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Geochemistry of Late Cretaceous phosphorites in Egypt: Implication for their genesis and diagenesis

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Abstract

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. Phosphatic grains in these deposites are classified into phosphatic mudclasts and phosphatic bioclasts. Phosphatic bioclasts are subdivided into fish bone fragments and shark tooth fragments. All phosphatic grains are composed of francolite.

Chemical mapping of the phosphatic grains using Electron Probe Microanalysis (EPMA) indicated that the phosphatic mudclasts are homogeneous in their chemical composition and no concentric texture nor chemical zoning are observed. Some of the bone fragments show Fe and S zoning. No significant difference in chemical composition is observed between the phosphatic mudclasts and bioclasts. Acid-insoluble residues of the phosphorites show lower values of the Chemical Index of Alteration (CIA) compared to the associated rocks. Structural CO_2 contents in the francolites range from 3.32% to 7.21% with an average of 5.3%. The $\delta^{13}C_{PDB}$ values range from −4.04‰ to −8.7‰, while the $\delta^{18}O_{PDB}$ values range from −4.3‰ to −10.3‰.

The compositional homogeneity of the mudclasts, Fe and S zoning in some of the bone fragments and the difference in the Chemical Index of Alteration between the acid-insoluble residues of the phosphorites and the associated rocks suggest that the phosphatic grains in the Duwi Formation are derived from pre-existing authigenic phosphorites, which reworked and concentrated afterward.

Negative $\delta^{13}C$ values of structural CO_2 suggest that the CO_2 was derived from degradation of organic matter. Low $\delta^{18}O$ values of structural CO_2 can be attributed to the influence of meteoric water.

Higher CO_2, SO_3 and F contents compared to the recent authigenic phosphorites and negative $\delta^{13}C$ and $\delta^{18}O$ values of structural CO_2 indicate that diagenesis plays an important role in the modification of the chemical composition of phosphatic grains and that the studied apatite was francolitized during diagenesis.

Keywords: Egypt; Phosphorites; Phosphatic mudclasts; Phosphatic bioclasts; Francolite; Diagenesis

1. Introduction

The geochemistry of phosphorites and their constituent mineral francolite have been widely studied owing to their economic importance (Jarvis et al., 1994) and the potential utility of their geochemistry to estimate paleo-marine chemistry (Donnelly et al., 1990). The chemical composition of carbonate fluorapatite is highly variable because its crystal structure allows a variety of substitutions (McClellan and Lehr, 1969). Variability in chemical composition of francolite may reflect difference in original composition, modification during diagenesis, or modification during weathering (Jarvis et al., 1994).

Sedimentary francolite contains up to 8% of structurally incorporated carbonate (McArthur, 1978). This carbonate can be analyzed for its carbon and oxygen isotope composition, which are highly instructive on the condition of the francolite precipitation (Jarvis et al., 1994). The source of this carbon and oxygen in authigenic francolite is generally

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considered as the pore-water at the time of its formation (Hudson, 1977). Because the amount of bicarbonate present in solution is small, its carbon isotope composition very sensitively reflects the degradation processes of organic matter during burial diagenesis. Consequently, authigenic francolite formed in anoxic sediments is expected to contain organically derived carbon released during bacterial degradation processes. The $\delta^{13}C$ of francolite should become light if it is precipitated in the sulfate-reduction zone whereas it should become heavy if it is precipitated in the fermentation zone (Hudson, 1977).

Carbon isotopic data from francolite may be used to help constraining where and when phosphorite formation occurs (Glenn, 1990). If francolite precipitates directly from seawater at the sediment–water interface, then the carbon isotopic composition of incorporated CO_2 should be characteristic of the bottom water. If, on the other hand, francolite precipitates within the sediments, the $\delta^{13}C$ values of lattice-bound CO_2 should record $\delta^{13}C$ of the pore-water total dissolved carbon (Glenn et al., 1988).

Degradation of marine organic matter typically contributes CO_2 with a carbon isotopic composition of about $-18‰$ to $-24‰$ (cf. Anderson and Arthur, 1983) while the carbon isotopic composition of modern deep water total dissolved carbon is about $-0.5‰$ to $+0.5‰$ (cf. Kroopnick, 1985). The depletion in total dissolved carbon-^{13}C in organic carbon-rich marine sediments takes place in suboxic to anoxic sulfate-reducing environments up to the point at which all dissolved sulfate has been used up by sulfate-reducing bacteria. Authigenic carbonate-bearing mineral phases that precipitate within these zones may thus exhibit values ranging from about $0‰$ for phases forming near the sediment–water interface, to values as low as $-24‰$ for phases forming under extensive sulfate-reduction. Concurrent with or following the sulfate-reduction processes, methane-producing bacteria use organic matter and/or total dissolved carbon in pore waters whereby extremely light (as light as $-100‰$) biogenic methane is produced, leaving a residual total dissolved carbon enriched in ^{13}C (Claypool and Kaplan, 1974). Therefore, below the zone of sulfate-reduction, methane production results in a progressive increase in total dissolved carbon-$\delta^{13}C$ from about $-24‰$ to $+25‰$, depending upon the extent of methanogenesis. Authigenic mineral phases precipitated in this zone exhibits a range in $\delta^{13}C$ from very low to very high values (Glenn, 1990).

The use of oxygen isotopes in marine carbonate minerals to estimate water paleotemperatures (Urey et al., 1951) and to determine diagenetic conditions (Hudson, 1977; Irwin et al., 1977) is well established. McArthur et al. (1980) interpreted $\delta^{18}O$ values of carbonate in apatite by using the calcite-water isotopic fractionation (Epstein et al., 1953), and reasonable temperatures were obtained for recent and young phosphorites. However, ancient phosphorites (from Jordan, South Africa, Phosphoria Formation) are consistently depleted in ^{18}O.

The Campanian-Maastrichtian phosphorite deposits in Egypt, named the Duwi Formation, form a portion of the Middle East to North Africa phosphogenic province of Late Cretaceous to Paleogene age (Notholt, 1985). This study aims to examine the mineralogical, chemical and isotopic compositions of the different phosphatic grains as well as temporal and spatial variations in the composition of phosphorites and associated rocks to assess their controlling factors.

2. Geological setting and studied localities

The Duwi Formation overlies a fluvial shale sequence of the middle Campanian Qusseir Formation, and is overlain by the deeper marine shales and marls of the middle Maastrichtian Dakhla Formation. Thus, deposition of the Duwi Formation represents an initial stage of the late Cretaceous marine transgression in Egypt. The precise age of the Duwi Formation is poorly known, and generally considered as either late Campanian to early Maastrichtian based on paleontological evidences (Glenn and Arthur, 1990).

According to Baioumy and Tada (2005), the Duwi Formation in the Red Sea, Nile Valley, and Abu-Tartur areas (Fig. 1) overlies non-marine, varicolored shale of the middle Campanian Qusseir Formation, and is comformably overlain by marine, laminated, gray, foraminefera-rich shale of the middle Masstrichtian Dakhla Formation. The Duwi Formation is subdivided into four members based on its lithology (Fig. 2). The lower member is composed of coarse phosphatic sandstone in the Abu-Tartur area whereas it is composed of quartzose sandstone and siliceous shale in the Nile Valley and Red Sea areas. The middle member is composed of soft, laminated, organic-rich, black shale in the three areas. The upper member is composed 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, respectively. The uppermost member is composed of hard, massive grayish brown to gray shale in the three areas. 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 occurs in the lower member in Abu-Tartur area where the phosphorite beds locally amalgamate to form a single seam averaging approximately 12 m thick. One common feature of nearly all Duwi phosphorites is extensive bioturbation. As a result, most of the phosphatic beds appear massive and internally structureless.

3. Samples and methods

Thin sections of phosphorites and the associated rocks were prepared and observed under the petrographic microscope to examine their grain composition and texture. A total of 42 phosphatic grains from seven polished thin