

Carbon and oxygen isotopic composition of lattice-bound carbonate of phosphorites ore in Egypt

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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. Based on the petrographical observation, the phosphatic grains in the Phosphorites are classified into phosphatic mudclast and phosphatic bioclast. Both of them are composed of francolite.

The structural CO₂ contents in the francolite range from 3.32 to 7.21 % with an average of 5.3 %. The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of the studied samples are highly variable but are, nevertheless, all large negative numbers. The $\delta^{13}\text{C}_{\text{PDB}}$ values range from -4.04 to -8.7 ‰ while the $\delta^{18}\text{O}_{\text{PDB}}$ values range from -4.3 to -10.3 ‰.

Negative $\delta^{13}\text{C}$ values and low $\delta^{18}\text{O}$ values of structural CO₂ suggest that the CO₂ was derived from degradation of organic matter. The linear relationship between $\delta^{13}\text{C}$ and CO₂ % indicates that as the medium became more negative with shallow burial there was a progressive increase in the substitution of CO₃ for PO₄ in the carbonate fluorapatite. These data along with the higher CO₂ contents in the apatite from Duwi Formation in Egypt compared to the recent authigenic phosphorites indicate that the chemical composition of apatite has been changed after the formation and during diagenesis by taking CO₂ into the structure

from the surrounding medium and the studied apatite was francolitized during diagenesis.

RIASSUNTO. — I depositi di fosforite dell'Egitto, noti come Formazione di Duwi, appartengono alla provincia fosfogenica estesa dal Medio-Oriente all'Africa settentrionale che ha un'età compresa tra il Cretacico superiore e il Paleogene.

Sulla base delle osservazioni petrografiche, i grani fosfatici delle fosforiti sono classificati come clasti fangosi e bioclasti. Entrambi sono costituiti da francolite.

I contenuti di CO₂ nella francolite oscillano da 3,32 a 7,21 % con valori medi del 5,3 %.

I campioni studiati hanno valori del $\delta^{13}\text{C}_{\text{PDB}}$ e del $\delta^{18}\text{O}_{\text{PDB}}$ molto variabili ma sempre negativi; i valori del $\delta^{13}\text{C}_{\text{PDB}}$ oscillano da -4,04 a -8,7 ‰ e quelli del $\delta^{18}\text{O}_{\text{PDB}}$ da -4,3 a -10,3 ‰.

I valori negativi del $\delta^{13}\text{C}$ ed i bassi valori del $\delta^{18}\text{O}$ della CO₂ strutturale suggeriscono una sua derivazione da degradazione di materiale organico. La relazione lineare tra i valori del $\delta^{13}\text{C}$ ed i contenuti percentuali di CO₂ indicano una correlazione tra la sostituzione del CO₃ al posto del PO₄ nella fluoroapatite carbonatica con l'aumento del seppellimento. Tali dati, unitamente al più elevato contenuto di CO₂ dell'apatite nella Formazione di Duwi nei confronti delle fosforiti autigene recenti, mostrano che la composizione chimica dell'apatite è variata durante la diagenesi che ha provocato una francolitizzazione del sedimento.

KEY WORDS: *Egypt, Duwi, carbon isotope, oxygen isotope, diagenesis, apatite, francolite.*

INTRODUCTION

Sedimentary francolite contains up to 8 % of structurally incorporated carbonate (Lehr *et al.*, 1967; McArthur, 1978; Baioumy, 2002). This carbonate can be analyzed for its carbon and oxygen isotope composition. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data are highly instructive on the physicochemical condition of the francolite precipitation (Jarvis *et al.*, 1994).

The source of this carbon and oxygen in authigenic francolite would be the pore water at the time of its formation. As the amount of bicarbonate present in solution is small, the carbon isotope composition very sensitively reflects the various organic degradation processes, which successively affect sediment during burial. Authigenic francolite, formed in anoxic sediments, therefore, is expected to contain organically derived carbon released during bacterial degradation processes. This should make it isotopically light if produced in the sulfate reduction zone or heavy if produced in the fermentation zone (Hudson, 1977). In contrast, the carbon isotopic composition of carbonate in diagenetic francolite should be much the same as its precursor.

Carbon isotopic data from francolite may be used to help constrain where and when phosphorite formation occurs (Glenn, 1990). The primary assumption is that as francolite phase grow, it keeps isotopic and chemical equilibrium with the total dissolved carbon in the waters from which it precipitates (Glenn, 1988). 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 (about 0 per mil). If, on the other hand, francolite precipitates within the sediments, the $\delta^{13}\text{C}$ values of lattice-bound CO_2 should mimic those of the pore-water total dissolved carbon and display relatively negative to positive values characteristic of suboxic to anoxic organic matter degradation processes.

The isotopic composition and abundance of total dissolved carbon in marine sediments depend primarily on the relative proportion of CO_2 derived from organic matter degradation in the sediments and that from the total dissolved carbonate in the bottom waters overlying the sediments. Degradation of marine organic matter typically contributes CO_2 with a carbon isotopic composition of about -18‰ to $+24\text{‰}$; while the carbon isotopic composition of modern deep water total dissolved carbon is about $\pm 0.5\text{‰}$. The depletion in total dissolved carbon- $\delta^{13}\text{C}$ in organic carbon-rich marine sediments takes place in suboxic to oxic sulfate-reducing environments up to the point at which all dissolved sulfate has been consumed 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 negative as -24‰ for phases forming with extensive sulfate reduction. Concurrent with or following the sulfate reduction processes methane-producing bacteria being to utilize organic matter and/or total dissolved carbon in pore waters whereby extremely high biogenic methane is produced leaving 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- $\delta^{13}\text{C}$ from about -24‰ to $+25\text{‰}$, depending upon the extent of methanogenesis. Authigenic mineral phases that precipitate in this zone may exhibit a range in ^{13}C from very depleted to very enriched (Glenn, 1990).

The use of oxygen isotope 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. Low $\delta^{18}\text{O}$ values are common in early diagenetic marine carbonate rocks that are associated with organic matter (Irwin 1980; Dix and Mullins, 1987; Thyne and Boles, 1989), and are conventionally explained as caused by carbonate formation under conditions of low salinity and normal marine water.

GEOLOGICAL SETTING

The phosphatic deposits of Egypt, named the Duwi Formation (Glenn and Arthur, 1990), are a part of the upper Cretaceous lower Tertiary sedimentary sequence, and widely distributed in the Eastern Desert, Nile Valley, and Western Desert areas (Fig. 1). The Duwi Formation overlies the 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. Upper Campanian to early Maastrichtian is assigned as the age of the Duwi Formation in Egypt (Baoumy 2001).

The Duwi Formation is sub-divided into four members (Baoumy 2001) based on the lithology and grain size (Fig. 2). The lower member is composed of coarse phosphatic sandstone in Abu-Tartur whereas quartzose sandstone and siliceous shale in the Nile Valley and Red Sea areas. The middle member is composed of soft, laminated, blackish in the fresh outcrop, shale in the three localities. The upper member is composed of coarse glauconitic sandstone at Abu-Tartur, phosphatic sandstone in the Nile Valley and phosphatic sandstone and oyster fragment-rich calcarenite in the Red Sea area. The uppermost member is composed of hard massive shale in the three localities. The productive beds occur in the lower member in Abu-Tartur area and in the upper member in the Nile Valley and Red Sea areas.

Individual phosphorite beds in the Duwi Formation range in thickness from a few millimeters to tens of centimeters. Thicker phosphorite beds are composed of accumulation of thinner individual beds. The thickest accumulation of minable phosphorites occurs in the lower member in Abu-Tartur area where the phosphorite beds locally combine to form a single seam about 12 m thick in average. In contrast to the deposits at Abu-Tartur, the phosphorites in the Nile Valley and Red Sea Coast areas are thinner and laterally discontinuous overall. One common feature of nearly all Duwi phosphorites is that they are extensively bioturbated. As a result, most of

these units appear massive internally structureless.

A detailed field work has been conducted for the upper Cretaceous phosphorite-bearing sequence in Egypt to examine stratigraphy of the phosphorite deposits and collect representative samples in three localities, Red Sea, Nile Valley, and Abu-Tartur areas (Fig. 2) since the Duwi Formation is well-developed and exposed, and phosphorites are economically produced in these areas.

SAMPLES AND METHODS

Approximately 100 phosphorites samples were collected from the Red Sea, Nile Valley, and Abu-Tartur areas. Thin sections were made for approximately ten representative samples. Powders were made for 24 samples and subjected to mineralogical and isotopic analyses.

Powdered samples were mounted on a glass holder and X-rayed from 2° to $80^\circ 2\theta$ by a MAC Science MXP-3 X-ray diffractometer equipped with $\text{CuK}\alpha$ tube and monochromator at the Department of Earth and Planetary Science, University of Tokyo. Tube voltage and current are 40 kV and 20mA, respectively. The replacement of the tetrahedral PO_4 by CO_3 anion changes the lattice parameter of the apatite unit cell (LeGeors *et al.* 1967). This relationship is used by Gulbrandsen (1970) and Schuffert *et al.* (1990) to estimate the CO_2 content of apatite. By increasing the substitution of phosphate by carbonate, the (410) plane shifts to a higher 2θ angle and (004) plane shifts to a lower 2θ angle; i.e. the angular distance between the two peaks decreased. This angular distance between the peak corresponding to (410) and (004) at approximately 51.6 and $53.1^\circ 2\theta$ respectively is used as a measuring for the CO_2 content of the separated phosphatic mudclasts and phosphatic bioclasts according to the equation of Schuffert *et al.* (1990):

$$Y = 10.643X^2 - 52.512X + 56.986,$$

Where $Y = \text{CO}_2 \%$ and $X = \Delta 2\theta_{(004)-(410)}$

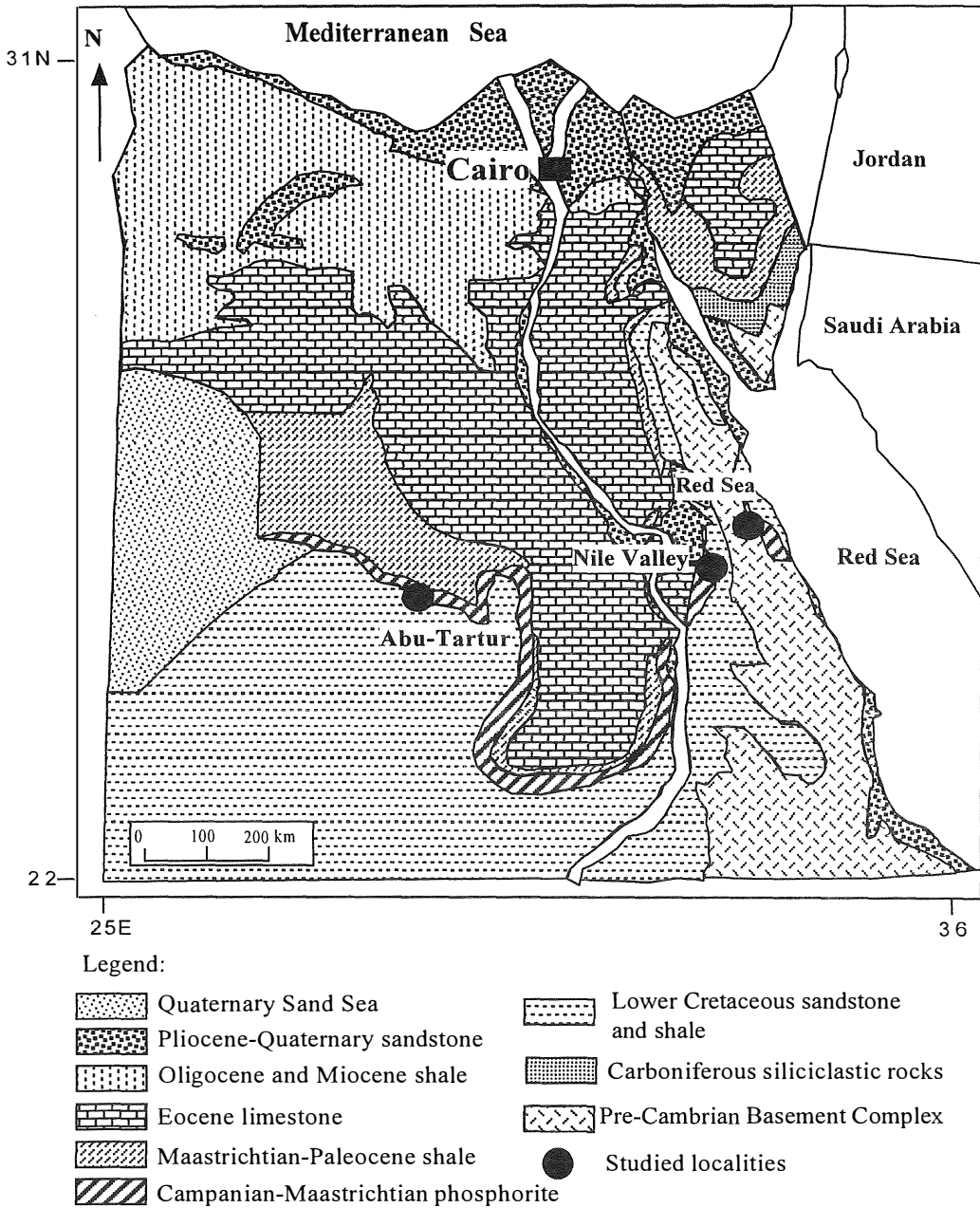


Fig. 1 – Geological map of Egypt with the localities of studied area (modified from Spanderashvilli and Mansour, 1970).

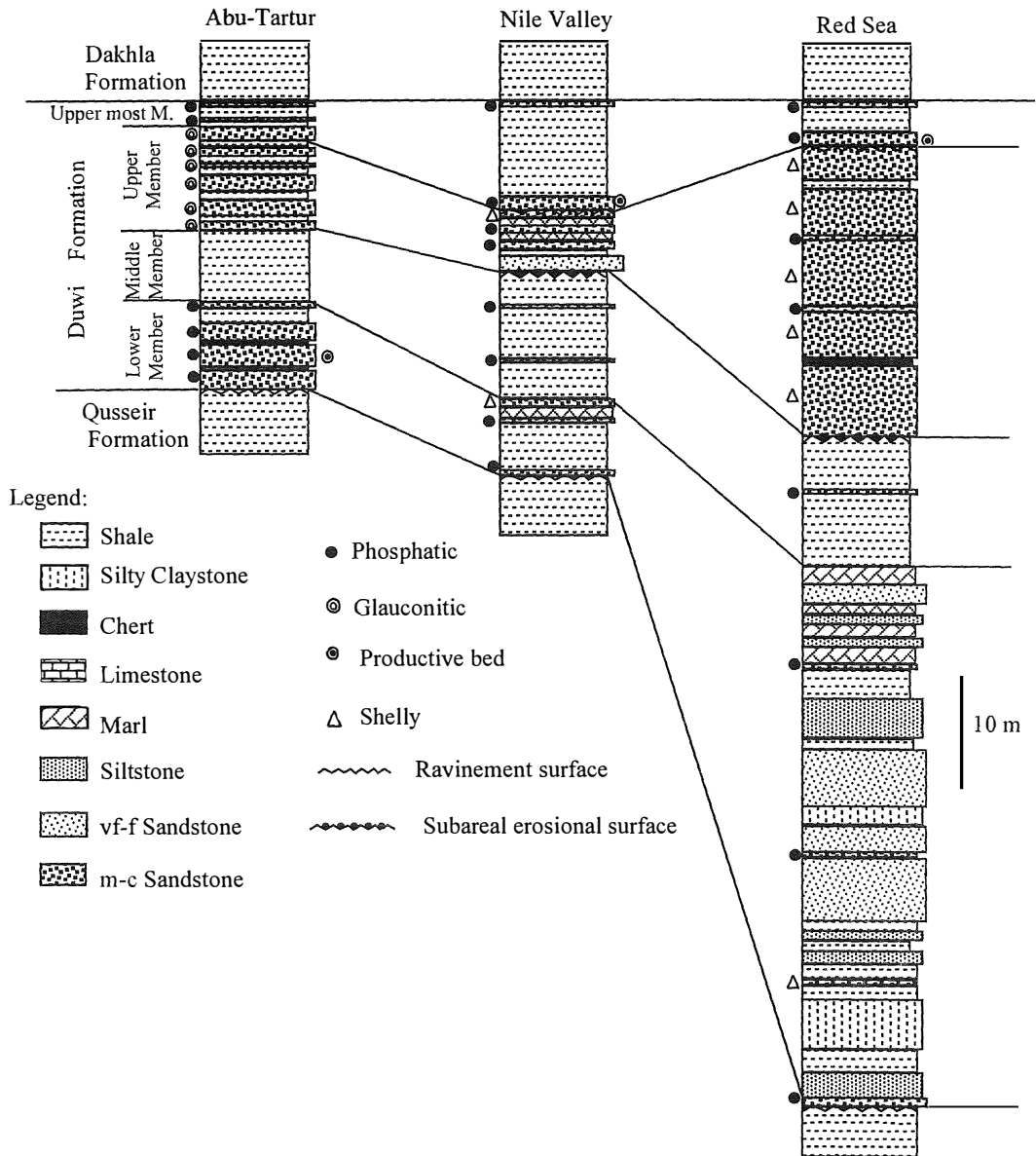


Fig. 2 – Detailed lithostratigraphy of upper Cretaceous Duwi Formation in the Red Sea, Nile Valley, and Abu-Tartur areas (after Baioumy 2001).

A total of 24 phosphorite samples from the Red Sea, Nile Valley and Abu-Tartur sections were analyzed for their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions. Samples are checked by XRD so that all samples are composed of phosphorites without any carbonates. To extract CO_2 for isotopic analysis, 20 mg of powdered samples were reacted with 2.5ml high concentrated phosphoric acid in reaction tube under vacuum condition at 25 °C for about 12 hours. CO_2 was recovered and extracted to be analyzed by a MAT252 mass spectrometer at the Earth and Planetary Science, University of Tokyo, Japan. Carbon and oxygen isotopes data are reported in ‰ notation relative to the PDB standard.

RESULTS

Petrography and mineralogy of phosphorites

Under the microscope, phosphorites are composed of phosphatic grains, non-phosphatic

grains, and cements. Phosphatic grains are composed of phosphatic mudclast and bioclasts (Baïoumy, 2001). Both of them are composed of francolite as it is indicated from the X-ray analysis (Baïoumy, 2002).

Phosphatic mudclasts are generally well rounded to subrounded, spherical in shape. Their size ranges from 40 to 100 mm in diameter, and colorless transparent through yellow to brown translucent. Black opaque varieties are confined to fresh samples from Abu-Tartur mine. Although spherical in shape, no concentric texture or any other internal structure is observed (Fig. 3). The percentage of phosphatic mudclasts in the phosphatic grains range from 45 to 67 volume % with an average of 51 volume % in the Duwi Formation. Phosphatic bioclasts are composed of fragments of fish bone and shark tooth. Fish bones fragments (Fig. 3) are angular to subangular and prismatic or irregular in shape. Their size ranges from 120 to 180 mm. Generally, bone fragments are colorless and

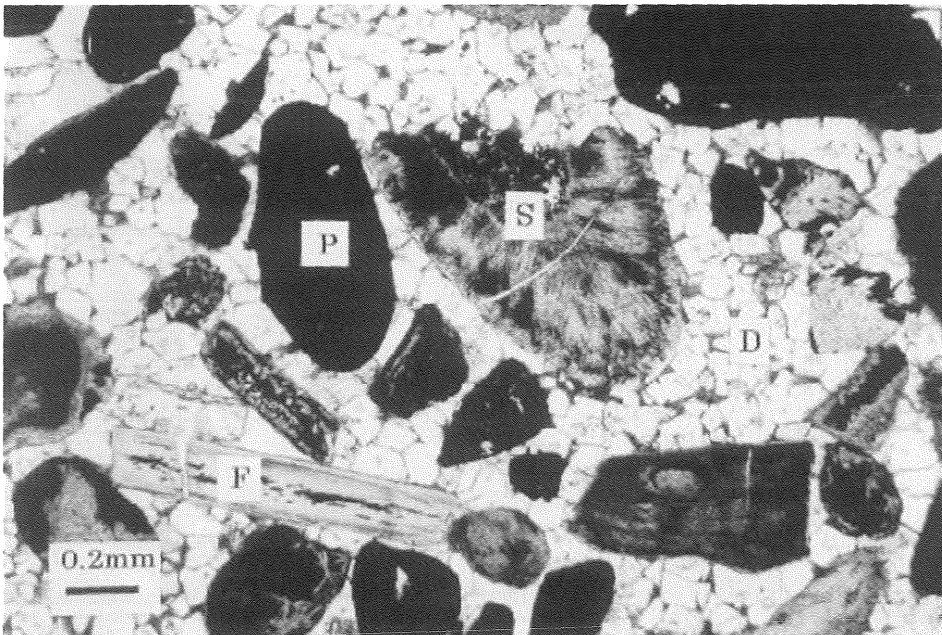


Fig. 3 – Photomicrograph shows the phosphatic constituents of the studied phosphorites. They are composed of phosphatic mudclasts (M), bone fragments (B), and shark tooth (S) that are cemented by dolomite (D).

transparent under the petrographic microscope. However, some of bone fragments show various shades of color ranging from yellow to gray. Bone fragments are generally anisotropic, but some show low birefringence and lamellar twinning. Elongated and prismatic bone fragments occasionally show extinction parallel to the elongated axis. The percentage of bone fragments in the phosphatic grains of the Duwi phosphorites range from 36 to 54 volume % with an average of 43.7 volume %. Tooth fragments (Fig. 3) are less abundant compared to bone fragments. The color of tooth fragments ranges from yellow to brown. Size of tooth fragments ranges from 150 to 200 μm . The percentage of tooth fragments in the total

phosphatic grains range from 0.25 to 2 volume % with an average of 1.3 volume %.

Non-phosphatic grains are mostly composed of subangular to subrounded, mono- and polycrystalline, colorless to pale gray detrital quartz and rounded green to greenish gray glauconite. Cements are composed of chalcedony, calcite, dolomite, pyrite, gypsum, anhydrite, and iron oxides.

Carbon and Oxygen Isotopes

The structural CO_2 contents in the studied samples range between 3.32 % and 7.21 % with an average of 4.9 % (Table 1). Carbon and oxygen isotopic compositions of the analyzed phosphorites from the Duwi Formation are

TABLE 1
Structural CO_2 , $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values of the Duwi phosphorites.

Locality	Samples	CO_2	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Temp.°C
Red Sea	PR8	6.58	-7.91	-6.4	101.02
	PR9	6.58	-7.74	-6.38	100.70
	PR14	7.21	-8.71	-5.9	93.13
	PR4	6.23	-7.71	-7.91	124.85
	PR12	6.21	-5.25	-5.96	94.07
	PR15	6.71	-6.18	-7.25	114.44
Nile Valley	PN37	4	-5.2	-9.9	156.26
	PN40	4.25	-4.75	-9.5	149.95
	PN48	5.21	-4.83	-9.41	148.53
	PN53	3.32	-4.04	-10.3	162.58
	PN54	6.7	-5.28	-8.8	138.90
	PN58	3.78	-4.51	-9.15	144.43
	PN60	3.68	-4.46	-9.44	149.00
	PN61	3.72	-4.65	-10.3	162.58
PN63	4.87	-5.55	-9.9	156.26	
Abu-Tartur	PA79	5.78	-6.31	-4.37	68.98
	PA85	5.95	-6.56	-6.33	99.91
	PA100	5.87	-6.45	-6.36	100.39
	PAW1	5.25	-6.1	-5.94	93.76
	PAW2	4.78	-5.67	-6.27	98.97
	PAb40	4.88	-6.1	-4.93	77.82
	PAb41	4.44	-5.94	-4.99	78.76
	PAb43	5.33	-6.21	-6.23	98.34
	PAb47	5.3	-6.1	-4.84	76.40

presented in Table 1. The $\delta^{13}\text{C}$ values range from -4.04 to -8.71 ‰ with an average of -5.93 ‰, while the $\delta^{18}\text{O}$ values range from -4.37 to -10.3 ‰ with an average of -7.37 ‰. Slight but clear differences can be observed in the CO_2 ‰, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ values among the studied localities (Fig. 4). Samples from Red Sea area have higher CO_2 ‰ and $\delta^{13}\text{C}$ values compared to those from the Nile Valley and Abu-Tartur areas, whereas, samples from Nile Valley area have lower CO_2 ‰ and higher $\delta^{18}\text{O}$ values compared to those from the Red Sea and Abu-Tartur areas. Abu-Tartur samples have intermediate values. Scatter diagram of CO_2 contents and $\delta^{13}\text{C}$ is shown in Figure 5. A linear relationship between $\delta^{13}\text{C}$ and CO_2 ‰ is

observed. Scatter diagram of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is shown in Figure 6. A lack of covariance is observed between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Paleotemperatures were calculated using the equation of Craig (1965) assuming $\delta^{13}\text{O}$ values of -1.2 ‰ for pre-glacial seawater (Shackleton and Kennett, 1975). Results are shown in Table 1. The values range between 76.4 °C and 162.3 °C with an average of 116.3 °C.

DISCUSSION

$\delta^{18}\text{O}$ values of the phosphorites are mainly a function of the isotopic composition and the temperature of the mineralizing fluids (Yeh,

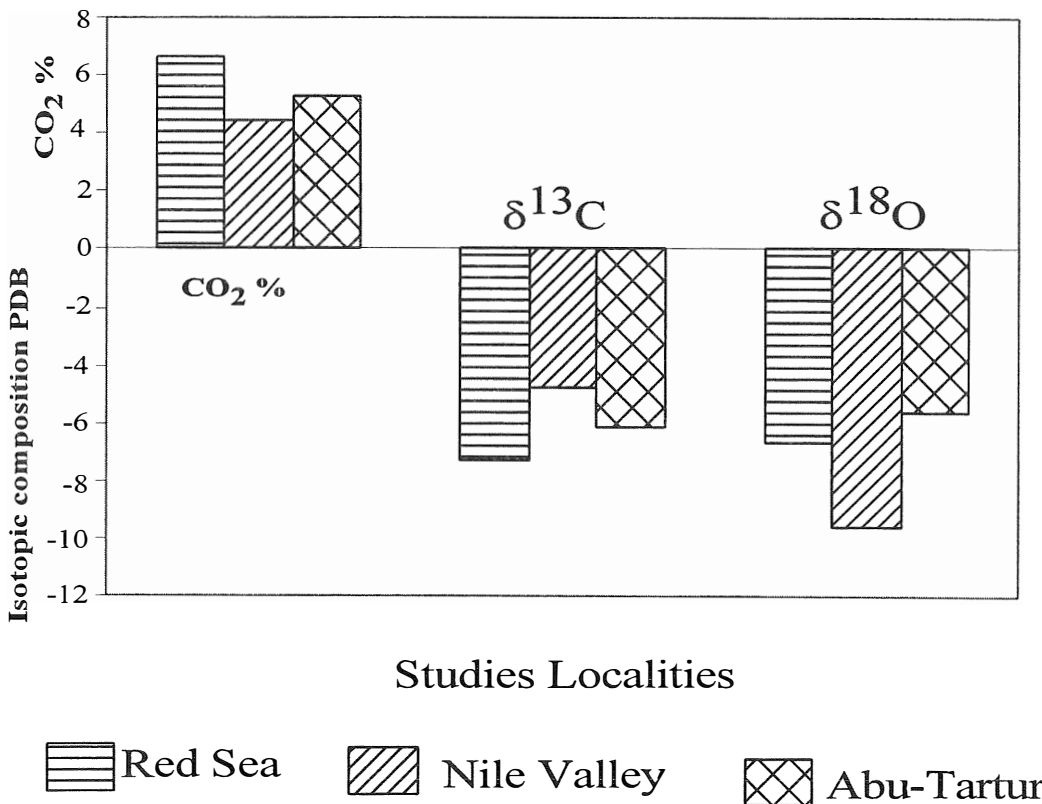


Fig. 4 – Histogram shows a comparison of the structural CO_2 ‰, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ average values of the studied phosphorites among the studied localities.

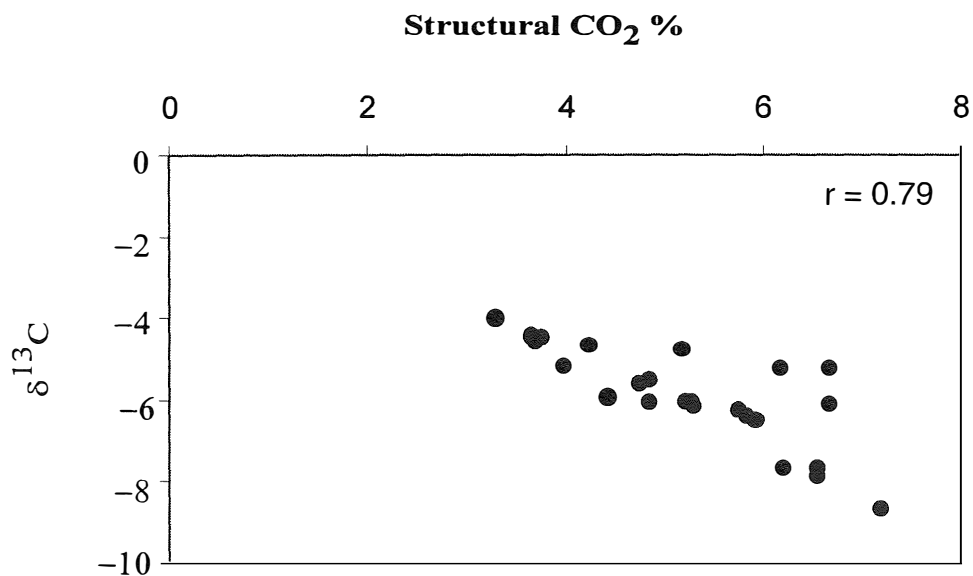


Fig. 5 – Scatter diagram of CO₂ contents and δ¹³C. A linear relationship between δ¹³C values and CO₂ % is observed.

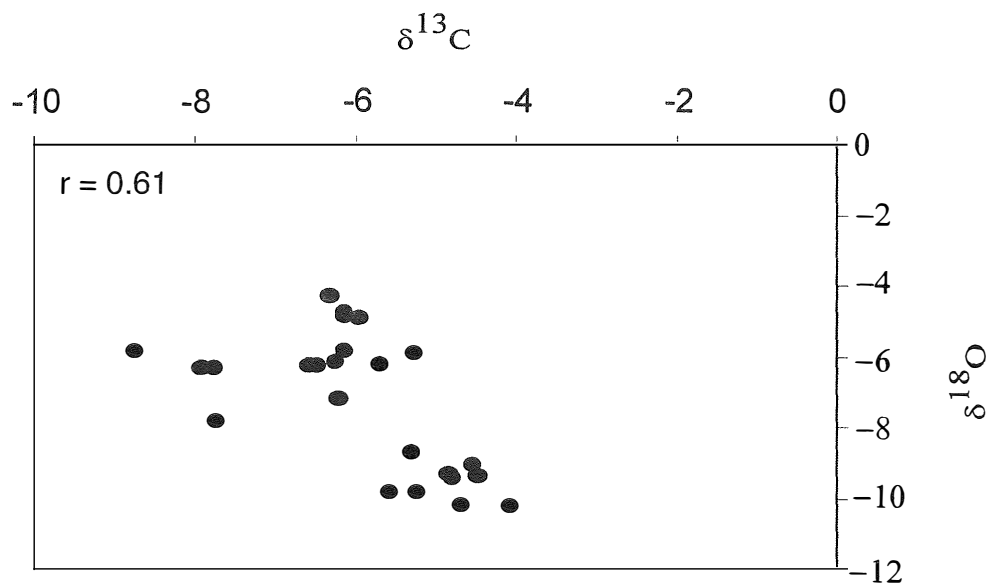


Fig. 6 – Scatter diagram of δ¹⁸O and δ¹³C values. A lack of covariance is observed between δ¹⁸O and δ¹³C.

1997). An increase in temperature and a decrease in the isotopic composition of the fluids both give rise to a decrease in the $\delta^{18}\text{O}$ values of the phosphate minerals. Hence the low values $\delta^{18}\text{O}$ of the Duwi phosphorites indicate either high temperature of formation, or formation in fluid with low $\delta^{18}\text{O}$ values or some combination of both of these. Additionally, the variations in the $\delta^{18}\text{O}$ values in the studied phosphorites definitely indicate the fluctuation in the formational environment parameters (Glenn *et al.*, 1988). The oxygen-isotope composition of seawater is generally homogeneous and enriched in $\delta^{18}\text{O}$ (Dansgaard, 1964; Craig and Gordon, 1965). Low $\delta^{18}\text{O}$ values are also typical of early diagenetic marine carbonate rocks associated with organic matter (Irwin 1980; Dix and Mullins, 1987; Thyne and Boles, 1989). The low $\delta^{18}\text{O}$ values are conventionally explained as caused by carbonate formation under conditions of low salinity and normal marine water isotopic composition. This means that the low and highly variable $\delta^{18}\text{O}$ values likely indicate the phosphate formed in high temperature and/or associated with organic matter degradation during early diagenesis. The calculated temperatures of the studied phosphorites exceed 150°C , which cannot be suitable conditions for the formation of phosphate minerals. This implies that the low $\delta^{18}\text{O}$ values can be attributed to the formation of phosphorites associated with organic matter degradation during early diagenesis rather than with high temperature conditions.

The most common CO_2 end-members, which contribute to the SCO_2 in the water system on the surface of the earth, are inorganic carbon and organic carbon. The inorganic carbon in the CO_2 derived from the dissolution of marine carbonate and/or dissolved CO_2 in seawater in equilibrium with atmospheric CO_2 . The organic carbon is the CO_2 derived from oxidation of the biogenic materials. The $\delta^{13}\text{C}$ values of the inorganic carbon are relatively homogeneous and close to zero, whereas the values of organic carbon are more variable and are generally large negative numbers (Deines, 1980; Savin and

Yeh, 1981; Sackett, 1989; Yeh *et al.*, 1995). Therefore, the negative and variable $\delta^{13}\text{C}$ values of phosphorites suggest that much of the phosphorites carbonate ions might be derived from oxidation of isotopically light organic carbon. Lack of covariance between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values argues for ^{12}C from sulfate reduction in marine waters (Budd, 1997).

In agreement with this interpretation and based on mineralogical and geochemical studies on the late Cretaceous phosphorites in Egypt, Baiomy (2001 & 2002) pointed out that the diagenetic alteration is the most important factor that controls chemical composition of the phosphorites in the Duwi Formation and that the phosphatic grains in the Duwi Formation have been francolitized during diagenesis by introducing CO_2 into the structure. The differences in the distribution of structural CO_2 %, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values among the studied localities support this idea, where the CO_2 introduced from different media and consequently showed different isotopic ratios.

CONCLUSION

The structural CO_2 contents in the francolite range from 3.32 to 7.21 % with an average of 5.3 %. The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of the samples studied are highly variable but are, nevertheless, all large negative numbers. The $\delta^{13}\text{C}_{\text{PDB}}$ values range from -4.04 to -8.7 ‰ while the $\delta^{18}\text{O}_{\text{PDB}}$ values range from -4.3 to -10.3 ‰.

Negative $\delta^{13}\text{C}$ values and low $\delta^{18}\text{O}$ values of structural CO_2 suggest that the CO_2 was derived from degradation of organic matter. The linear relationship between $\delta^{13}\text{C}$ and CO_2 % indicates that as the medium became more negative with shallow burial there was a progressive increase in the substitution of CO_3 for PO_4 in the carbonate fluorapatite. These data along with the higher CO_2 contents in the apatite from Duwi Formation in Egypt compared to the recent authigenic phosphorites indicate that the chemical composition of apatite has been changed after the formation and during

diagenesis by taking CO₂ into the structure from the surrounding medium and the studied apatite has been francolitized during diagenesis.

REFERENCES

- BAIOUMY H.M. (2001) — *Origin of late Cretaceous phosphorites in Egypt*. Ph.D. dissertation, the University of Tokyo, Japan, 160 p.
- BAIOUMY H.M. (2002) — *Structural CO₂ in the Apatite of the Late Cretaceous Phosphorite Resources in Egypt: Effect on the Crystal Chemistry and Geologic Implications*. Res. Geol. **52** (3), 231-238.
- BUDD D.A. (1997) — *Cenozoic dolomites of carbonate islands: their attributes and origin*. Earth Sci. Rev. **42**, 1-47.
- CLAYPOOL G.E. and KAPLAN I. R. (1974) — *The origin and distribution of methane in marine sediments*. In «Kaplan, I.R., ed., *Natural Gases in Marine Sediments*» New York, Plenum, 240 p.
- CRAIG H. (1965) — *The measurement of oxygen isotope palaeotemperatures*. In: «Tongiorgi, E. (ed.). *Stable isotope in oceanographic studies and palaeotemperatures*». CNR, Pisa, 3-24.
- CRAIG H. and GORDON L. (1965) — *Deuterium and oxygen-18 variations in the ocean and the marine atmosphere*: In: «*Symposium on marine geochemistry, Graduate School of Oceanography, University of Road Island, Providence*» Occ. Publ., **3**, 122 p.
- DANSGAARD W. (1964) — *Stable isotopes in precipitation*. Tellus., **16**, 436-468.
- DEINES P. (1980) — *The isotopic composition of reduced organic carbon*. In: «*Handbook of environmental isotope geochemistry ed. Fritz and Fontes, The terrestrial environment A*» Elsevier, New York, Chapter **9**, 329-406.
- DIX G.R. and MULLINS H.T. (1987) — *Shallow, subsurface ground and burial alteration of Middle Devonian calcite concretions*. J. Sed. Petrol. **57**, 140-152.
- GLENN C.R. (1990) — *Depositional sequence of the Duwi, Sibaiya and Phosphate Formations, Egypt: phosphogenesis and glauconitization in a late Cretaceous epeiric sea*. In: «*Phosphorite Research and Development (ed. By Notholt A.J.G and Jarvis, I.)*». Geol. Soc. Spec. Publ. **52**, 205-222.
- GLENN C.R., ARTHUR M.A., YEH H.W. and BURNETT W.C. (1988) — *Carbon and oxygen isotopic composition and lattice-bound carbonate of Peru-Chile margin phosphorites*. In: «*Phosphorite Research and Development (ed. By Notholt A.J.G and Jarvis, I.)*». Geol. Soc. Spec. Publ. **52**, 270-286.
- GULBRANDSEN R.A. (1970) — *Relation of carbon dioxide content of apatite of the Phosphoria Formation to regional facies*. US Geol. Survey Prof. Paper **700-B**, 9-13.
- HUDSON D.J. (1977) — *Stable isotope and limestone lithification*. J. Geol. Soc. London. **133**, 637-660.
- IRWIN H. (1980) — *Early diagenetic carbonate precipitation and pore fluid migration in the Kimmeridge Clay of Dorset, England*. Sed. **269**, 209-213.
- IRWIN H., CURTIS C.D. and COLEMAN M. (1977) — *Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments*. Nature **269**, 209-213.
- JARVIS I., BURENTT W.C., NATHAN Y., ALMBAYDIN S.M.F., ATTIA A.K.M., CASTRO L.N., FLICOTEAUX R., HILMY M.E., HUSAIN V., QUTAWAH A.A., SERJANI A. and ZANIN Y.N. (1994) — *Phosphorite geochemistry: State-of-the-art and environmental concern. In concepts and controversies in phosphogenesis. «Proceeding of the Symposium and Workshop held on 6-10 September, 1993» Switzerland, 643-700.*
- LEGEROS R.Z., TRAUTZ O.R., LEGEROS J.P. and EDWARD K. (1967) — *Apatite crystallites-Effects of carbonate on morphology*: Sc. **155**, 1409-1411.
- LEHR J.R., MCCLELLAN G.H., SMITH J.P. and FRAZIER A.W. (1967) — *Characterization of apatite in commercial phosphorite rocks. «Internat. Colloquium Solid Inorganic Phosphates»*. Toulouse, France, 29-44.
- MCCARTHER J.M. (1978) — *Systematic variations in the contents of Na, Sr, CO₃ and SO₄ in marine carbonate-fluorapatite and their relation to weathering*. Chem. Geol., **21**, 89-112.
- SACKETT W.M. (1989) — *Stable carbon isotope studies on organic matter in the marine environment*. In: «*Handbook of environmental isotope geochemistry ed. FRITZ and FONTES, The terrestrial environment A*». Elsevier, New York, Chapter **4**, **3**, 139-169.
- SAVIN S.M. and YEH H.W. (1981) — *Stable isotopes in ocean sediments*. In: «*The Sea, ed. C. Emiliani, Wiley Interscience*» New York **7**, 1521-1554.
- SCUFFERT J.D., KASTNER M., EMANUELE G. and JANHNKE R.A. (1990) — *Carbonate-ion substitution in francolite: A new equation*. Geochim. Cosmochim. Acta, **54**, 2323-2328.
- SHACKLETON N.J. and KENNETT J.P. (1975) — *Palaeotemperature history of the Cenozoic and the initiation of Antarctic glaciation oxygen and carbon isotope analyses in DSDP Sites, 277, 279, and 281*. In: «*Kennett, J. P., HOUTZ, R. E. et al. (eds.). Initial Report Deep Sea Drilling Project, U.S. Government Printing Office Washington*». **27**, 743-756.

- SPANDERASHVILLI G.I. and MANSOUR M. (1970) — *The Egyptian phosphorites*. In: «MOHARRAM *et al.* (eds.), *studies on some mineral deposits of Egypt*», 89-106.
- UREY H.C., LOWENSTAM H.A., EPSTEIN S. and MCKINNEY M.H. (1951) — *Measurements of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark and the south-eastern U.S.* Geol. Soc. Amer. Bull. **62**, 399-416.
- THYNE G.D. and BOLES J.R. (1989) — *Isotopic evidence of the Moeraki septarian concretions, New Zeland*. J. Sed. Petrol. **59**, 272-279.
- YEH H.W., CHEN S.H., CHANG W.C. and KAO W.Y. (1995) — *Paleolimnology of Yuen-Yang Lake based on the isotopic composition of organic carbon*. J. Geol. Soc. China. **38**, 125-139.
- YEH H.W. (1997) — *Stable isotope study of insular phosphate deposits: Preliminary C- and O-isotope results on the deposit of the Lau Group, Fiji*. J. Geol. Soc. China. **40**, 401-414.