite crystals, and took the percentage of them.

2.3 Sample collection

Due to the hummocky topography and the low accessibility of the site, samples were selected using the convenient sampling method from the boulders which had the easiest access. 15 samples were collected representing 12 rock samples and 3 soil samples from 3 calcite boulders representing the top, middle and bottom levels of the boulders, and the samples were weighed around 1 kg.

Table 1 - Defining the type of sample according to the sample number

Sample number	Sample type
1 - 12	Rock
13 - 15	Soil

Rock samples were taken to analyze the geochemistry of the carbonatite matrix and soil samples to analyze the condition after weathering of the boulders.

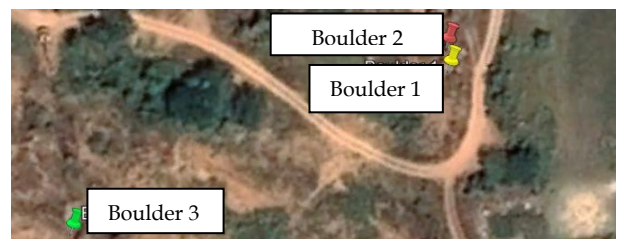


Figure 2 - The southern part of the Eppawala deposit and the sampling points



Figure 4 - Large calcite outcrops in the southern part of the deposit

2.4 Sample Preparation

Rock samples were firstly crushed using the hammer and then by the laboratory jaw crusher. Crushed samples (<10 mm) and soil samples were ground using a laboratory Tema mill and sieved using 90 µm and 63 µm ASTM sieves.

2.5 Sample Analysis

The samples were analyzed using colorimetric methods, titration, fluoride electrode, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis by aqua regia digestion to determine the ion and elemental concentrations.



Figure 5 - Large apatite grains in calcite matrix

3. Results and Discussion

The current mining method which is being applied in the southern part of the Eppawala deposit is selective mining. The calcite intrusions are the reason for going for this method. To go further mining in that area it is necessary to remove these calcite boulders while extracting the phosphate ore.

The oxides percentages gained from the calcite matrix in the southern part were compared with the specification values mentioned in different industries as follows.

Table 2 - Major oxides of the calcite matrix determined by X-ray fluorescence (XRF) analysis in six different locations (Sample location numbers are not included in [8], thus herein they are numbered as L1, L2,..L5)

Major Oxides						
Wt. %	[8]			[9]		
CaO	40.01	39.6	37.82	52.01	51.82	41.98
MgO	11.78	11.14	13.11	3.21	3.54	10.64
SiO ₂	2.46	2.41	3.84	0.04	0.09	2.03
Al ₂ O ₃	0.06	0.05	0.06	0.06	0	0.04
FeO	1.8	1.48	1.71	1.02	0.65	-
Fe ₂ O ₃	-	-	-	-	-	0.23
MgO+CaO	51.79	50.20	50.93	55.22	55.36	52.62

Table 3 - Calcite specifications for glass, cement, and fertilizer industry uses [6]

Industry	CaO Wt. %	MgO Wt. %	SiO ₂ Wt. %	Al ₂ O ₃ Wt. %	Fe ₂ O ₃ Wt. %
Glass	53	MgO + CaO > 54.5	<2.5	-	0.2(max colour) & 0.02 (colorless)
Cement	42<	<4	2 - 4	12 - 6	1 - 2
Fertilizer	CaO + MgO > 50		5	-	-

This comparison (Table 2 & Table 3) results from the ability to apply the calcite matrix only for the fertilizer industry in its natural form. Due to the higher alumina percentage, it is not suitable for the glass industry and for the cement industry also it shows deviations from the required values.

Table 4 - Calcite specifications for the chemical industry [13]

Characteristics	The requirement in percent by mass for			
	Bleaching Powder	Caustic Soda	Calcium Carbide	Sugar
LOI	46.00	46.00	46.00	44.00
CaO	54.00	53.00	54.00	50.00
SiO (Max.)	0.75		1.00	2.00
Fe ₂ O ₃	0.15		0.25	
MgO	2.00	1.00	0.80	1.00

Comparison of the major oxides results from Table 2 with the specifications of the chemical industry from Table 4 presents the inability of applying the calcite matrix directly for bleaching, caustic soda, calcium carbide, or sugar industries due to the higher silica amounts of calcite matrix.

By doing further upgrading, the gap between the required percentages and this calcite matrix composition may be able to be removed and used for those industrial applications.

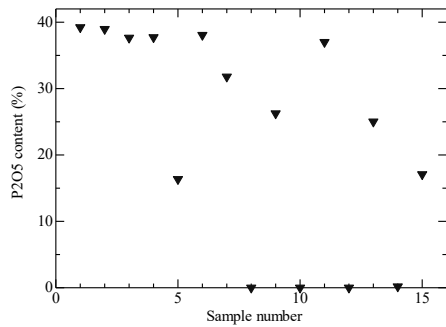


Figure 4 - P₂O₅ content of the samples

According to the results in Figure 4, the P₂O₅ content of the apatite crystals shows the highest value at 39.23% and around 16 percent of the apatite mineral phase is embedded in the calcite matrix according to the 2D image calculation (Figure 2). Among the three soil samples, 13 and 15 samples show higher P₂O₅ content, and this might be a reason that the soil samples have resulted from the weathering of the calcite matrix. If we are going to apply the powder form of these calcite bodies into the soil as a fertilizer the higher P₂O₅ content coming from the large apatite crystals would be an added advantage since there is an apatite phase of around 16 percent in it.

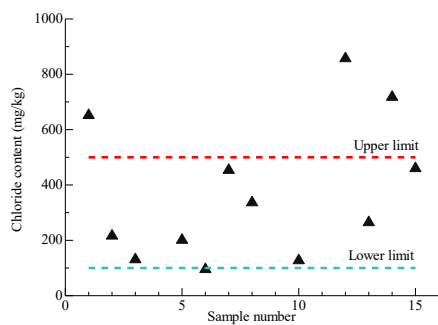


Figure 5 - Chloride content of the samples with permissible limits

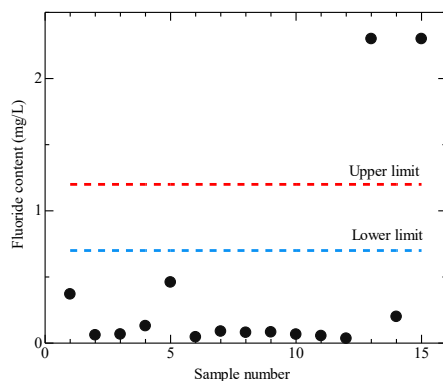


Figure 6 - Fluoride content of the samples with permissible limits

As in Figure 6, the highest fluoride content is shown by a soil sample (sample 13) and other samples do not show a remarkable deviation from each other while the highest chloride content (Figure 5) is shown by a calcite sample. Some apatite samples do not consist of a detectable amount of chloride (Figure 5), but they have fluoride ions in them (Figure 6). The soil sample with the highest chloride content shows a very lower amount of P₂O₅ (Figure 4).

Plant tissues itself has the desired chloride content important for growth. But when that amount falls below 100 mg/kg, it is considered a deficiency level, and going beyond 500 mg/kg is toxic [10]. According to Figure 5, the majority of the samples are fallen within the desired range and it reveals the ability to apply this calcite matrix as a chloride source for plants.

The permissible limit for fluoride in soil may vary from 0.7 mg/L to 1.2 mg/L and the maximum allowed concentration is 1.5 mg/L [11]. All the samples except two soil samples are fallen below the maximum permissible Levels (Figure 6). Therefore, we can say that soil samples contain more fluoride than expected and fresh carbonatite matrix is the most suitable one as a fertilizer.

When comparing the ICP-MS results, as in Table 5, Sr shows the highest amounts almost in all the samples while Cd, Cs, and U show lower values. When comparing rock and soil samples, higher content of heavy metals has been added to the soil and sample number 13 shows it clearly with the results. But the other soil sample (sample 14) has a little deviation from those values.

Here the most important heavy metals we were concerned about were Cd and Pb because they are extensively toxic for plant growth.

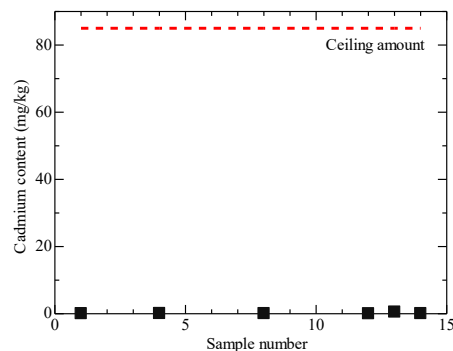


Figure 7 - Cadmium content in samples with ceiling amount

Table 5 - ICP-MS results of the selected samples representing calcite matrix, apatite crystals, and soil

ICP-MS Results (mg/kg)						
Sample number	1	4	8	12	13 (Soil)	14 (Soil)
Cr	2.84	2.99	2.02	0.89	39.70	4.12
Ni	276.86	250.75	251.60	214.90	668.89	348.07
Co	25.63	23.25	20.25	16.52	35.08	21.60
Ga	2.61	0.82	1.54	ND	48.08	1.50
As	27.51	24.99	13.91	8.12	31.62	15.39
Sr	5,814.47	4,069.44	2,502.81	2,177.69	4,984.66	3,145.60
(112)Cd	0.09	0.12	0.10	0.07	0.55	0.10
(114)Cd	0.07	0.04	0.03	0.02	0.23	0.09
Cs	0.03	0.01	ND	ND	0.73	ND
Ba	118.10	48.04	80.00	21.99	1,540.50	77.83
Pb	13.03	6.69	3.86	1.05	34.74	3.92
Th	451.52	319.88	15.61	4.31	218.28	48.58
U	6.97	5.21	0.31	0.12	3.90	0.74

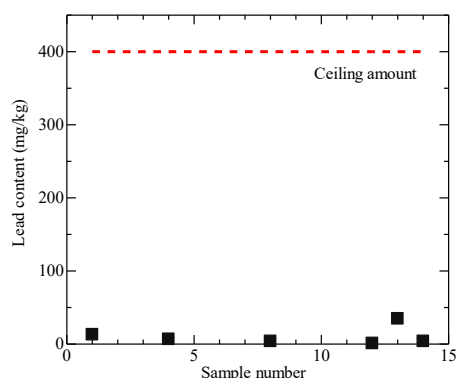


Figure 8 - Lead content in the samples with a ceiling amount

According to the Environmental Protection Agency (United States), the ceiling amount for Cd is 85 mg/kg [12]. Therefore, no toxicity occurs from the calcite matrix according to Figure 7. This limit for Pb is 400 mg/kg and it also results from no toxicity to the environment (Figure 8).

4. Conclusion

The calcite intrusion in the southern part of the Eppawala phosphate deposit has approximately lower than 16 percent apatite crystals embedded in it. This is comprised of more than 40 percent of calcite and lesser amounts of other accessory minerals such as dolomite and apatite.

There is no toxicity in the calcite matrix and can be used only as a fertilizer in its natural form.

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