

A Note on the Chemistry and Mineralogy of Apatite Crystals of Eppawala and Ridigama Phosphate Deposits

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Abstract

The mineralogy, chemistry and solubility of apatite from two rock phosphate deposits in Sri Lanka were studied. The larger deposit is located at Eppawala in the North Central Province, and the newly discovered smaller deposit is at Ridigama, in the North Western Province. Both ores show enrichment of phosphorous by way of primary and secondary components, developed in two stages. The primary component consists of coarse, primary apatite crystals, whereas the secondary component has a finer matrix. The primary apatite crystals of both deposits contain at least two types of apatite: chloro-fluoro-hydroxylapatite (CFHA) as the major type and fluorapatite (FA) as the minor one. Although the mineralogical composition of the primary apatite of the two deposits is similar, their a-axis dimensions are different. Further, it was revealed that the crystal structure of the primary apatite from Eppawala is more stable than that of Ridigama. Therefore, a greater chemical reactivity is expected of the primary apatite from Ridigama than that from Eppawala. This explanation is consistent with the solubility data obtained for the primary apatite of two deposits, primary apatite from Ridigama being more soluble than that from Eppawala. In addition, chemical studies show that the primary apatite from both locations, with low Fe and Al contents, has a better potential as a fertilizer than that of their finer matrices.

Key Words : Apatite, Phosphate, Solubility, Mineralogy

Introduction

A large and important phosphate deposit was discovered in 1971 at Eppawala, in the Anuradapura District, about 200 km north of the Sri Lankan capital city of Colombo (Figure 1). This deposit is being currently mined as fertilizer for direct application with a product having an average P₂O₅ content of 30 per cent. The Eppawala phosphate deposit occurs as a thick, weathered profile underlain by a apatite-rich carbonate rock. Due to intensive weathering conditions, the parent apatite-rich carbonate rock has been weathered and leached, and in the process the capping material has been enriched with mineral apatite and other secondary products. Essentially, the deposit consists of yellowish green, sub-hedral, large apatite crystals as a primary mineral in the fine matrix. The matrix itself is composed of finer primary apatite and still finer secondary phosphatic matrix (Dahanayake and Subasinghe, 1988). The deposit is a leached, apatite-bearing phoscrete type phosphorite, which has developed on an apatite-bearing carbonate rock with a possible igneous origin. However, it should be noted that the apatite-bearing rock is interbanded with gneisses, which form a series of hillocks directing in a N-S direction across the Eppawala-Talawa road (Jayawardena, 1976; Dahanayake and Subasinghe, 1989). The parent carbonate rock contains yellowish green apatite, calcite and dolomite as major minerals and spinel, pyrite, ilmenite and magnetite as important accessories.

Another rock phosphate deposit was recently discovered at Kawisigamuwa, near Ridigama, on the Mallawapitiya - Ridigama road, south-east of the town of Kurunegala, 105 km away from Colombo (Figure 1). The phosphate occurrence at Ridigama is restricted to a smaller area, in comparison with the surficial distribution of the Eppawala deposit. The deposit is overlain by a lateritic crust. Field evidence suggests an extension to the ore body along the NS direction up to a distance of one kilometer along the NS direction.

As at Eppawala, yellowish green apatite crystals with high amounts of hematite and magnetite are embedded in a secondary, fine-grained matrix (Hewawasam and Dahanayake, 1995). Near the deposit, some igneous intrusions with primary apatite, hematite and magnetite have been emplaced into the surrounding Precambrian terrain (Hewawasam and Dahanayake, 1996). The mineralogical, chemical and solubility characteristics of the yellowish green primary apatite and their associated matrix in both deposits are studied and compared in this paper.

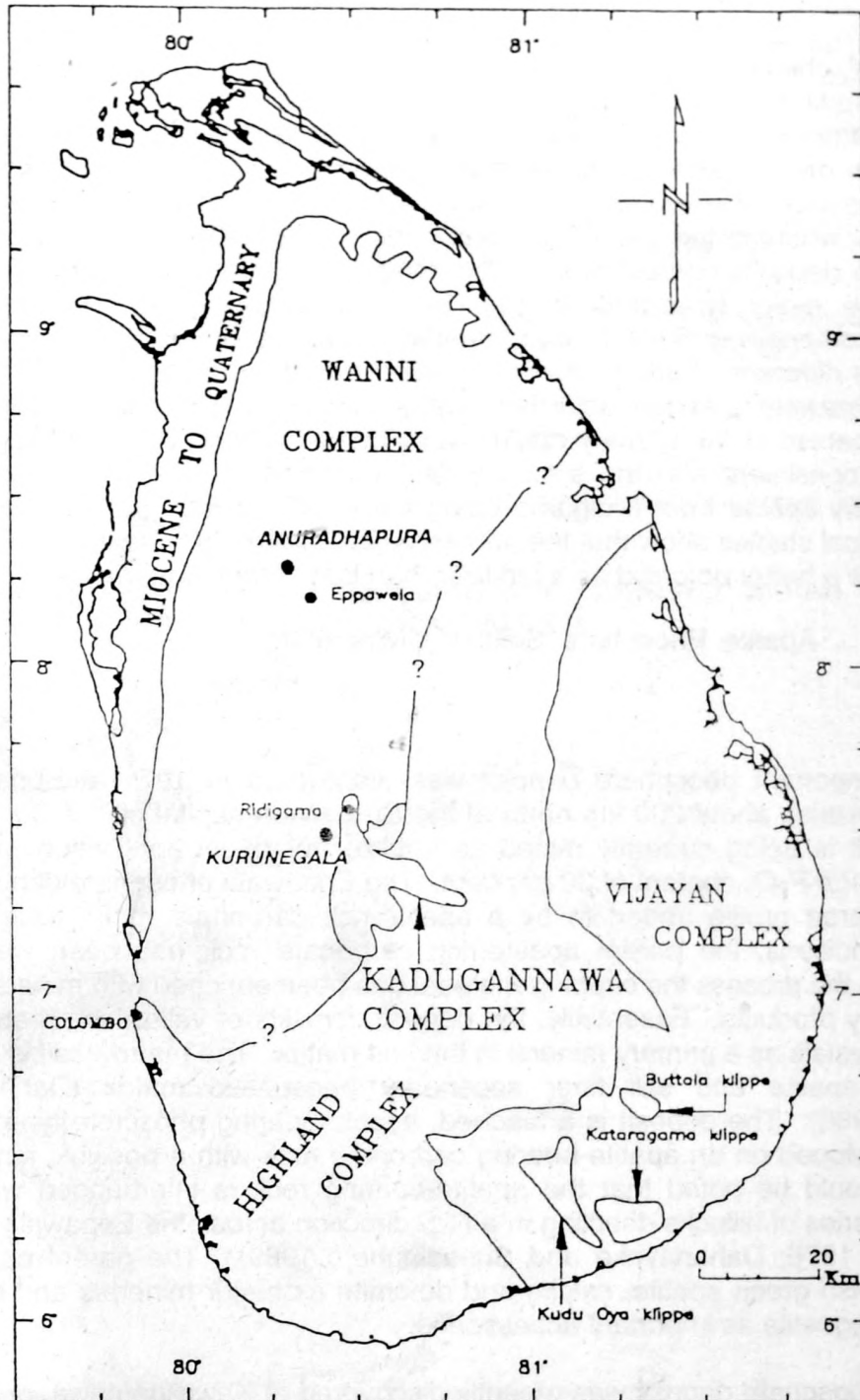


Figure 1 Geological Subdivisions of Sri Lanka and Locations of Phosphate Deposits (Kroner et al., 1991)

Materials and Methods

X-Ray Diffractometry: Apatite varieties and mineralogical compositions in the primary crystals and the fine matrix were detected by X-ray powder diffraction method (Moore and Reynolds, 1989; Whiston, 1987).

Wet Chemical Analysis : Chemical composition of the dissolved samples was determined by atomic absorption spectrophotometry(AAS), inductively coupled plasma spectrophotometry(ICPS) and colorimetry. For solubility analyses, the powdered samples were dissolved in relevant solvents and filtrates were used (Jeffery and Hutchison, 1981; Yoshida et al., 1976; Watanabe and Olson, 1965).

Mineralogy and Chemistry of the Deposits

1. Eppawala

In the Eppawala deposit, yellowish green, euhedral, primary apatite crystals are distributed in the brown coloured matrix. According to XRD studies, these apatite crystals contain chloro-fluor-hydroxylapatite (CFHA) and fluorapatite (FA) as major and minor components (Figure 2). The unit cell a-dimensions of CFHA and FA are 9.46Å and 9.37Å respectively (Table 1). The finer matrix of the Eppawala deposit is rich in minerals such as carbonate fluorapatite (CFA), CFHA, goethite, kaolinite, crandallite and quartz (Table 1).

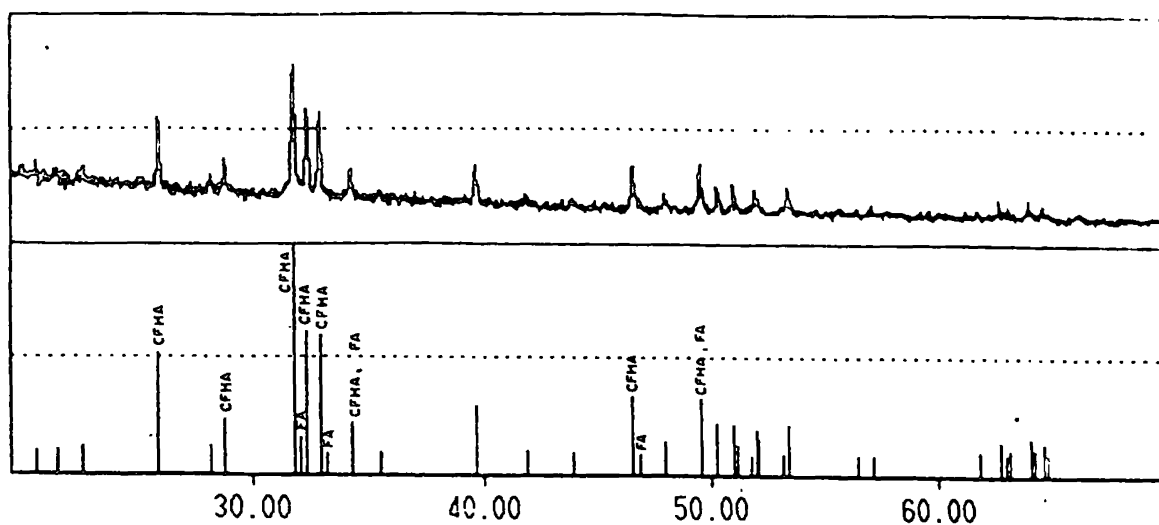
Table 1 Comparison of mineralogy of two apatite varieties in two phosphate deposits

Location	Mode of Occurrence	Mineralogy
Eppawala	Yellowish green primary apatite crystals occur in fine grained matrix.	<p>Primary Apatite major - CFHA (<i>a axis</i>: 9.46Å) minor - FA (<i>a axis</i>: 9.37Å).</p> <p>Fine Matrix CFA, CFHA, goethite, kaolinite, crandallite, quartz</p>
Ridigama	Yellowish green primary apatite crystals occur in fine grained matrix .	<p>Primary Apatite major - CFHA (<i>a axis</i>: 9.48Å) minor - FA (<i>a axis</i>: 9.35Å)</p> <p>Fine Matrix CFA, CFHA, randallite, hematite, goethite, kaolinite</p>

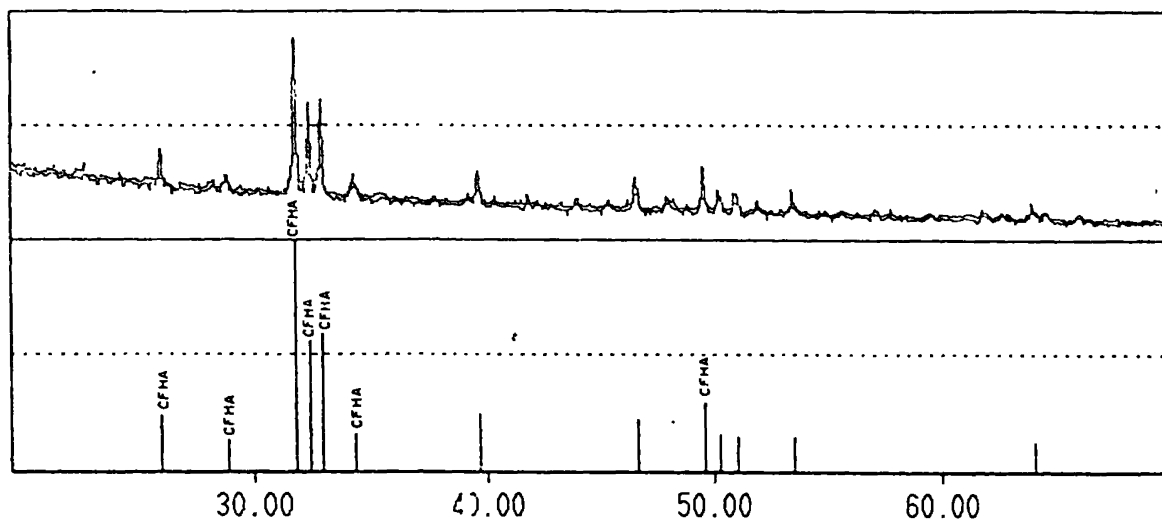
CFHA - Chlor-fluor-hydroxylapatite, FA - Fluorapatite, CFA - Carbonate fluorapatite

The average P₂O₅ of primary apatite lies between 38 to 40 per cent based on analysis of randomly selected samples, and it varies from 30 to 35 per cent in the matrix. The 2 per cent citric acid solubility is around 6 per cent for primary crystals and it ranges from 3 to 5 per cent for the matrix (Tables 2 and 3). The water solubility of primary apatite and the fine matrix is around 0.06 (P₂O₅ by weight) and 0.04 (P₂O₅% by weight), respectively.

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(A)



(B)

Table 2 Chemical composition of primary apatite and fine matrix from Eppawala and Ridigama phosphate deposits

	Eppawala Primary Apatite %	Eppawala Fine Matrix %	Ridigama Primary Apatite %	Ridigama Fine Matrix %
P ₂ O ₅	40.18-38.72	33.22-28.26	40.73-39.63	30.26-24.39
CaO	53.80-51.38	43.19-34.90	54.62-53.21	38.36-32.32
F	02.39-02.09	02.72-02.06	01.48-01.29	01.32-01.28
SiO ₂	00.19-00.11	00.79-00.14	00.19-00.12	00.43-00.23
Al ₂ O ₃	00.05-00.02	02.02-01.38	00.26-00.18	02.72-02.06
Fe ₂ O ₃	00.38-00.32	12.21-10.78	00.76-00.42	22.33-14.56
Na ₂ O	00.16-00.11	00.19-00.12	00.15-00.05	00.23-00.19
K ₂ O	00.05-00.02	00.04-00.02	00.05-00.02	00.08-00.04
MgO	00.18-00.11	00.19-00.13	00.11-00.03	00.16-00.11
Cl	01.98-01.84	01.41-01.16	02.31-02.12	01.52-01.29

2. Ridigama

Yellowish green, subhedral, primary apatite crystals are found in a secondary, fine grained sedimentary matrix, which is composed of secondary phosphate minerals, aluminous, ferruginous and siliceous materials. The size of the primary apatite crystals varies from a few mm to several cm. In the matrix, high amounts of hematite and magnetite are present. The colour of the secondary matrix varies from yellow and yellowish brown to dark brown. The XRD studies revealed that CFHA and FA are the major components in the primary crystals (Figure 2). The unit cell a-dimension of CFHA is 9.48\AA whereas that of FA is 9.35\AA (Table 1). According to XRD analyses of the fine matrix, it contains CFA, CFHA, hematite, crandallite, goethite and kaolinite (Table 1). The total P_2O_5 of primary apatite is around 40 per cent (by weight) whereas it varies from 25 to 30 per cent (by weight) in the matrix. The 2 per cent citric acid solubility of primary crystals is around 7 per cent (P_2O_5 by weight) and it is around 3 per cent (P_2O_5 by weight) for the matrix. The water solubilities of primary crystals and matrix are around 0.05 ($\text{P}_2\text{O}_5\%$ by weight) and around 0.04 ($\text{P}_2\text{O}_5\%$ by weight) respectively (Tables 2 and 3).

Table 3 Solubility of primary apatite crystals and fine matrix from Eppawala and Ridigama Phosphate deposits

	Eppawala Primary Apatite	Eppawala Fine Matrix	Ridigama Primary Apatite	Ridigama Fine Matrix
2% Citric Acid Solubility (as $\text{P}_2\text{O}_5\%$)	6.32-5.81	4.72-2.85	7.32-6.64	4.21-2.32
Water Solubility (as $\text{P}_2\text{O}_5\%$)	0.06-0.04	0.04-0.03	0.06-0.05	0.04-0.03
Neutral Ammonium Citrate Solubility (as $\text{P}_2\text{O}_5\%$)	2.20-2.10	2.10-1.90	2.70-2.60	1.60-1.70

The chemical studies reveal that the total P_2O_5 content in the primary apatite of Eppawala and Ridigama exceeds 40% (Table 2). In the fine matrix of both deposits, relatively low P_2O_5 content was recorded and it ranges from 25 to 35 per cent P_2O_5 . The chemical studies show that the CaO content of all the primary apatite samples exceeds 50 per cent whereas that of the fine matrix ranges from 30 to 45 per cent. The F content of the primary apatite from Eppawala (2.0-2.4%) is higher than that of the Ridigama ore (1.25-1.40). A low SiO_2 content was observed in the primary apatite but that value is higher in the fine matrix. The contents of Al_2O_3 and Fe_2O_3 of primary apatite of both locations are very low when compared with their fine matrices. Higher values of Al_2O_3 and Fe_2O_3 were observed for primary crystals of Ridigama than that of Eppawala (Table 2).

The values of the Fe_2O_3 for the matrix of Ridigama are significantly higher than those of Eppawala, due to the abundance of Fe rich minerals. The 2 per cent citric acid, neutral ammonium, citrate and water solubilities of these deposits were compared (Table 3). This study reveals that the 2 per cent citric acid and neutral ammonium citrate solubilities of primary apatite crystals from Ridigama are higher than those of Eppawala. The solubility and the total phosphorous content of the fine matrices are low, due to the presence of high amounts of non-phosphatic materials.

Discussion and Conclusions

It is noted that both the Eppawala and Ridigama residual sections have developed through several stages of weathering, both physical and chemical, followed by precipitation, deposition and consolidation, resulting in the present stage of the profiles. The existing profiles are characterized by a number of horizons, starting from the parent rock to loose unconsolidated top soil. Primary phosphate minerals have been subjected to weathering, forming new components, and the nature of the new minerals depends on the composition of the parent rock and the weathering environment.

Primary apatite crystals from both deposits have CFHA and FA as major and minor components, respectively. However, the ratio of abundance of CFHA to FA in the primary crystals ranges considerably for the two deposits. It was noted that when the content of FA increases, the solubility, or the reactivity of the primary crystals also increases significantly. This shows that the minor apatite mineral component (i.e., FA) is more soluble than the major apatite mineral component (i.e., CFHA). Therefore, the abundance of FA is much more important than that of the CFHA in determining the reactivity of the primary apatite crystals.

Although FA is present as a minor component in the yellowish green crystals, their a-axis dimensions are different for the two locations. The length of the a-axis (9.37\AA) of the primary apatite from Eppawala corresponds closely with that of the pure fluorapatite (9.372\AA), whereas this value is lower for the primary crystals from Ridigama (9.35\AA). Therefore, the crystal structure of primary crystals from Eppawala is more stable than that of the Ridigama crystals. In addition, mineralogical investigations have revealed that the abundance of FA in the primary crystals of Ridigama is higher than that of Eppawala. This evidence suggests a greater chemical reactivity and, thus, an increased solubility of the primary crystals from Ridigama compared to Eppawala. This explanation is consistent with the solubility data and it was noted that the primary apatites from Ridigama have higher solubilities than Eppawala.

Acknowledgments

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