

Preliminary data on cadmium and arsenic geochemistry for some phosphorites in Egypt

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Abstract

Phosphorite deposits in Egypt, contained in the Duwi Formation, are a part of the Middle Eastern to North African phosphogenic province of Late Cretaceous to Paleogene age. They are mainly composed of phosphatic, structureless pelloids and bioclasts of francolite composition. Three localities were sampled.

Results of inductively coupled plasma (ICP) analyses indicate that the cadmium contents range from 0.37 to 11.55 ppm with an average of 3.2 ppm. Arsenic contents range from 0.1 to 2.1 ppm with an average of 0.95 ppm. Red Sea phosphorites show higher cadmium contents compared with the Nile Valley and Abu-Tartur phosphorites. The Abu-Tartur phosphorites show higher arsenic contents compared with the Red Sea and Nile Valley phosphorites. Nile Valley phosphorites have the lowest cadmium and arsenic contents.

Lack of correlation between Cd and As suggests different sources and/or diagenetic behavior. Correlation between both elements and Al_2O_3 is also lacking, suggesting that both Cd and As do not have a detrital origin. Lack of correlation between Cd and As and CaO and P_2O_5 indicates there is no genetic relationship between Cd and As and francolite. Lack of correlation between Cd and TOC suggests that Cd does not have an organic origin, while the relatively strong positive correlation between As and TOC indicates that As contents may be related to the organic fraction. Relatively strong positive correlation between As and S is suggestive for the occurrence of As as sulfide.

The geochemistry of Cd and As is completely different and diagenesis seems to be the most important controlling factor of their distribution.

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1. Introduction

The geochemistry of phosphorites and their constituent mineral francolite have been widely studied, owing to their economic importance and the potential utility of their geochemistry to estimate paleo-marine chemistry (Cathcart, 1980). The chemical composition of francolite (carbonate fluorapatite) is highly variable because its crystal structure allows a variety of substitutions

(McConnell and Lehr, 1969; McArthur, 1990; McClellan, 1980; McClellan and Van Kauwenbergh, 1990). Cadmium (Cd) is one of the trace elements highly enriched in phosphorites (Nathan et al., 1996, 1997; Soudry et al., 2002). The average Cd concentration in phosphorites, 18 mg g^{-1} , is 60 times its average concentration in shales, 0.3 mg g^{-1} (Altschuler, 1980). This enrichment is even more evident if the value of 0.1 mg g^{-1} is taken as the average Cd concentration in shales (cf. Heinrichs et al., 1980). Some phosphorite deposits contain significantly higher average Cd concentrations than the average for world phosphorites, such

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as 80 mg g^{-1} in Togo (Johanson, 1987). In phosphorites, discrete samples with Cd concentrations of hundreds of mg g^{-1} are not uncommon (Nathan et al., 1996).

It appears that Cd does not replace Ca in the apatite structure, since as a rule no correlation is found between P_2O_5 and Cd in phosphorites (sedimentary apatite) (Bock, 1987; Prevot, 1990; Nathan et al., 1996). This is similar to what was found in magmatic apatite (Vincent and Bilefewld, 1960). The lack of a Cd–Ca substitution in both sedimentary and magmatic apatites (although the radii of Cd^{2+} and Ca^{2+} are almost identical) is probably due to the same reason: the high degree of covalence present in the Cd–O bond (Brooks and Ahrense, 1961).

The prevalent opinion is that Cd, in phosphorites, is related to organic matter (Gulbrandsen, 1966; Baturin and Oreskin, 1981, 1985). Heinrichs et al. (1980) showed clearly a general relation of Cd with organic matter in shales. The average Cd concentration increases from 130 mg g^{-1} in shales with less than 0.5% organic C, to 210 mg g^{-1} in dark shales with 0.5–2% organic C, and to 1450 mg g^{-1} in black shales with more than 2% organic C. Very high Cd concentrations have been reported from black shales, e.g. 230 mg g^{-1} Cd in such a shale from the Upper Pennsylvanian Stark Shales Member, USA (Hatch and Leventhal, 1992).

The geochemistry of Cd in phosphorites has many aspects. Cd is a biologically mediated trace constituent of seawater and is distributed analogously to the nutrients such as phosphate. Significant differences in the Cd/P ratio in rocks of the same sequence may help to unravel the geological history of these rocks. The toxicity of cadmium (Nomiya, 1975) and the fact that the major route of Cd addition to soils is through phosphate fertilizers (Cook and Ferney, 1988; Merry and Tiller, 1991) adds another incentive to this study.

Arsenic is a ubiquitous element that ranks 20th in abundance in the earth's crust, 14th in seawater and 12th in the human body. It is used in various fields such as medicine, agriculture, livestock, electronics, industry and metallurgy (Nriagu et al., 1998). It is now well recognized that consumption of arsenic, even at low levels, leads to carcinogenesis (Mandal and Suzuki, 2002). In most rocks arsenic ranges from 0.5 to 2.5 mg kg^{-1} through higher concentrations are found in finer-grained argillaceous sediments ($3\text{--}490 \text{ mg kg}^{-1}$) and phosphorites ($0.4\text{--}188 \text{ mg kg}^{-1}$) (Kabata-Pendias and Pendias, 1984).

Arsenic naturally occurs in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts and the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic (Onishi, 1969).

The Campanian–Maastrichtian phosphorites in Egypt, contained in the Duwi Formation, form a portion of the Middle Eastern to North African phosphogenic province of Late Cretaceous to Paleogene age. The province holds the greatest accumulation of phos-

phorites in the geological record, possibly in excess of 70 billion metric tons (Cook and McElhinny, 1979). The phosphate resources in Egypt alone exceed an estimated 3 billion metric tons (Notholt, 1985). The age of the Duwi Formation most likely ranges from late Campanian to early Maastrichtian. The phosphate deposits are widely distributed in the Eastern Desert, Nile Valley, and Western Desert. They occur in two main horizons separated by a thick shale interval. The lower horizon is productive in the Abu-Tartur area, and the upper horizon is productive in the Nile Valley and Red Sea areas (Fig. 1). Based on the petrographical observations, the phosphorite grains are classified into phosphatic structureless peloids and bioclasts. Phosphatic bioclasts are subdivided into fish bone fragments and shark tooth fragments. These phosphatic grains are genetically different, so their chemical and mineralogical compositions are expected to be different.

This preliminary study aims to examine the geochemistry of cadmium and arsenic in the Egyptian phosphorites and to discuss briefly their controlling factors.

2. Geological setting and studied localities

Detailed fieldwork has been conducted on the Duwi Formation in the Red Sea, Nile Valley, and Abu-Tartur areas (Fig. 1) to collect samples that represent different localities and horizons. The Duwi Formation in these areas overlies non-marine, varicolored shale of the middle Campanian Qusseir Formation, and is conformably overlain by marine, laminated, gray, foraminefera-rich shale of the middle Maastrichtian Dakhla Formation. According to Baioumy (2001, 2002, 2003), the Duwi Formation is sub-divided into four members, based on lithology and grain size (Fig. 2). The lower member is composed of coarse phosphatic sandstone in the Abu-Tartur area, but of quartzose sandstone and siliceous shale in the Nile Valley and Red Sea areas. The second member (cf. middle member in Fig. 2) is made of soft, laminated, blackish shale in all three localities. The third member (cf. upper member in Fig. 2) consists of coarse glauconitic sandstone at Abu-Tartur area, phosphatic sandstone in the Nile Valley area, and phosphatic sandstone and oyster fragment-rich calcarenite in the Red Sea area. The uppermost member is built of hard, massive shale in the three localities. The productive beds occur in the lower member in the Abu-Tartur area, in the third member in the Nile Valley area and in the uppermost member in the Red Sea area. Individual phosphorite beds in the Duwi Formation range in thickness from a few millimeters to tens of centimeters. Thicker phosphorite beds are formed by amalgamation of thinner individual beds. The thickest accumulation of minable phosphorites occur in the lower member in the Abu-Tartur area, where the phosphorite beds locally

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