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FULL LENGTH ARTICLE

Mineralogical, geochemical characteristics and origin of Late Cretaceous phosphorite in Duwi Formation (Geble Duwi Mine), Red Sea region, Egypt

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Abstract The Late Cretaceous Duwi Formation in Egypt overlies non-marine, varicolored shale of the middle Campanian Quseir Formation. It is conformably overlain by gray, laminated, foraminiferal-rich marine shale of the middle Maastrichtian Dakhla Formation. Detailed mineralogical and geochemical studies were carried out on the phosphate rocks of the Duwi Formation in Quseir-Safaga province (Geble Duwi Mine) to infer their source rocks, paleo-weathering and provenance of the sources. The importance of the effect of phosphate rock depends on the chemical form of phosphorus in which this element is combined. This information is important in the assessment of possible radiological hazards to human health; due to the presence of uranium in the apatite structure. The phosphatic rock materials may be used as building stones or as phosphatic fertilizers and animal feed ingredients. Mineralogically, they are composed mainly of apatite (fluor-apatite), calcite and quartz with minor amounts of pyrite. The studied Duwi phosphates are authigenic in origin, comparable to those of phosphatic nodules of Peru and Chile margins. They are most probably derived from pre-existing authigenic phosphorites. Provenance, they originate from reworked older sedimentary phosphorites and biogenic sources. The geochemical data, CIA values suggested that the Duwi Formation phosphates were subjected to low chemical weathering.

Generally, the enrichment of the trace elements, REEs and uranium may have occurred during diagenesis. The studied phosphate samples were compared to the average of the Average World Phosphorite (AWP) and the Average Shale Composition (ASC). The major, trace and rare earth elements contents are compared with those in Egypt, North African, Asian and other localities. The ratios V/Cr, V/(V + Ni) and Mo/Al and the high concentrations of the redox sensitive elements revealed that the studied phosphates were deposited under anoxic reducing marine environments coupled with hydrothermal solutions, which is comparable to the environmental condition of

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the associated black shales. The concentration of the trace and toxic elements in the studied samples are considered to be below the limits for most field-grown crops.

1. Introduction

Composition of the phosphate rocks mostly depends on their type and origin. About 90% rocks are used in the production of P-fertilizers and the remains 10% is used as a source of phosphorous for chemical and food industries [1]. Phosphate resources are distributed, according to their type, approximately as follows: 75% from sedimentary marine deposits, 15–20% from igneous, metamorphic and weathered deposits, and 2–3% from biogenic sources (bird and bat guano accumulations) [2]. Its current abundance in the earth's crust is approximately 0.12%; and almost all of the phosphorus on earth is found in the form of minerals including chloro and fluoro-apatite, vivianite, wavellite, and phosphorites [3,4].

Sedimentary rocks contain high concentrations of heavy metals. These deposits occur in the form of ore bodies or lenses in one thick bed or several beds intercalated with sedimentary non-phosphate materials. Sedimentary phosphate ores show a wide diversity in the composition of their gangue materials, but generally fall into one of the three categories: siliceous, clayey and calcareous ores. It is known that most sedimentary calcareous phosphate rocks contain considerable quantities of carbonates and are considered to be carbonate-apatite or francolites. Because of the increasing use of phosphate in industry worldwide, it is interesting to investigate the elemental concentration in phosphate ores. The trace element content of certain phosphate rocks is critical for their utilization and consequently, determination of the concentration of Ni, Zn, and U (environmental pollutants i.e. toxic elements), and the common elements (Co, K, Mg, Mn, Na) in phosphate rocks used for the production of fertilizers in Egypt.

In the present study the authors focus on the geochemical composition of phosphates of the Duwi Formation, in an effort to recognize its provenance, source weathering history, and the depositional environment. These factors are evaluated using major oxides, trace, and rare earth element (REEs) data, weathering indices, elemental ratios, and other geochemical indicators.

2. Geological setting

Most of the known world phosphate rock reserves are found in sedimentary marine deposits of the Upper Cretaceous and Eocene ages of the Mediterranean phosphogenic province; which exist in Morocco, Spain, Sahara, Algeria, Tunisia, Egypt, Israel, Jordan, Syria, Saudi Arabia, Turkey and Iraq. They are made of deposits laid down in the ancient Tethys Sea of the Mesozoic and Tertiary ages. The importance of the phosphate rock deposits in the Upper Cretaceous and Eocene ages is that they form more than 70% of the total world phosphate reserves [5,6].

Phosphorite deposits in Egypt, known as the Duwi Formation, are a part of the Middle East to North Africa phosphogenic province of Late Cretaceous to Paleogene age. They are found in: the Nile Valley, between Idfu and Wadi Qena, the Red Sea Coast, between Safaga and Quseir, Abu Tartur plateau in Western Desert and Sinai. These deposits belong to the Duwi Formation and its equivalent formations of Campanian–Maastrichtian age. The Duwi Formation in the Red Sea, Nile Valley, and Abu-Tartur areas overlies non-marine, varicolored shale of the middle Campanian Quseir Formation, and is conformably overlain by gray, laminated foraminiferal-rich marine shale of the middle Maastrichtian Dakhla Formation [7]. These sediments are reflecting deposition under inner neritic to outer shelf conditions and repeated sea level changes [8]. Abd El-Gabar et al. [9] reveal the presence of uranium phosphate mineral phosphuranylite, belovite and phosphoferrite in all phosphate rocks in the Red Sea, Nile Valley and Western Desert. Moreover, they indicated that the uranium contents increase as P_2O_5 exceeds 15% with an average of 107 ppm. These values drop to an average of 36 ppm with P_2O_5 less than 15%. Individual phosphorite beds in the Duwi Formation range in thickness from a few millimeters to tens of centimeters. One common feature of nearly all Duwi phosphorites is the extensive bioturbation. As a result, most of the phosphate beds appear massive and internally structureless.

Quseir-Safaga areas are part of the Eastern Desert of Egypt at the Red Sea Coast, and gained importance since the phosphate deposits of the Gebel Duwi Range were discovered and exploited. The region extends in a northwest direction along the western coast of the Red Sea from south of Quseir to Safaga, between Longitudes 33°45′–34°25′ E and Latitudes 25°50′-26°67′ N, covering an area of about 500 km^2. Typically, the Egyptian phosphates are shallow marine deposits of Upper Cretaceous age. Their maximum intensity of deposition was associated with a transgressive shoreline of the Late Campanian or Early Maastrichtian Sea which encroached from north to south over the northern slope of Africa [10,11]. The chosen area is located at Longitudes 34°03′12″–34°03′24″ E and Latitudes 26°11′27″–26°11′37″ N (Figs. 1 and 2), [12,13].

3. Mineralogy

The mineralogical composition was identified using the X-ray technique with a Phillips X-ray diffractometer model and Ni-filtered Cu-Kα radiation at the Metallurgical Center for the Research and Development Institute (Tebbin, Egypt). The XRD analysis showed the dominance of apatite (fluor-apatite) in the tested samples while the associated gangue minerals are calcite and quartz with minor amounts of pyrite. Apatite $\{Ca_5(PO_4)_3[F, OH \text{ or } Cl]\}$ in most sedimentary calcareous phosphate rocks contains considerable quantities of carbonates and is considered to be carbonate-apatite or francolites. Many authors presented evidence that, as in a typical sedimentary ore in the Duwi Formation, its main phosphate mineral is francolite (carbonate fluorapatite). In addition, many accessory phosphate minerals were also reported in Abu-Tartur such as fluor-apatite, hydroxyapatite, dolomite, quartz,

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