ISOTOPE SIGNATURES IN PHOSPHATE DEPOSITS: FORMATION AND DIAGENETIC HISTORY

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Most sedimentary rocks contain less than 1% of P. The formation of rocks that are highly enriched in P_2O_5, and in which apatite is the main mineralogical constituent, requires special conditions, during both deposition and diagenesis. Our interest in phosphate rocks is not only academic. Phosphorus is an essential nutrient of both plants and animals; hence, repeated growth of crops on limited land, demands the artificial addition of P to the soil. Application of phosphate fertilizers became an essential part of modern agricultural techniques. The combined scientific and economic importance of phosphate rocks made them an object of extensive geological, mineralogical and geochemical research for over a century. Research has intensified after World War II, and peaked in the seventies and eighties. The results of these studies are summarized in several thorough reviews and books (Cook, 1976; Cook and McElhinny, 1979; Bentor, 1980; Kolodny, 1981; Sheldon, 1981; Baturin, 1982). The present chapter is a summary of the contribution which has been made by the application of isotopic methods to the study of phosphate rich

rocks, as well as an attempt to outline those isotopic methods that may be applied in the future to that purpose. The central theme of this chapter will be phosphorites, but at several points attention will be drawn to the study of phosphatic biogenic components of non-phosphatic sedimentary rocks: biogenic apatite of fish (ichthyoliths), bones and teeth of other vertebrates, conodonts, brachiopods.

The main mineral in phosphate rich rocks is apatite, more specifically *francolite* - the carbonate-fluoride variety (CFA) of apatite. Both, the structure and the chemical composition of francolite have been the subject of extensive research and dispute. The extremely small size of francolite crystallites combines with a very extensive range of substitutions in the lattice. The key substitution seems to be that of a distorted $(CO_3 \cdot F)^{-3}$ tetrahedron replacing a tetrahedral PO_4^{-3} ion (Altschuler et al., 1952; Borneman-Starynkevitch and Belov, 1940; Bacquet et al., 1980). To resolve both structural and charge imbalance, additional substitutions, such as F^-, OH^- for PO_4^{-3}, and Ca^{2+} for Na^+, have been proposed. The general formula that has been suggested for francolite is

$$Ca_{10-a-b}\ Na_a\ Mg_b\ (PO_4)_{6-x}\ (CO_3)_{x-y-z}\ (CO_3 \cdot F)_y\ (SO_4)_x\ F_2$$

where $x=y+a+2c$, and x varies from near zero to 1.5, $y=0.4x$ on the average and $b=0.4a$. (McClellan and Lehr ,1969; Nathan, 1984).

Marine rocks in which apatite is the main mineralogical constituent are referred to as *phosphorites*. Phosphorites are found in sediments of practically all geological ages from the Proterozoic (2,200 m. y. B.P.) to the present. The distribution of phosphorites in space and time does not seem to be random, however. Cook and McElhinny (1979) have shown that phosphorites are confined to specific, phosphogenic epochs, and form phosphogenic provinces, the most prominent of which are the Cambrian deposits of the Karatau (Kazakhstan) and the Georgina Basin (Australia), the Permian Phosphoria Formation and associated formations in the Western U.S., the Upper Cretaceous to Eocene Tethyan province of the Mediterranean, and the Plio-

Miocene deposits of the southeastern U.S. On the other hand, it has been noticed (Strakhov, 1970; Kolodny, 1980) that phosphorites occur in a characteristic lithologic association - most frequently accompanied by cherts and organic rich deposits. It is quite likely that the latter association, can be explained by the biolimiting nature of P and Si (Broecker, 1974, p.21), and by the connection between these elements and areas of high biological productivity in the ocean. Most recent theories, which aim at explaining the genesis of phosphorites, have made use of the strong relationship between organic productivity and P. The problem of explaining phosphorite formation may be reduced to the location of a break in the oceanic cycle of upwelling - high productivity - raining out of organic matter to the sediment - organic matter rich sediment - decomposition of the organic matter into interstitial water. Kazakov (1937) was the first to stress the importance of the marine cycle of P for understanding phosphorite formation. Practically all phosphate is extracted from sea-water by organisms in the photic zone. The P-containing, organism-produced particles are then oxidized while falling to the sea-floor. A sharp concentration gradient in dissolved phosphate is thus formed between surface water and the deep water masses. It was Kazakov's suggestion that phosphorites may form when "phosphate rich", cold, deep water rises to the surface in areas of upwelling; upon reaching the surface, such water warms up, loses CO_2, and therefore precipitates apatite.

Ever since Kazakov, theories of phosphorite genesis have been intimately tied with studies and speculations on marine upwelling. The main advocate of Kazakov's theory in its "chemical " form has been the phosphate group of the U.S. Geological Survey (McKelvey et al., 1953, 1967; Sheldon, 1964). The correlation between occurrences of phosphorite nodules on present day marine shelves and areas of upwelling, has been extended to equating upwelling and phosphorite formation. In the sixties and seventies, it became obvious that whereas upwelling is very likely a necessary requirement for many phosphorite deposits, it is certainly neither a sufficient nor a sole condition for their formation. The reasons for this realization were several: (a) most phosphorites occur among sedimentary sequences with clear

imprints of rather shallow water deposition, not leaving much room for upwelling from great depth; (b) when Recent phosphorite formation was identified off the coasts of Namibia and Peru (Baturin, 1969, Veeh et al., 1973; Burnett and Veeh, 1977; see below), there were many indications that the apatite of these nodules is forming interstitially within the uppermost few centimeters of sediment, rather than by precipitation from the bottom water (Froelich et al., 1988); and (c) in laboratory studies, Mg has been shown to inhibit crystallization of apatite from sea-water. Thus Kazakov's "classical" theory of phosphorite precipitation from sea-water has been gradually replaced by a strongly altered version of it - his compatriot's G.N. Baturin's theory of phosphorite formation by ocean dynamics (Baturin, 1971a, b, 1982).

Baturin's theory envisages the formation of a phosphorite rock in two principal stages:

(1) *the formation of apatite pellets*, which form within the sediment, by growth from interstitial water, during a relatively high sea stand, by remobilization of organic matter phosphorus. The apatite pellets are at this stage sparsely distributed within the sediment;

(2) *the formation of a phosphorite rock*, which is principally a mechanical concentration stage. It is tied to a lower sea level stand, and is a stage of winnowing in which apatite is enriched to a major rock component. Compton et al. (1990) suggested that as long as 10 Ma could have separated the two stages which finally resulted in the enormous phosphorite deposits of the southeastern U.S.

Even in Baturin's version of phosphogenesis the connection between phosphorites and upwelling remains strong. Once such a relationship has been established, it may be used both as a means for explaining the origin of phosphorites, or in its inverse form - the distribution of phosphorites may be used for the tracing of past areas of upwelling. The latter approach has been applied by J. Parrish and her co-workers in recent years (Parrish, 1982; Parrish et al., 1982) for the reconstruction of upwelling zones in Paleozoic oceans. The relationship between phosphatic sediments and upwelling also encompasses the other bioproductive

constituents of sedimentary sequences - chert and organic rich rocks. It is hence not surprising that phosphorites have been related to petroleum-producing source rocks as well (Waples, 1982). The occurrence of phosphorite deposits in areas where no evidence for simple, west-coast-type upwelling can be found is problematic in this context. Such are the young phosphorites of the southeast United States. In most proposed models, these "east-coast" type phosphorites are explained by invoking paleo-ocean dynamics that could result in large scale upwelling (Riggs, 1984; Compton et al., 1990).

Current ideas of phosphogenesis are based upon petrological observations. The two-stage model of Baturin is supported by the occurrence of two essentially different types of phosphatic rocks.

1. Phosphatic micronodules, nodules, pellets and lenses are common in brown or black shales or carbonates (Garrison et al., 1987; 1990). These rocks are laminated, organic rich, and usually contain large amounts of biogenic carbonate and/or silica. They bear distinct evidence of having been diagenetically formed in a reducing environment. The P_2O_5 content of such rocks does usually not exceed a few percent.

2. In contrast to these rocks, economic phosphorites are usually rocks which bear clear evidence of clastic reworking, winnowing and enrichment. Phosphorites were most probably formed in oxidizing conditions. They show mechanical sorting and traces of boring.

Most apatite in sedimentary rocks occurs as grains. Fine grained phosphorites, sometimes termed phospholutities were also described, but are by far less common. The majority of phosphatic grains are francolitic pellets. Those which are ovular, with no discernable internal structure, are usually referred to as "ovules", "ovulites", or just "pellets". When an internal concentric structure is observed in the pellet, the term oolite or "ooid" is usually applied. Another common type of apatitic grains are fossil fragments. These are common in practically all phosphorites, but sometimes they reach such predominance in the rock that it is referred to as a "bone bed " or "bone phosphorite". The cement or matrix in such rocks is usually

calcitic, sometimes siliceous, and in the high grade phosphorites - francolitic. The association between phosphorites and apatitic skeletal fragments has been interpreted, by some investigators (e.g. Penrose, 1888; Gulbrandsen, 1969) as reflecting cause and effect. In the extreme case phosphorite formation was related to mass mortalities of fish (Brongersma-Sanders, 1957). Later studies influenced by Kazakov stressed the chemical aspects of phosphorite formation and viewed the apatitic pellets in phosphate rocks as principally inorganic formations. In recent years this tide has turned again: more and more cases of apatitic pellets and cements have been identified as biological precipitates. Thus, Williams and Reimers (1983) identified sulfur-oxidizing bacteria of the genus *Beggiatoa* in sediments off California, and from the Gulf of California. They suspect similar structures in phosphate rich sediments of the Miocene Monterey Formation of California. Bacterial structures were identified both in Cretaceous phosphorites of the Negev, (Israel) and in East Australian continental margin phosphorites (Soudry and Champetier, 1983; Soudry, 1987). A sequence of studies by Lucas and Prévôt (e.g. 1985) experimentally demonstrated bacterial mediation in replacement of Ca carbonate by apatite.

STABLE ISOTOPES AS RECORDERS FOR THE ORIGIN OF PHOSPHATES

The understanding of conditions under which phosphatic sediments form is a challenge of dual nature. On one hand, we aim a better understanding of the different stages of phosphogenesis, an apparently difficult and challenging task in itself. On the other hand, phosphorites and apatitic fossils are records of <u>oceanic</u> conditions. In this aspect the chemical (and isotopic) composition of a sedimentary apatite is not a reflection of a repeatedly recurring set of conditions which result in the formation of these rocks, but rather it reflects the ever changing oceanic environment. Table 1 is a preview of such an approach.

Table 1: Isotopes in apatite: what do they tell us?

Element	Measured Parameter	Genesis of phosphorites	About the world
Ca-sites			
Sr	$^{87}Sr/^{86}Sr$	Sr - Stratigraphy	
Nd	ε_{Nd}		Land-sea distribution
U	U(IV)/U(VI) $^{234}U/^{238}U$ $^{230}Th/^{234}U$ $^{231}Pa/^{235}U$	Age, Rate of growth, Redox, Submarine weathering	
PO_4 sites			
O	$\delta^{18}O_p$, $\delta^{18}O_c$	Temp. of formation, T of diagenesis	Paleoclimates
C	$\delta^{13}C$	Diagenetic mode	
S	$\delta^{34}S$	Diagenetic mode	

All stable and radioactive isotopes that are used as tracers or time measuring devices in the study of phosphatic deposits occur as trace constituents in the apatitic rocks. However, whereas the isotopic composition of O, C and S refer to constituents of CFA itself, being a part of its major structural components, several other isotopic tracers such as U, Sr and Nd are constituents that replace some major elements in the lattice. These latter elements are captured by or admitted to the lattice. The unique feature of sedimentary apatite is the ability to accommodate a large number of different trace elements in its lattice by coupled substitutions. Thus, as explained above, divalent carbonate may replace phosphate, the charge difference being balanced by a fluoride ion. Similarly, trivalent rare earths or tetravalent U may substitute for Ca^{2+} accompanied by a charge balancing substitution such as Na^{+} for Ca^{2+} or CO_3^{2+} for F^{-}. Below, we shall treat the different tracers, element by element, and then we shall attempt to summarize our conclusions into an integrated

picture of what isotopes can tell us about phosphorite formation and about the world in which they formed.

Oxygen Isotopes

Oxygen occurs in apatite as four oxyanions. The major site is in the phosphate ion, the other ones are in carbonate, sulfate and hydroxyl. Fortunately it is rather simple to isolate the O from the major two of these sites: carbonate in apatite can be separated by reaction of the mineral with phosphoric acid, and evolution of CO_2 (McCrea, 1950; Kolodny and Kaplan, 1970b). Oxygen in the phosphate can be analyzed by dissolving the mineral, precipitating the phosphate as ammonium phosphomolybdate and Mg-phosphate to ensure purity, and finally precipitating Bi-phosphate (Tudge, 1960; Longinelli, 1965; Kolodny et al., 1983; Karhu and Epstein, 1986). Throughout this procedure, O in the phosphate does not exchange isotopically with O in the aqueous solutions. Hence, the final $BiPO_4$ precipitate can be fluorinated and the resultant O analyzed, assuming that it adequately represents the isotopic composition of the original apatite. The recently developed procedure by Crowson et al. (1991) in which Ag_3PO_4 is used, is less time consuming, and yields identical, yet more precise results. The idea of using the isotopic composition of phosphate O as a geochemical indicator is almost as old as stable isotope geochemistry. When Urey and his co-workers (1951) presented the first paleotemperature estimates of the Upper Cretaceous, they noted its dependence on the knowledge of the isotopic composition of ancient sea water. Their suggestion for the elimination of this problem was the analysis of coexisting phosphate and carbonate in sediments. The fractionation of O between the two solid phases would then be independent of water composition. The first measurements were made by Longinelli (1965) using the procedure of Tudge (1960). Longinelli analyzed trace amounts of phosphate in carbonate shells, measured $\delta^{18}O$ of the environmental water in which they deposited their shells, and determined the growth temperature from $\delta^{18}O$ of the carbonate. The initial efforts of this pioneering research were marred by experimental difficulties, and it was not until eight years later

(Longinelli and Nuti, 1973), that the following phosphate - water temperature equation was proposed:(1)

$$t^{o}C = 111.4 - 4.3\ (\delta_p - \delta_w) \qquad (1)$$

where δ_p refers to the $\delta^{18}O$ of O in the phosphate and δ_w to that of the water, both on the SMOW scale (Fig. 1a). Kolodny et al. (1983) confirmed Eq.1 by analyzing bones and teeth of living fish. (Fig 1b).

A major advantage of the phosphate O paleothermometer is that isotope exchange between phosphate O and water is extremely slow in inorganic systems, but is very rapid in biochemical enzyme-catalyzed reactions (Kolodny et al., 1983). The sluggishness of inorganic exchange is best demonstrated by the validity of the laboratory method for apatite isotopic analysis: it involves several steps of dissolution and precipitation, some of them at elevated temperatures.

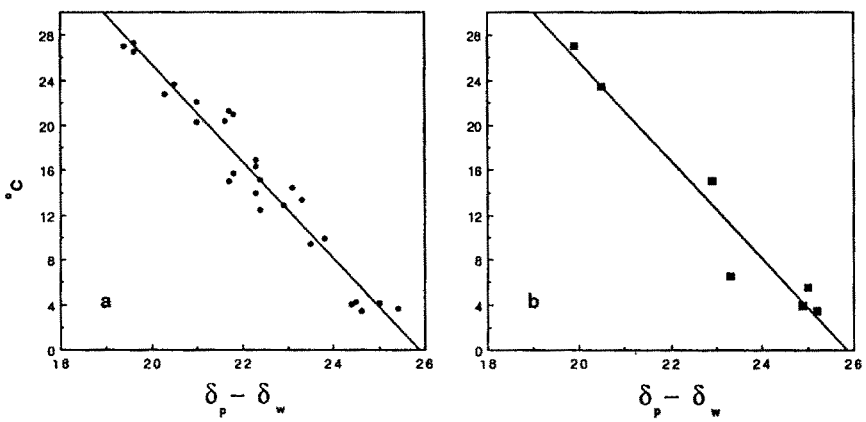


Figure 1: Temperature vs. $(\delta_p-\delta_w)$ of mollusc shells. After Longinelli (1965) and Longinelli and Nuti (1973a). (b) Average temperature vs. $(\delta_p-\delta_w)$ of fish bones and teeth. Data from Longinelli and Nuti (1973a) and Kolodny et al. (1983). Data points in which the temperature range is larger than 5°C, were rejected. After Luz and Kolodny (1989)

Throughout those steps the isotopic composition of the phosphate in apatite is preserved and remains unchanged in the laboratory precipitated $BiPO_4$, which is the precipitate one fluorinates in the procedure given by Tudge (1960). This

sluggishness suggests that isotopic exchange between solid apatite and water at low temperatures should be extremely slow even on a geologic time scale. On the other hand, researchers of biochemical mechanisms have shown (e.g. Boyer at al., 1977) that isotopic exchange between water and dissolved phosphate is rapid when enzymatically catalyzed. Although the exact mechanism of phosphate biomineralization is not clear, similar reactions catalyzed by such enzymes as alkali-phosphatase, probably affect exchange of O between water and phosphate in bones, teeth, and apatitic shells. Kolodny et al. (1983) demonstrated the high rate of this exchange in an experiment with trout growing in a pond with constant temperature and δ_w. The trout were fed marine fish meal with much heavier O. Still, the isotopic composition of the trout bones is determined only by the temperature-dependent fractionation between bone-phosphate and water. Thus, biogenic apatites have the properties required for an ideal geochemical recorder: they respond sensitively during their formation to the aqueous environment, and they preserve very well their record after death of the organism.

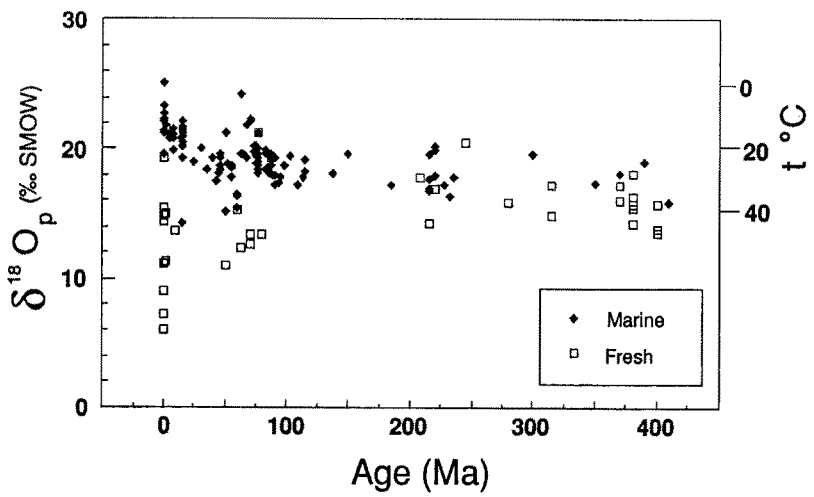


Figure 2: The secular change of $\delta^{18}O$ in phosphate of marine and fresh-water fish; Devonian to Recent. After Kolodny and Luz (1992)

The calibration of the phosphate thermometer enabled the application of this method to the fossil record. This application included the analysis of δ_p in conodonts of the North American

Paleozoic (Luz et al., 1984), of fossil fishes from the Cretaceous and Tertiary of Israel and from other Mediterranean countries (Kolodny and Raab, 1988). The latter analysis yields information about temperatures that prevailed during the Late Mesozoic-Early Cenozoic in the tropical parts of the Tethys. The thermal record is well correlated with the record obtained by carbonate O isotope thermometry of foraminifers from the deep Pacific (Douglas and Woodruf, 1981) and with the contemporaneous record for Northern Europe (Loewenstam, 1964). The deduced temperatures for the Cretaceous range between 20°C and 34°C, some 10° higher than Cretaceous surface water temperatures in Northern Europe. A survey of the isotopic record of phosphate in fish from their earliest appearance in the geological record to the Recent has recently been completed (Kolodny and Luz, 1992). Figure 2 is a plot of δ_p in fresh water and marine fishes in the last 400 million years. Throughout this time fresh water fishes had δ_p values which are lower than δ_p of contemporaneous marine fish. This is not only a demonstration of the very long term persistence of the hydrological cycle as we know it but also a reconfirmation of the essential lack of post depositional exchange in apatite O. No clear time trend in δ_p, and hence in temperature, is evident from figure 2.

Much effort has also been directed towards isotopic analysis of phosphate of non-skeletal origin. Shemesh et al. (1983) showed that ichthyoliths in phosphorites of the Campanian Mishash Formation have the same $\delta^{18}O$ as apatitic pellets from the same rocks. In a study of phosphorites from the Tethyan-Mediterranean Mesozoic province, Shemesh and Kolodny (1988) showed that δ_p of phosphorites were close to those of fish (Kolodny and Raab, 1988). Furthermore, a stratigraphic analysis of δ_p in the Mishash Formation of Israel shows that the major phosphorite-forming event is correlated with an increase in δ_p, which can be interpreted as an onset of an upwelling regime in the area. A similar conclusion, i.e. the onset of upwelling in the Tethys phosphogenic province, has been proposed by Grandjean et al. (1987, 1988) on the basis of REE pattern analysis.

Longinelli and Nuti (1968) noted a trend of decreasing δ_p in phosphorite whole rocks with increasing geological age. Similarly, Shemesh et al. (1983) have shown that whereas $\delta^{18}O$ in Recent phosphorites varies between 20 and 25 per mil, it decreases to 15-20 per mil in Mesozoic rocks, and drops further

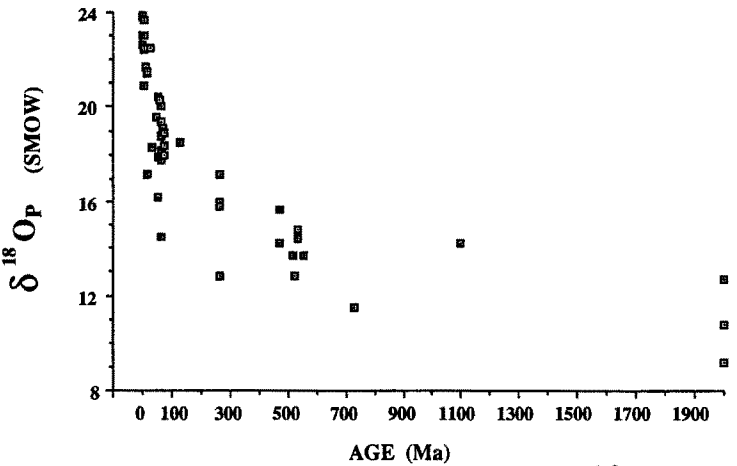


Figure 3: The secular change of $\delta^{18}O$ in phosphate of phosphorites. After Shemesh et al. (1988)

to about 10 per mil in the Archean (Fig. 3). A similar trend has been observed for $\delta^{18}O$ of carbonates, cherts and glauconites (Degens and Epstein, 1962; Knauth and Epstein, 1976; Keppens and O'Neil, 1984). Four alternative explanations have been offered for the isotopic time trends: (1) post-depositional isotopic exchange with fresh water, (2) changing $\delta^{18}O$ of sea-water with time, (3) changing temperature of deposition of phosphorite with time, and (4) high temperature alteration. Whereas the first explanation was favored for carbonates by Degens and Epstein (1962) and for phosphorites by Longinelli and Nuti (1968), the main proponent of an ocean with changing isotopic composition has been E.C. Perry and his co-workers (e.g. Chase and Perry, 1972). Shemesh et al. (1983) rejected the first hypothesis; they were strengthened in their belief in the resistance of phosphate to late isotopic exchange by evidence such as the narrow range of δ_p in the Mishash apatites compared to the broad range of $\delta^{18}O$ in coexisting carbonates and cherts (see also Vengosh et al., 1987). Hence they favored higher temperatures of deposition for ancient phosphorites. Such higher temperatures could be either a reflection of a global phenomenon, i.e. of warmer oceans in the

geological past, or of a shift in the site of phosphorite formation in the ocean. A warmer ocean in the past 100 Ma has been suggested on the basis of $\delta^{18}O$ in carbonates (Savin, 1977); much debate has however been caused by the proposition of Knauth and Epstein (1976) that Precambrian oceans might have been as warm as 60-70°C (Veizer et al., 1986). The resolution of the dilemma of whether it was temperature or $\delta^{18}O$ of ocean water that caused the low δ_p in ancient rocks could be achieved by analyzing O in cogenetic phases. This is the approach taken by Karhu and Epstein (1986) who analyzed Precambrian and Phanerozoic cherts for both $\delta^{18}O$ of the silica in the chert and that of the very small amounts of phosphate in them. They concluded that: " The early Precambrian temperatures were as high as 80°C and decrease with time". A corollary of that conclusion was that: "The $\delta^{18}O$ value of the ocean has not varied more than a few per mil over the past $3x10^9$ years" (see also Perry, 1990, and Epstein and Karhu, 1990).

If chert and phosphate can be treated as two coexisting phases, then the two types of O in apatite (δ_p the $\delta^{18}O$ of PO_4^{3-}, and δ_c the $\delta^{18}O$ of CO_3^{2-}) may be even better candidates for such a pair. In such a treatment, δ_c of CFA-CO_2 is assumed to behave as in $CaCO_3$. Compare the phosphate paleothermometer (Eq. 1) to the carbonate paleothermometer (Eq. 2, after Epstein et al., 1953)

$$t = 16.5 - 4.3\ (\delta_c - \delta_w) + 0.14\ (\delta_c - \delta_w)^2 \qquad (2)$$

The striking similarity of the slope coefficient in the carbonate and phosphate paleothermometers was a disappointing observation for any attempt to estimate marine paleotemperatures independently of water isotopic composition. Karhu and Epstein (1986) pointed out that such parallelism is impossible over the entire temperature range, because at room temperature the $\delta^{18}O$ of marine calcite is about 10 per mil higher than apatite precipitated from the same water, whereas they must achieve zero fractionation at high temperature.

The establishment of a phosphate-water paleothermometer over a broad temperature range requires experimental equilibration of

phosphate water pairs at different temperatures. Preliminary results (Shemesh et al., 1988), yielded the following equation:

$$1000\ln\alpha = 2.12\ (10^6/T^2) - 2.98 \qquad (3)$$

where $1000\ln\alpha \cong (\delta_p - \delta_w)$, and T is the temperature in °K. The slope here of 2.12 should be compared with that of 2.78 from the analogous equation for calcite (O'Neil et al., 1969):

$$1000\ln\alpha_{(c-w)} = 2.78\ (10^6/T^2) - 2.89 \qquad (4)$$

By subtracting (3) from (4), we obtain (5) which is a paleotemperature equation in $\delta^{18}O_p - \delta^{18}O_c$ space, independent of δ_w:

$$1000\ln\alpha_{(c-p)} \approx 0.66\ (10^6/T^2) + 0.09 \qquad (5)$$

where again $1000\ln\alpha_{(x-y)}$ equals about $(\delta_x - \delta_y)$. Initially, Shemesh et al. (1983) were reluctant to use the $\delta_c - \delta_p$ pair, because the carbonate O appeared to be much more exchangeable than the phosphate one. Later however it was shown that δ_c and δ_p are very well linearly correlated (Fig. 4), so that if post depositional exchange is to be assumed, it must occur for both sites in a comparable (though not necessarily equal) degree. If δ_c and δ_p of figure 4 are equilibrium pairs, then both temperature and δ_w can be estimated. In figure 3 isotherms (with unity slope) and lines of constant $\delta^{18}O_w$ (with a slope of 0.76 = 2.12/2.78) are plotted as an overlay on the data points. Assuming isotopic equilibrium, temperature of formation and $\delta^{18}O$ can be estimated from each $\delta^{18}O_c - \delta^{18}O_p$ pair. Most points in the upper part of figure 4 yield temperatures and $\delta^{18}O_w$ well within the range of recorded earth surface values. However, most data points in the lower left part of the diagram indicate temperatures well above 100°C. The δ_w of water in equilibrium with these samples, had to be well above zero. Shemesh et al. (1988) concluded therefore that the isotopic composition of O in both apatite sites is a reflection of late diagenetic (to early metamorphic?) interactions between the apatite and fluids. It is also suggested that such interaction took place at a relatively low water/solid

ratio in a semi closed system of pore waters. We can conclude by stating that although temperature may be recorded by phosphorites, it is not always the depositional temperature. Most phosphorites as well as phosphate bearing rocks may thus not tell us much about temperatures of ancient seas (Karhu and Epstein, 1986). Rather they tell us about conditions of burial. The latter conclusion is supported by the location of phosphorites from the Miocene Monterey Formation on figure 4 (Kastner et al., 1990).

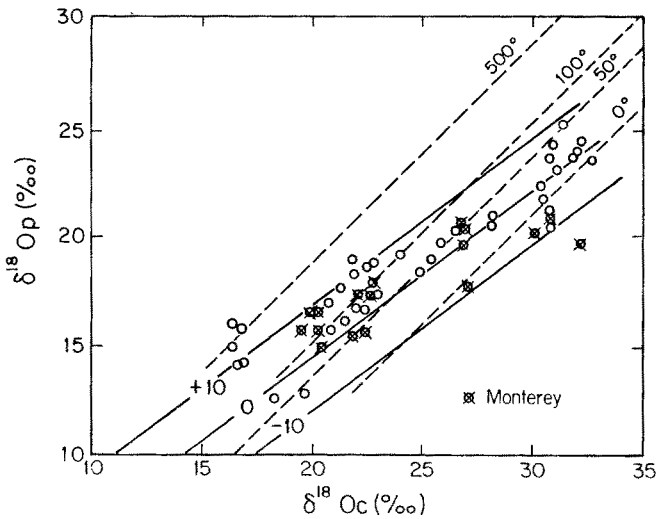


Figure 4: Relationship between $\delta^{18}O_p$ and $\delta^{18}O_c$ in Phanerozoic phosphorites. Iso-$\delta^{18}O_w$ lines and isotherms (=isoΔ_{c-p}) are overlaid upon the data points. Note the spread of Monterey data which cover the entire sample range. The high temperature data are all in the field of positive $\delta^{18}O_w$ values. After Shemesh et al. (1988)

The Monterey phosphorites were certainly **not** deposited in a very warm ocean, as there is good evidence that they were deposited from rather cold, upwelling water: δ_p of fishes from the Monterey yield temperatures of 16-21°C. Yet, the δ_p (and δ_c) values of the Monterey samples spread almost over the entire range of figure 4. Curiously the temperatures indicated by the O in the phosphate of Monterey phosphorites are very close to temperatures indicated by the isotopic analysis of dolomite concretions in the same beds. The concretions are clearly diagenetic, and the isotopic composition of their C bears indications of equilibration with

methane (high $\delta^{13}C$ in carbonates). It is thus possible that the post-depositional interaction between phosphate and fluids was bacterially mediated, by the methanogenic bacteria.

The isotopic study of phosphatic sedimentary rocks should by no means include only the phosphatic phases. The availability of δ_p isotopic data opens the possibility of multi-phase isotopic analysis (Vengosh et al., 1987). Such studies should be especially useful as tracers of diagenesis. The Mishash Formation of Israel is a sequence of alternating cherts, porcellanites, chalks, limestones and phosphorites. A combination of chemically selective analytical methods with handpicking of textural components enables one to reconstruct a diagenetic sequence of events. Three isotopically concordant assemblages were identified: (a) a depositional assemblage formed in normal seawater at temperatures between 23°C and 30°C is reflected by benthic foraminifera (*Nodosaria*) skeletons ($\delta^{18}O_{SMOW}$ = +27.5 to 29.5 per mil) and apatitic bio-detritus (δ_p= +18 to +19.5 per mil), (b) an early diagenetic assemblage formed in equilibrium with a marine solution is recorded by calcite of micritic cement (+26 to +27.5 per mil), silica in opal-CT (porcellanite) (+31.5 to +33.3 per mil), silica as quartz in homogeneous cherts (+29 to +32 per mil), silica as quartz in "fragments" of chert breccias (+31 to +33 per mil), and some quartzose matrix in silicified phosphorites, and (c) a later diagenetic assemblage contains calcitic spar infilling of fossils (+20 to +26.6 per mil), silica in "matrix" of chert breccias (+21 to +33 per mil) and coarse quartz matrix in silicified phosphorites (+20 to +30 per mil). This last assemblage has been interpreted by Vengosh et al. (1987) as representing a late fresh water fluid.

One of the most striking constraints of isotopic paleothermometry is its limitation to reconstructing marine conditions. A necessary assumption of paleothermometry is the knowledge of the isotopic composition of paleo-seawater. In paleothermometry of non-Glacial periods, δ_w is assumed constant and equal to about -1 per mil. Such assumption can be justified by several approaches (Savin, 1977; see Holland, 1984, p. 241-251). In contrast, the isotopic composition of water in lakes,

rivers, and groundwaters, all of which originate from meteoric water, is highly variable both in space and in time even in the present world (Dansgaard, 1964; Yurtsever and Gat, 1981). Thus, if continental, aquatic paleothermometry is to become operative, means for estimating δ_w of paleo-meteoric waters must be found. A possible way of solving the problem of the dependence of δ_p on two variables, temperature and δ_w, is fixing one of the two. In warm blooded animals the isotopic composition of O in bone phosphate should depend only on the isotopic composition of the body fluid, since the temperature of deposition is fixed (Longinelli 1984). Unlike in aquatic organisms (e.g. foraminifera, molluscs, fish), the isotopic composition of body fluids of mammals is not equal to δ_w of the drinking water. $\delta^{18}O$ of the body fluids (δ_{BW}) depends on the total flux of O through the body water reservoir (Lifson and McClintock, 1966; Luz et al., 1984). The major inputs are: drinking water, air O, metabolically produced O, and water in foods. Oxygen leaves the body by the following routes: as liquid water (urine, sweat), as water vapor, and as exhaled CO_2. When such a balance is performed the interesting result is that to a first (and good) approximation the slope of δ_{BW} versus δ_w does not depend on the isotopic composition of the different reservoirs (Eq. 6):

$$\delta_{BW} = \frac{F_1}{F_1+F_4+F_5}\,\delta_W + \frac{8(1-x)(F_1+F_4) - F_2\delta_{Ox} + F_3\delta_F + 38F_5}{F_1+F_4+F_5} \qquad (6)$$

where F_1 is the flux of O in drinking water (and water in food) with an isotopic composition δ_w, F_2, with an isotopic composition δ_{Ox}, is the influx of atmospheric O and F_3, with δ_F, is the input of O from organic food compounds. Similarly, F_4 is the metabolic water formed within the body (hence possessing δ_{BW}); a fraction x of the water leaving the body is in liquid form and has a composition similar to body water, whereas a fraction (1-x) is in the form of water vapor and is hence depleted by 8 per mil with respect to body water. F_5 is the flux of respiratory CO_2 out of the body; its $\delta^{18}O$ being δ_{BW} +38 per mil.

The relationship between a mammal's drinking water and the composition of its body water is thus crudely dependent on the ratio between the amount of "drinking" to "drinking plus metabolism". Luz et al. (1984) verified the above relationship in a controlled experiment using laboratory rats. Only δ_w of the drinking water of the rats was modified, and a good linear fit between drinking water and body water was observed:

$$\delta_{BW} = 0.53\ \delta_w - 0.39 \quad (r = 0.99) \qquad (7)$$

the slope of eq. (7), 0.53, agrees remarkably well with the ratio of "drinking" to "metabolic" fluxes for rats as obtained from physiological literature. Eq. (6) is thus a guide for selecting optimal organisms for paleoenvironmental studies: animals which drink much and have a low metabolism should be the best recorders of environmental δ_w. As stated above, the isotopic composition of a mammal bone should be determined solely by δ_w, since body temperature is fixed. Moreover, according to Eq. (1), $(\delta_p - \delta_{BW})$ should not be far from 17.3 in most mammals, since their body temperatures are around 37°C. Indeed, in a controlled experiment, bones and teeth of rats were on the average 17.9 per mil heavier than their body water (see Fig. 5), close enough to the expected value (Luz and Kolodny, 1985). Although in principle it has been demonstrated that mammals can serve as good monitors of paleo-δ_w, several points remain unexplained and cause difficulties: (1) in some cases, a slope of unity or even larger has been observed for the δ_{BW} vs. δ_w relationship, suggesting that the model of Luz et al. (1984) might be an oversimplification (D'Angela and Longinelli, 1985); (2) Longinelli (1984) observed $(\delta_p - \delta_{BW})$ values quite different from the expected 17.3 per mil; he found 20.9 per mil in man and 21.4 per mil in pigs, and (3) in a study of well documented human teeth from locations over a broad range of latitudes and hence δ_w, Levinson et al. (1987) found a good linear correlation (r = 0.93) between the isotopic composition of local tap water and δ_p of the human teeth. The slope of the regression line was much lower (0.46) than that expected from physiological data (0.7). Mixing of water sources due to dietary habits of modern man has been suggested as an explanation. Luz et al. (1990) showed that when a significant part of intake water in

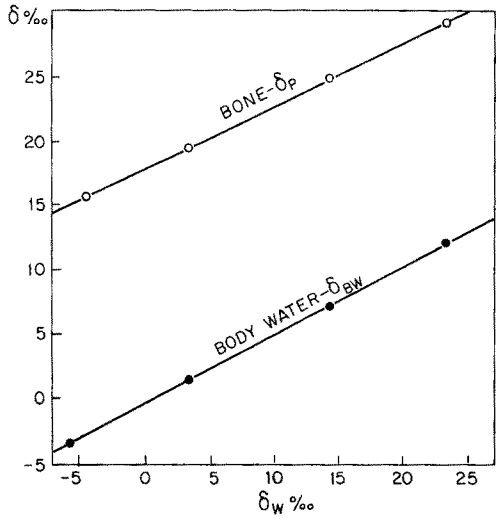


Figure 5: Plots of δ_{BW} ($\delta^{18}O$ of body water) and δ_p ($\delta^{18}O$ of bone phosphate) vs. δ_w ($\delta^{18}O$ of drinking water) of experimental rats. The separation between the two nearly parallel lines indicates equilibrium apatite precipitation at 37°C, and the slope of both lines is less than unity indicating metabolic activity (see text). After Luz and Kolodny (1985)

a mammal is obtained from leaves, relative humidity becomes a significant factor in determining the δ_w of the body fluid and hence of δ_p. Multiple regression of the isotopic composition of phosphate O of white tailed deer from North America yields a high correlation with local relative humidity and precipitation. The relative uniformity of δ_w over Australia, coupled with the variance of climate in this continent allowed L. Ayliffe and her co-workers (Ayliffe and Chivas, 1988, 1990) to isolate humidity as a variable which *via* its influence on leaf water isotopic composition is reflected in δ_p of Australian kangaroos. The isotopic composition of O in the carbonate of mammal bone apatite (δ_c) is probably also determined by the composition of body fluids and should hence also bear climatic information, albeit it is probably more susceptible to alteration. Land et al. (1980) demonstrated that δ_c of deer bone is correlated to local meteoric water δ_w values. More recently, Koch et al. (1989) have interpreted laminae in tusk and molar dentine of late Pleistocene mastodonts and mammoths as annual growth bands. They suggested that the variation in δ_c observed between these bands is a

reflection of seasonality. The low $\delta^{18}O$ values representing winter growth.

Carbon Isotopes in Apatite Carbonate

We have shown above that $\delta^{18}O$ of apatite CO_2 can essentially be treated as representing a separate carbonate phase. Similarly $\delta^{13}C$ of CFA can be treated as a useful tracer of depositional and diagenetic conditions. The three following assumptions are necessary for a genetic interpretation of $\delta^{13}C$ in CFA.

1. There is little or no C isotope fractionation upon incorporation of dissolved CO_2 into the CFA lattice. This would mean that the isotopic composition of the CFA-CO_2 is representative of the bulk total of the CO_2 dissolved in the water from which the apatite formed. Although there are no experimental data for isotopic fractionation factors of carbonate ions between solutions and apatite, one can expect a rather small fractionation by analogy with inorganic Ca-carbonate precipitation.

2. An implicit assumption is that CO_2 enters the CFA lattice at the time of its formation. This is not as obvious as it may seem. Price and Calvert (1978) indicated that CO_2 content in phosphorites increases from 1.4% in poorly consolidated nodules to 4.2% CO_2 in concretionary and pelletal phosphorites, respectively. A similar trend was observed by Romankevich and Baturin (1972). Mineralogical and isotopic analysis of fossil fish bones suggests that not only must CO_2 be introduced *post mortem* into lattices of fish bones, but it is quite likely that the stable CFA phase in fish fossils is a result of a dissolution-reprecipitation process of an original hydroxyapatite phase.

3. If the isotopic analysis of CO_2 is to be used for reconstruction of depositional or diagenetic environments then one must assume that the CO_2 is well preserved in the lattice after its formation.

There are principally two different approaches to the role of CO_2 in the apatite lattice: the CO_2 content decreases with weathering and diagenesis from an initially uniform value of

about 6% (McArthur, 1978; McClellan, 1980; McClellan and Saavedra, 1986; Jahnke, 1984), and the CO_2 content reflects a spectrum of formation conditions. Thus, Gulbrandsen (1970) attributed the variation in CO_2 content in Phosphoria Formation apatites to regional variations in the temperature of the Permian water column. Similarly, McArthur (1985) suggested that "the chemical composition of francolite reflects that of its formational environment". The relative constancy in Na, Sr, Mg, and SO_4 content are then a reflection of the constancy of composition of Phanerozoic seawater, whereas "the variable contents of CO_2 in unaltered francolite are a response to the pH of its formational environment". Romankevich and Baturin (1972), on the other hand, suggested that the carbonate content is controlled by its supply from degradation of organic matter in pore waters during apatite precipitation.

Isotopic analysis of CFA-CO_2 can be used to distinguish the role of these processes, as well as to elucidate several related problems. Benmore et al. (1983), McArthur et al.(1986) and Glenn and Arthur (1990) applied the approach of Goldhaber and Kaplan (1974), Irwin et al. (1977) and Froelich et al. (1979) to estimate the depth of formation of a carbonate beneath the sediment-water interface. The crux of this approach is the tracing of the relative amount of organic-matter-derived C in the C that is dissolved in the pore water. The organic-matter-derived C is labeled by low $\delta^{13}C$ (about -24 per mil) values. With increasing depth in a marine sediment, one observes a transition from the zone of oxidation of organic matter, through a suboxic zone, to an anoxic zone of (bacterial) sulfate reduction. The $\delta^{13}C$ of the total dissolved CO_2 decreases along this depth profile. When sulfate is exhausted at depth, organic matter is decomposed by methanogenic microorganisms, and part of the total dissolved CO_2 is reduced to form methane (which is highly depleted in ^{13}C). The remaining CO_2 is thus enriched in ^{13}C. McArthur et al. (1980) attempted to distinguish between "authigenic" apatites precipitated in anoxic sediments, and "diagenetic" apatite formed by limestone replacement. They proposed using ^{13}C as a discriminating indicator of mode of formation. According to McArthur et al. (1980) a strong depletion in $\delta^{13}C$

indicates void-filling apatite formation in organic rich sediments, whereas phosphatized carbonates retain the $\delta^{13}C$ value of their precursors, which lie around 0 per mil PDB. Such a simple relationship may hold only in rock dominated systems, where the amount of dissolved C species that are derived from oxidation of organic C is negligible. In systems with a high water/rock ratio, and a high organic matter content, such a distinction is no longer possible.

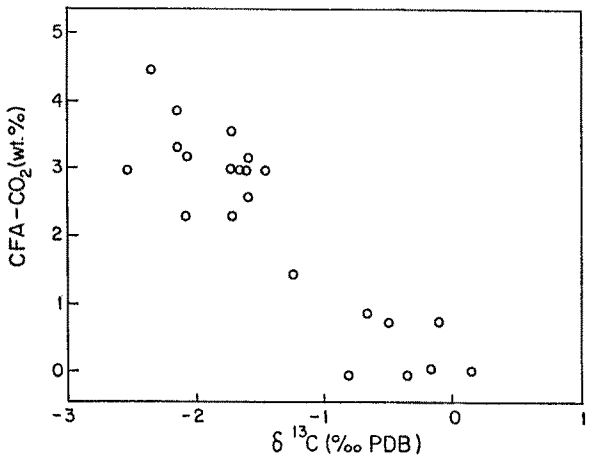


Figure 6: $\delta^{13}C$ vs. wt% CO_2 in CFA, in grains of young phosphorite from off Peru. Note the negative correlation. After Glenn et al. (1988)

Glenn and his co-workers (1988, 1990) compared $\delta^{13}C$ and CO_2 contents of phosphorite grains and crusts with $\delta^{13}C$ and concentration of total dissolved carbon, PO_4^{3-} concentration, and total alkalinity in pore waters of cores from the same area. They concluded that the amount of CO_2 in CFA depends mainly on the carbonate content of the pore water. It thus primarily reflects carbonate concentration (and thus carbonate alkalinity, but not pH), rather than the CO_3^{2-}/PO_4^{3-} ratio. The increased pore-water carbonate alkalinity is the result of microbial oxidation of organic matter. Increased carbonate substitution in CFA increases its solubility and limits the extent of its crystallite growth. Thus CFA with higher than about 6% CO_2 becomes unstable in typical pore waters. The $\delta^{13}C$ values indicate that most of the Peru-Chile phosphorite grains form between 5-10 cm below the sediment-water interface, in suboxic, perhaps anoxic, sediments.

The combination of the above processes results in a general negative correlation between $\delta^{13}C$ and the CO_3^{2-} content of CFA (see Fig. 6).

Since the turn of the century, the insular phosphorite deposits of Nauru, Ocean Island, Ebon Island and Makatea in the Pacific have yielded the main fertilizer demands of Australia and New Zealand. All these phosphorites are guano related. In an attempt to explain their formation, Aharon and Veeh (1984) measured δ_c and Ayliffe et al. (1991) determined δ_p in these apatites. They showed clear geochemical and petrological differences between the young phosphorites of the low islands and the >200 ka old deposits of the elevated, karstic islands. Whereas the former (δ_c = 32.4, δ_p = 21-23) are the result of interaction of seabird guano with slightly evaporated rain water, the latter (δ_c = 24.7, δ_p = 17-19) apparently formed by diagenetic reaction between ^{18}O depleted rain water, guano and karstic limestone.

Sulfate-Sulfur Isotopes

The presence of sulfate, probably substituting for PO_4^{3-} as a structural component within the CFA lattice, is today a well established fact (McConnell, 1973; Nathan, 1984). Similarly to the case of carbonate, the degree of isomorphous replacement of PO_4^{3-} by SO_4^{2-} depends on the sulfate content of the aqueous phase that was in equilibrium with the phosphate precipitate during its formation. (Bliskovskiy et al., 1977; McArthur, 1985). Hence, the S content and especially its isotopic composition ($\delta^{34}S$), become useful indicators of the depositional and diagenetic history of a phosphorite. The key observations here are the reduction of sulfate ions to hydrogen-sulfide by certain anaerobic bacteria which is associated with a strong fractionation (10-60 per mil) of S isotopes; the reduced phase being enriched in ^{32}S, while residual SO_4^{2-} in solution can be highly enriched in ^{34}S, the removal of sulfate into solid apatite which may, by analogy to evaporite sulfate precipitation, be assumed to have a rather small isotopic effect, and the sea-water

sulfate $\delta^{34}S$ which has undergone significant secular variation in the Phanerozoic. The $\delta^{34}S$ of marine evaporites of different ages records these variations (Holser and Kaplan, 1966; Anderson and Arthur, 1983; Holser, this volume). Hence, the concentration and isotopic composition of sulfate sulfur can vary greatly in an organic-rich sediment, as a result of both $\delta^{34}S_{SW}$ and degree of reduction.

CFA-sulfur that formed in contact with seawater in an oxic environment, should thus have $\delta^{34}S$ values close to marine sulfate of contemporaneous seawater. Francolite that formed in the anoxic zone, where sulfate reduction was the controlling reaction, should contain sulfate enriched in ^{34}S. Generally, one should expect an association between negative $\delta^{13}C$ values and positive $\Delta^{34}S$ ($=\delta^{34}S_{CFA}-\delta^{34}S_{SW}$). Figure 7 demonstrates such a relationship. Data points with high $\delta^{13}C$ and $\Delta^{34}S$ near zero form a tight cluster in the oxic zone. The $\delta^{13}C$ is generally low and uniform in the anoxic zone, while (with one exception) $\Delta^{34}S$ varies from high to low positive values. This latter variation is related to the variable extent of reduction of sulfate.

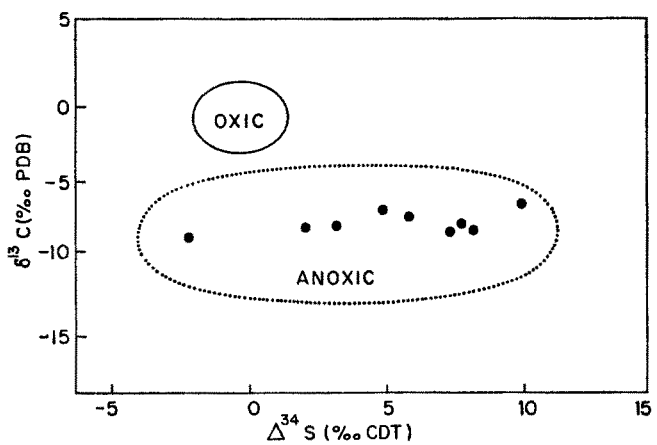


Figure 7: Variation of $\delta^{13}C$ and $\Delta^{34}S$ ($\delta^{34}S_{CFA}$ - $\delta^{34}S_{seawater}$) in oxic vs. anoxic sediments. After McArthur et al. (1986)

The first $\delta^{34}S$ measurements in apatite were performed by Bliskovskiy et al. (1977), followed by studies of Nathan and Nielsen (1980), Benmore et al. (1983), and McArthur et al. (1986). $\delta^{34}S$ of most young apatites (Miocene to Recent from Aghulas Bank, Blake Plateau, the California Borderland) are +20

to +23 per mil, and are indistinguishable from the modern seawater value. Most phosphorites ranging in age from the Precambrian to the Miocene have $\Delta^{34}S \geq 0$. Thus, Nathan and Nielsen (1980) drew the conclusion that whereas the phosphorites with $\Delta^{34}S \cong 0$ were apparently deposited from oxic ocean water, those with $\Delta^{34}S > 0$ formed in reducing environments. They supported the latter conclusion by the observation that gypsum associated with phosphorites is often isotopically very light, suggesting that it might have formed from aqueous sulfate released by the oxidation of biogenic Fe-sulfide. A decrease in sulfate concentration in interstitial water should thus be correlated with an increase in $\Delta^{34}S$. This, indeed, is the case for phosphorites of the Phosphoria Formation (Piper and Kolodny, 1987), where all $\delta^{34}S$ values are heavier than 14 per mil, (the value of Permian seawater), and negatively correlated with $\log(SO_4^{2-}/P_2O_5)$ supporting a "Rayleigh distillation" type reduction of sulfate to sulfide.

The simple relationship outlined above may be complicated at interfaces between reducing and oxidizing zones by the upward diffusion of ^{34}S depleted H_2S. In the absence of reactive Fe, this sulfide is oxidized to sulfate (in the suboxic or oxic zones), thus lowering $\delta^{34}S$ from its ambient value. An alternative explanation for the range of $\Delta^{34}S$ values between +6 and -2 is that these reflect different fractionations due to different rates of sulfate reduction (McArthur et al., 1986; Kaplan, 1983).

RADIOGENIC ISOTOPES AS RECORDERS FOR THE ORIGIN OF PHOSPHATES

Strontium and Neodymium Isotopes

The last decade has seen a sequence of impressive achievements in the application of isotopic ratios of Sr and Nd in sedimentary rocks for the understanding of the geological history of paleo-seas. The variations of both Sr and Nd isotopic

ratios in seawater are the results of a combination of the relative amounts and the isotopic compositions of the sources that contribute these elements to the oceans. In this case, variations in the isotopic composition of the sources are the result of radioactive decay, not of mass-dependent fractionation. The concentrations of Sr and Nd in seawater are very different, reflecting their different balances of input/removal rates. Whereas the residence time of Sr in seawater is about 10^6 years (Turner and Whitfield, 1979), several orders of magnitude longer than oceanic mixing time, the residence time of Nd is only tens to hundreds of years (Piepgras et al., 1979), much shorter than the oceanic turnover time. The oceans are therefore well mixed with respect to Sr, but heterogeneous with respect to Nd. Whereas a single ocean-wide curve has been established for the variation of $^{87}Sr/^{86}Sr$ in seawater with age (Peterman et al., 1970; Burke et al., 1982; Koepnick et al., 1985), no such curve has been proposed, or should be expected for $^{143}Nd/^{144}Nd$ (expressed as εNd).

Apatitic fossils are good indicators of $^{87}Sr/^{86}Sr$ in paleo-oceans, and probably the best available material for obtaining $^{143}Nd/^{144}Nd$ in paleo-seawater. Sr occurs in rather high concentrations (1100-2300 µg/g; Garavelli et al., 1979, Schmitz et al., 1991) in bones of living marine fish, and in comparable concentrations in apatitic fossils. Thus, it is reasonable that $^{87}Sr/^{86}Sr$ ratios in ichthyoliths reflect seawater values. Unlike Sr, Nd is apparently introduced into apatite during early diagenesis. The REE occur in extremely low concentrations in living fish bones, but reach rather high values relatively early after the organism's death (Arrhenius et al., 1957; Bernat, 1975; Shaw and Wasserburg, 1985). The concentration of REE in apatitic fossils is higher than in any other sedimentary mineral; it is 5-6 orders of magnitude higher than in seawater, and 2-5 orders of magnitude higher than in marine carbonates. Based on mass balance considerations, Grandjean et al. (1987) and Grandjean and Albarède (1989) have shown that REE must have been introduced into fish debris during very early diagenesis, via a carrier phase (probably biogenic particulates such as zooplankton fecal

pellets and oxihydroxides) which transported REE into the near-bottom water.

The Sr isotopic composition of apatitic fossils is often in reasonably good agreement with the $^{87}Sr/^{86}Sr$ ratio in contemporaneous seawater. Such agreement has been demonstrated for conodonts, ichthyoliths and inarticulate brachiopods (Kovach, 1980; Shaw and Wasserburg, 1985; Staudigel et al., 1985; Keto and Jacobsen, 1987; Grandjean et al., 1987). Whereas Staudigel et al. (1985) concluded that about 70% of their analyses fall within the range of the seawater curve, the data spread of about half of the fish fragments analyzed by Grandjean et al.(1987, 1988) was larger than that of contemporaneous carbonates. Practically all of these deviations were towards higher than expected $^{87}Sr/^{86}Sr$ ratios. A similar spread has been recently observed by Schmitz and coauthors (1991), who attempted to distinguish between marine and fresh-water fossil fish by means of the Sr isotopic composit-

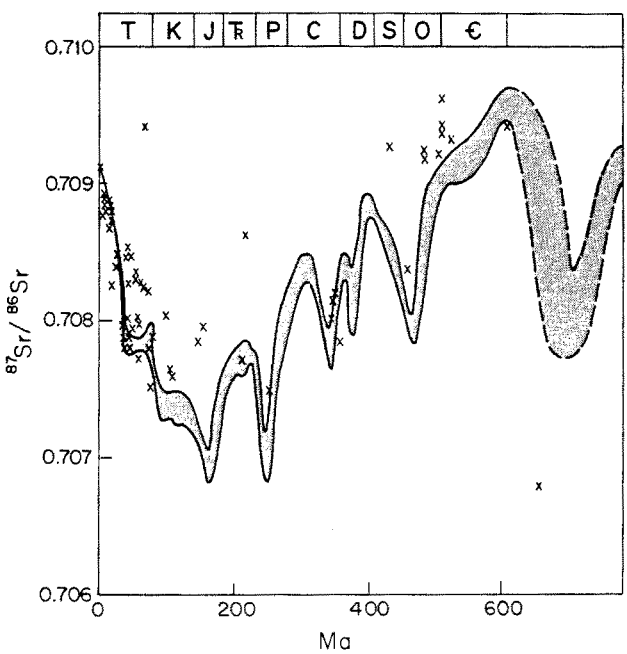


Figure 8: $^{87}Sr/^{86}Sr$ in phosphorites and fish debris plotted on the curve of the isotopic composition of Sr in seawater vs. time. Note the general agreement between phosphate and contemporaneous seawater; practically all deviations from the curve are towards more radiogenic values. Data from Shaw and Wasserburg (1985), Staudigel et al. (1985), and Grandjean et al. (1987, 1988)

ion. Most fossils that were presumed (on paleontological grounds) to be marine, plotted within error of the $^{87}Sr/^{86}Sr$ seawater curve. However, whereas living fresh-water fishes contain less than 100 µg/g Sr, the Sr content of the fossils was in the range of their marine counterparts. Hence, one cannot escape the conclusion that post-burial interaction between apatitic fossils and their surrounding fluids is common. Figure 8 is a summary of $^{87}Sr/^{86}Sr$ ratios in phosphorites and apatitic fossils. An attempt to date phosphogenesis by Sr isotopes has recently been been made (McArthur et al., 1990; Compton et al., 1990). This approach is supported by three observations: (1) $^{87}Sr/^{86}Sr$ ratios of modern phosphorites are within error of modern marine Sr, (2) during phosphatisation of carbonate the Sr isotopic composition of the newly formed apatite is not inherited from the carbonate but reflects seawater Sr, and (3) the $^{87}Sr/^{86}Sr$ ratio in shallow marine pore waters is indistinguishable from modern seawater. The age determinations for phosphorites from four different areas are in good agreement with geological reasoning and previous estimates. Compton and co-workers (1990) suggested on the basis of $^{87}Sr/^{86}Sr$ ratios in francolites and biogenic carbonates from Florida that phosphogenesis in the southeastern United States occurred in the Oligocene and early to middle Miocene. The apatites were reworked and weathered, *a la* Baturin during later Miocene regressions. These authors also suggested that whereas the depositional stage of apatite formation, which is basically a stage of deposition of organic rich sediments on the shelves, resulted in a global positive $\delta^{13}C$ excursion, the winnowing stage is the result of a regression, massive oxidation of organic carbon, and a return of $\delta^{13}C$ to its preexcursion values.

The reasonably good agreement between ichthyolith Sr isotopic values and the secular Sr-isotope curve should be considered in view of the demonstration (Nelson et al., 1986) that bones of prehistoric marine organisms (seals) acquire a "terrestrial" $^{87}Sr/^{86}Sr$ ratio after being exposed to freshwater diagenesis. Apparently this observation reflects an early dissolution-precipitation step in biogenic apatite diagenesis. The fossilized apatite ultimately acquires the chemical signatures of its very early diagenetic environment. If as in the "experiment" of Nelson

et al. (1986) that environment is drastically different from the depositional environment, the preserved information may be misleading. However, if as in the great majority of cases, the early burial site is identical, or very similar to the environment of life, then $^{87}Sr/^{86}Sr$ (and perhaps $\delta^{18}O$ as well) reflect that environment. The influence of late alteration on the Sr isotopic composition of phosphorites was considered by McArthur et al. (1987). They found phosphorites of the Upper Varswater Formation (Cape Province, South Africa) to be enriched in radiogenic Sr as their alteration is intensified (reaching $^{87}Sr/^{86}Sr = 0.70929$ in the most weathered sample). The alteration can be detected from the change in Sr concentration: weathering reduces the Sr content of the phosphorite from a Sr/Ca ratio of 3.7×10^{-3} in unaltered phosphorites to less than half that value in the most altered ones. An independent criterion for the degree of alteration of apatites has recently been suggested by Shemesh (1990). He used the crystallinity index as determined by infrared spectroscopy (FT-IR) as an indicator to distinguish between pristine samples and those strongly affected by diagenesis and recrystallization. As the crystallinity index increases, both $\delta^{18}O_P$ and the Sr content decrease.

$^{143}Nd/^{144}Nd$ ratios were measured in conodonts (Wright et al., 1984; Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987, 1988), ichthyoliths (Staudigel et al., 1985; Grandjean et al.,1987), phosphatic brachiopods (Keto and Jacobsen, 1987) as well as phosphorites (Shaw and Wasserburg, 1985; Keto and Jacobsen, 1988). Recent biogenic apatites from geographically separated localities bordering on a common sea, record approximately the same εNd. $^{143}Nd/^{144}Nd$ ratios in fish teeth separates from the Pacific and Atlantic oceans are similar to those ratios in Mn nodules, which in turn probably reflect some time-integrated values in the corresponding large water masses. The analysis of $^{143}Nd/^{144}Nd$ in apatitic fossils yields a rather consistent picture (Fig. 9). The present day oceanographic pattern seems to have existed for about the last 50 Ma. Throughout this time the Atlantic was characterized by relatively low $^{143}Nd/^{144}Nd$ (εNd between about -12 and -6) whereas the Pacific water masses had significantly higher ratios (εNd from -6 to 0). This difference

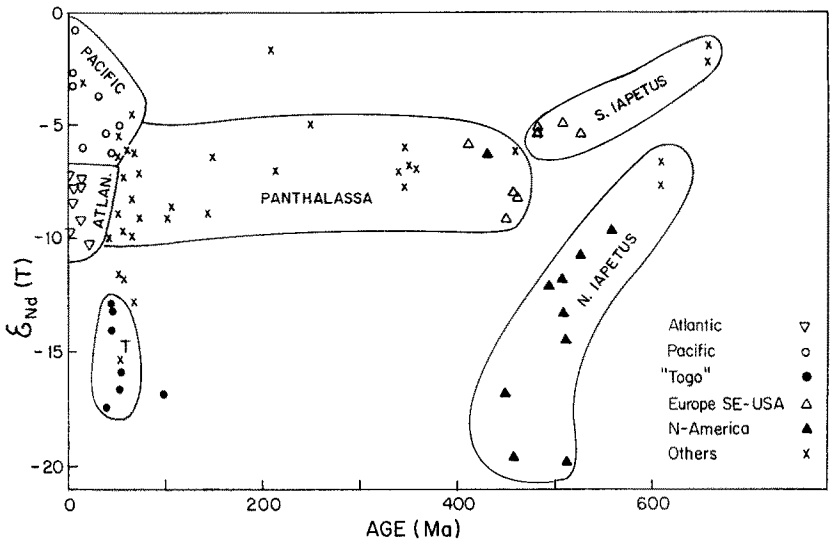


Figure 9: εNd(T) vs. time for Phanerozoic phosphatic fossils. Note two periods of geochemical provincialism: (a) between 0 and 50 Ma - the Pacific and Atlantic provinces (for data in field "T", see text), and (b) 400-650 Ma - the southern and northern Iapetus provinces (see text). Accordingly, data points from Pacific, Atlantic, North America, and SE-USA+Europe are marked. Data from Shaw and Wasserburg (1985), Staudigel et al. (1985), Grandjean et al. (1987, 1988), and Keto and Jacobsen (1987)

difference apparently reflects the dominance of old, LREE enriched crust as the source of Atlantic Nd, as opposed to relatively young crust as well as hydrothermal sources that supply Nd to the Pacific. Shaw and Wasserburg (1985) considered the convergence of εNd to a narrower spread prior to 100 Ma, as evidence for the existence of "Panthalassa", the uniform ocean which surrounded Pangea prior to its breakup. The studies of Keto and Jacobsen (1987, 1988) of $^{143}Nd/^{144}Nd$ in Phanerozoic apatitic fossils and phosphorites suggest that the picture of a single Paleozoic world ocean is an oversimplification. The Pacific/Panthalassa Ocean has been the largest Phanerozoic and Late Precambrian paleo-ocean (averaging 80% of world ocean area), but not the only one. Between the Middle Cambrian and the Middle Ordovician, geochemical provincialism shows up again. $\varepsilon Nd_{(T)}$ values in samples from Europe and the Southeastern United States (-5 to -9) differ sharply from those in the rest of North America (-10 to -20). The proposed interpretation is the existence of two separate oceans between North America and Baltica, with a barrier

between them. Keto and Jacobsen refer to these as the Southern and Northern Iapetus Seas, respectively. Only with the onset of the Taconic Orogeny did this barrier apparently disappear, and a uniform ocean (in εNd terms) form.

Further insight into paleoceanographic connections between different oceanic basins of younger age is provided by the isotopic analysis of Nd by Grandjean et al. (1987). Thus it appears that the Middle Eocene was a critical period in establishing modern oceanic circulations. Prior to that time an isolated basin (with εNd of about -13.5) existed in the South Atlantic. Sediments exposed in Togo, Guinea and Angola were deposited in that basin (Fig. 9, field "T"). In some cases the ichthyoliths have $^{87}Sr/^{86}Sr$ ratios of contemporaneous seawater, but $^{143}Nd/^{144}Nd$ values of an isolated basin. This probably is a reflection of good mixing and connection with the world ocean on a time scale of the residence time of Sr, (about 4 Ma) but insignificant interaction with other basins on the scale of Nd residence time (about 100 a; Fig.9). It should be stressed that in many cases the analyzed fossils do not actually sample an open oceanic environment. They usually represent marginal seas and carbonate platforms with poorly known connections to the major ocean water masses.

Uranium Isotopes and its Daughter Nuclides

The significant enrichment of sedimentary apatite in U has been noted early in this century. R. J. Strutt (later Lord Rayleigh) was inspired by Ernest Rutherford to study the helium content of numerous uranium bearing rocks and minerals, aiming at establishing methods for calculating their ages. As part of this project Strutt discovered the exceptional radioactivity of fossil bones and phosphorites. Later it was shown that while igneous apatite is enriched in both U and Th, the radioactivity of sedimentary phosphates is due almost entirely to U alone (Altschuler et al., 1958). This discrimination is apparently related to the relative solubility of some uranyl ions, leading to U enrichment in seawater, compared to the extreme insolubility

of Th compounds. The enrichment of phosphorites in U is so strong, that mapping the radioactivity of the sea floor by means of a deep-towed scintillometer proved an effective method for defining the distribution of phosphatic sediments in many parts of the oceans (Jones, 1989).

Phosphorite contains between 10 and 500 µg/g U. The average content is 120 µg/g, enriched by a factor of 30 over an average shale (Altschuler 1980). The study of the location of U in phosphatic sediments has been principally carried out by nuclear (though not necessarily isotopic) methods. In 1958 Altschuler et al. applied alpha-track autoradiography to demonstrate that practically all of the U in phosphorites is associated with the CFA. They further showed that much of the U in phosphorites is tetravalent, and proposed that U substitutes for Ca^{+2} in CFA as U^{+4} which has a similar ionic radius to that of Ca^{+2}. The structural location of hexavalent U in CFA is less clear. The uranyl $(UO_2)^{2+}$ ion is too large to fit structurally into any of the major lattice sites of CFA; hence its association with phosphorites has been explained by chemisorption of uranyl ions on growing apatite crystallites, or as a result of post-formational oxidation of primary U^{+4}.

The fission-track technique has also been successfully applied to the study of U distribution in phosphorites. Burnett and Veeh (1977), Kress and Veeh (1980), Kozlov (1970), Berzina et al. (1981) confirmed the early findings that U is CFA-related. A fission track study by Avital et al. (1983) of Israeli phosphorites enabled them to map concentrations of U in various textural components of a phosphorite. Optically anisotropic bone fragments have the lowest U concentration of all apatitic grains in the rock (80-150 µg/g); replaced isotropic bones are richer in U (120-260 µg/g), as are isotropic ovulites (140-300 µg/g). Non-apatitic grains and calcitic matrix and cement are U poor (usually less than 5 µg/g). A related study (Stein et al., 1982) dealt with the behavior of U in phosphorites during phosphate ore calcination. It has been found that during ore calcination at about 600°C, all the U is oxidized to the hexavalent state, and at about 900°C it migrates into U-rich phases that can be

preferentially extracted with acid, without dissolving the entire rock. The significance of such a study is in providing background information for attempts to extract U as a side product during industrial treatment of phosphorite ores.

Extremely few radiometric age determinations have been carried out on pre-Pleistocene phosphatic rocks. Early attempts to apply fission track dating to phosphorites failed because the crystallites of CFA in phosphorites are too small to record tracks (D. Lal, personal communication). Soviet scientists were the first to attempt Pb isotope studies of Proterozoic phosphatic sediments (Tugarinov et al., 1963). These were followed by two age determinations of uraniferous phosphorites (Vaasjoki et al., 1980; Bell and Thorpe, 1986), in both of which good Pb-Pb isochrons were obtained. Kovach and Zartman (1981), reported a U-Th-Pb date on conodonts. They obtained a concordant age of about 325 Ma for conodonts of Upper Carboniferous age.

Uranium Series Dating of Young Phosphorites.

In contrast to the, so far, limited success in dating ancient phosphorites, isotope geochemistry was central to the intensive study of young, sea-floor phosphorites. The success in establishing their ages, rates and modes of growth, and the understanding of the environment of Recent and young phosphogenesis led to a better understanding of how phosphorites formed through time. The distribution of submarine phosphorites, especially along the western margins of continents, has been tacitly assumed by many workers, notably by Sheldon (1964) and McKelvey (1967), to represent sites of Recent phosphorite formation. This in turn was accepted as proof of Kazakov's theory of phosphogenesis. The development of U series disequilibrium dating techniques (See Faure, 1986, and Ivanovich and Harmon, 1982, for summaries and thorough treatment of methods), brought many sedimentary events in the range of tens of thousands to hundreds of thousands of years within the capability of precise dating. The original methods were based on high resolution alpha-spectrometry; the recent introduction of mass-spectrometric

determination of $^{234}U/^{238}U$ ratios (Chen et al., 1986; Edwards et al., 1987), makes the prospects of the disequilibrium methods even more promising, though no mass-spectrometric measurements of phosphatic sediments have been reported so far.

In order to date a U-bearing phosphorite one must assume that: (1) U (but little if any Th) enters the apatite lattice at a time close to the mineral's formation, (2) this U is of marine origin with an initial $^{234}U/^{238}U$ activity ratio close to that of modern seawater, and (3) the apatite has remained a closed system with respect to U and Th isotopes. Kolodny and Kaplan (1970a) made these assumptions and attempted to date phosphorites from off California, Chatham Rise, and Aghulas Bank. None of these contained an excess of ^{234}U. In fact, many of the phosphorites showed $^{234}U/^{238}U$ ratios below unity, indicating that many phosphorites exposed now on the sea-floor are not forming at the present time, and are most likely even being leached. Thus it was concluded that none of the sea-floor phosphorites that have been studied by the end of the sixties, were Recent. When Recent phosphorite genesis was suspected in organic rich diatomaceous sediments beneath areas of intensive upwelling off the coasts of Namibia, Peru and Chile, it was by applying U-disequilibrium dating that their Recent age was confirmed (Baturin et al., 1972; Veeh et al., 1973; Veeh et al., 1974; Burnett and Veeh, 1977). It was found that these phosphorites contain U with a $^{234}U/^{238}U$ activity ratio very close to present seawater, and that although some ^{232}Th was found in the phosphorites, it could be assumed safely that none of it, and no ^{230}Th entered the apatite lattice.

The successful dating of young phosphorites began a sequence of radiochemical studies of phosphatic sediments, thanks to which our understanding of the modes of phosphogenesis increased greatly. These studies resulted in not only the location of further young phosphorites in zones of upwelling (off South Africa, Birch et al., 1983), the dating of very young insular (guano related) phosphorites on Ebon atoll in the Marshall Islands (Veeh and Burnett, 1978), but also the discovery of currently forming phosphorites off New South Wales, Australia (Kress and Veeh, 1980; O'Brien and Veeh, 1980; O'Brien et al.,

1986). This latter case was the first evidence for Holocene phosphogenesis not linked to strong upwelling. The Australian continental margin is an area of very limited seasonal upwelling and low biological productivity. This deposit as a possible analog of an "east coast" type phosphogenic province (McKelvey, 1967), eliminates the necessity to assume paleo-upwelling in areas where phosphorites are found with no indications of Recent upwelling. McArthur and co-workers (1988) dated phosphorites off western South Africa and concluded that phosphogenesis was episodic between the Eocene and 62 ka. Isotopic analysis of C and S suggested to those authors that phosphogenesis had occurred in oxic sediments and was probably unrelated to enhanced coastal upwelling.

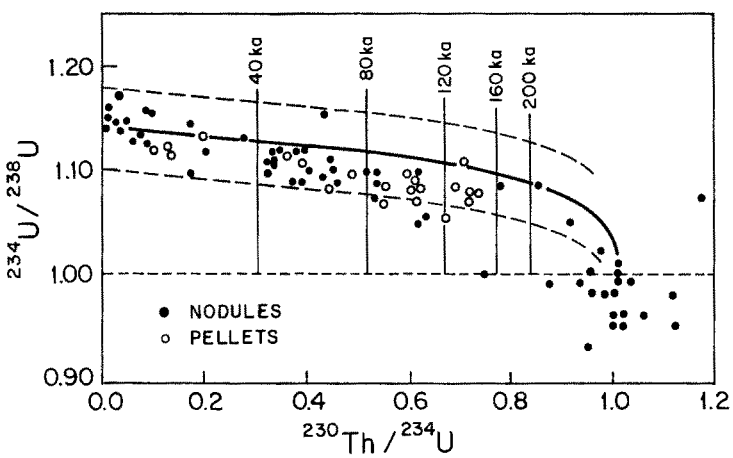


Figure 10: Ideal development in time or "Concordia (heavy curve) of $^{234}U/^{238}U$ activity ratios vs. $^{230}Th/^{234}U$ with analytical results of young pellets and nodules. Note the initial $^{234}U/^{238}U$ activity ratio of >1.14, and the occurrence of old nodules with $^{234}U/^{238}U$ <1.0. The two curves enclose a deviation of 2σ from the Concordia path. After Burnett et al. (1988), Burnett and Veeh (1977), and Veeh and Burnett (1982)

The U system offers several opportunities to test for concordance of radioactive dates. The decay of the two long-lived isotopes of U (^{235}U and ^{238}U) into a sequence of short lived daughters enables one to check concordance by comparing ages obtained by applying two different clocks. The graphical tool for

such a check is the construction of "concordia" type diagrams, so that the location of data points within analytical error of the calculated concordia curves indicates system closure, and increases one's confidence in the obtained date. Figure 10 represents the evolution in time of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ for radioactive decay in a closed system with an initial $^{230}Th/^{234}U$ ratio of zero and a constant initial $^{234}U/^{238}U$. These are conditions approximated by many phosphorites. It can be seen from figure 10 that the initial $^{234}U/^{238}U$ activity ratio in phosphorites is slightly higher than that in seawater (1.14), in contrast to corals which show no such difference. Veeh and Burnett (1982), suggest that this is the result of phosphorite formation in anoxic, organic-rich sediments. Uranium in such environments is incorporated into CFA from interstitial waters, which may be enriched in ^{234}U by diffusion from the solid grains. A further conclusion from the plot is that again, unlike in the case of corals no complete system closure can be assumed for phosphorites. The spread of the data points can be best explained as the result of a radioactive decay of excess ^{234}U in a semi-closed system from which a small fraction of ^{234}U is continuously lost; it is this fraction which diffuses into the interstitial water and enriches it in ^{234}U. This semi-closed 'valve type' mechanism of isotopic fractionation was first proposed by Kolodny and Kaplan (1970a), and was later confirmed and elaborated by Burnett and Veeh (1977) and O'Brien and his co-workers (1980, 1987). We shall deal with it in more detail below.

^{230}Th is daughter of ^{238}U and ^{231}Pa of ^{235}U. Figure 11 is a $^{230}Th/^{234}U$-$^{231}Pa/^{235}U$ concordia plot. The solid curve represents concordance which is expected if the system remained closed to all relevant isotopes, and no initial ^{230}Th and ^{231}Pa were included in the apatite. It can be seen from figure 11 that several phosphorite samples from non-upwelling environments (New South Wales) or young samples yield concordant $^{230}Th/^{234}U$-$^{231}Pa/^{235}U$ ages (Veeh, 1982; Birch et al., 1983). On the other hand many of the phosphorite nodules from off Peru-Chile have an excess of ^{231}Pa, as compared to their $^{230}Th/^{234}U$ age (Roe et al.,1982). An excess of ^{231}Pa is probably the result of adsorption of both Th and Pa during the nodules exposure to

seawater and pore-water at the sediment water interface. These bottom waters have a $^{230}Th/^{231}Pa$ activity ratio of less than the production ratio of 11.2, because ^{230}Th is preferentially scavenged by particulates in such a high productivity area; hence the apparent "excess" of ^{231}Pa. An other kind of openness is demonstrated by the pellets from the Peru shelf (Burnett et al., 1988). Their data points on figure 10 are predominantly below the concordia. Normally such tendency to plot below the concordia path would be explained by addition of U, preferential addition (relative to Pa) of Th, loss of Pa or a combination of these effects. Analyses of bones from limestone caves in South Australia (Ayliffe and Veeh, 1988) also plot below the concordia line. They were interpreted as representing episodic U assimilation, a conclusion supported both by fission track mapping and by $^{234}U/^{238}U$ analysis.

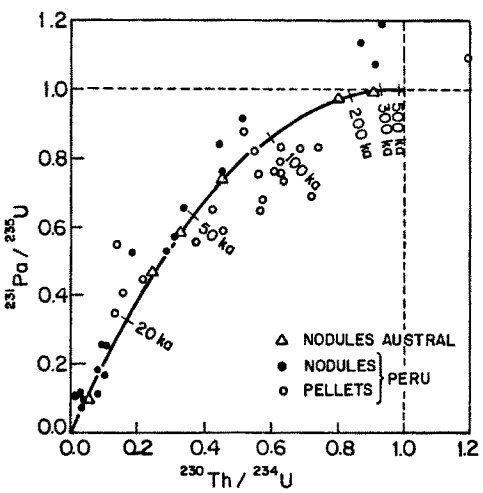


Figure 11: Ideal development in time or "Concordia" of activity ratios $^{230}Th/^{234}U$ with analytical results for young phosphatic pellets and nodules. Compare concordant ages of nodules from Australia to "excess Pa" in nodules from Peru, to "excess Th" in pellets from Peru. After Veeh (1982), Burnett and Roe (1983), and Burnett et al. (1988)

The geochronology of the Peru-Chile sea-floor phosphorites suggested to Burnett and Veeh (1977), that phosphorite formation was largely restricted to times of high sea level. This conclusion was not supported by the Eastern Australia data (Kress and Veeh, 1980; O'Brien and Veeh, 1980; O'Brien et al., 1986),

where phosphogenesis seems to have been a more or less continuous process for the last 180,000 years. It is too early to tell whether the difference between the two groups is the result of inadequate sampling, or it is real, indicating different mechanisms of phosphorite formation in "west coast" and "east coast" type phosphorites.

Modes and Rates of Growth

The establishment of modes and rates of growth of phosphorites is essential to a better understanding of mechanisms of phosphogenesis. The discovery of young phosphorites has made this task possible. In addition it is now possible to compare rates of growth of pellets, nodules and crusts with the surrounding sediments. In their study, Burnett and his co-workers (1982, 1983) cut phosphorite nodules and crusts from off Peru into several slices, each of them a few millimeters thick, in a direction perpendicular to their suspected growth axis. The $^{230}Th/^{234}U$ age was then established for each slice. The top and bottom of the dredged nodules was inferred from an oxidized layer on the exposed surface. In a later study, Kim and Burnett (1986) succeeded in sampling from the Peruvian sea floor an undisturbed, oriented 20 mm thick, phosphatic crust, together with its overlying (14 cm) and underlying sediment. They concluded that whereas phosphate nodules located at the sediment water interface, grow *down* into the soft underlying mud, the direction of growth of the buried crust is *upward*.

Growth rates turn out to be slow relative to the surrounding sediment. The fastest growing nodule grew at a rate of 10 mm/1000 yrs.; the slowest - at a fraction of a mm per thousand years. It is therefore surprising that such nodules remain at the sediment-water interface in sediments that accumulate at a rate of about 1 mm per year. Even the fastest growing nodule should have been buried under about 2 meters of sediment. Burnett and his co-workers suggested that either burrowing activity by benthic organisms or intermittent periods of non-deposition could explain the interface location of the nodules. Burnett et al. (1988)

applied an analytically improved version of U-disequilibrium dating, combined with accelerator mass spectrometry (AMS) ^{14}C dating of structural CFA-CO_2 in Peruvian shelf phosphatic *pellets* (as opposed to nodules). Calculated rates of phosphate uptake are somewhat higher than rates for nodules. The pellets seem to form very quickly, probably within less than 10 years after growth is initiated.

Redox, Uranium Oxidation States and its Isotopic Composition

The effect of ^{234}U diffusion outward from the solid apatite into interstitial water upon the dating system of phosphorites has been mentioned above. Such diffusion is an expression of a fractionation of the U isotopes ($^{234}U/^{238}U$) between different oxidation states. Chalov and Merkulova (1966) found that the $^{234}U/^{238}U$ ratio in the tetravalent fraction of uranium oxides is always lower than that ratio in the hexavalent fraction. Kolodny and Kaplan (1970a) showed that upon chemical separation of U into its two oxidation states in apatite, the ratio of U isotopes varies as follows:

$$^{234}U/^{238}U(IV) \; < \; ^{234}U/^{238}U(T) \; < \; ^{234}U/^{238}U(VI)$$

where (IV), (T), and (VI), designate the tetravalent U, the total U, and the hexavalent U fractions respectively. The scheme which has been proposed in order to explain these differences is shown in figure 12. It is assumed that a fraction of the radiogenic ^{234}U in the tetravalent U in apatite is relocated due to alpha recoil, and then oxidized to hexavalent U. Hence there is a continuous leakage of ^{234}U from $U_{(IV)}$ to $U_{(VI)}$. If that fraction (termed "R") remains constant with time, then the $^{234}U/^{238}U_{(IV)}$ varies with time according to:

$$(^{234}U/^{238}U)_{IV} =$$

$$(1-R)\,[1-e^{(\lambda 238-\lambda 234)\,t}]+(^{234}U/^{238}U)_{IV0}\cdot e^{(\lambda 238-\lambda 234)\,t} \qquad (8)$$

where t = time since phosphorite formation and $(^{234}U/^{238}U)_{IV0}$ is the initial activity ratio at $t = 0$. When t becomes sufficiently large (> 1Ma), the right-hand side of Eq. (8) becomes equal to (1-R). Thus R can be estimated from:

$$R = 1 - (^{234}U/^{238}U)_{IV} \qquad (9)$$

by measuring the activity ratio of tetravalent U in sufficiently old phosphorites. In Kolodny and Kaplan's phosphorites this activity ratio averaged 0.7. They therefore estimated R as being 0.30, indicating that about 30% of the tetravalent ^{234}U atoms produced within the phosphorites are oxidized to the hexavalent state. Kolodny and Kaplan (1970a) considered the constant R to be the combined probability of a radiogenic ^{234}U atom in the tetravalent state to be displaced and then oxidized to hexavalent U. They showed that in order to produce the leakage of recoil $^{234}U_{(IV)}$ an oxidant is necessary, and that in sea-floor weathered, outer oxidized rims of phosphatic nodules, both $U_{(VI)}$ and $(^{234}U/^{238}U)_{IV}$ are lower than in their un-oxidized centers. Both the general model, and the estimate of the best value for "R" as 0.3, has since been confirmed by Burnett and Veeh (1977), O'Brien and Veeh (1980), and Veeh and Burnett (1982).

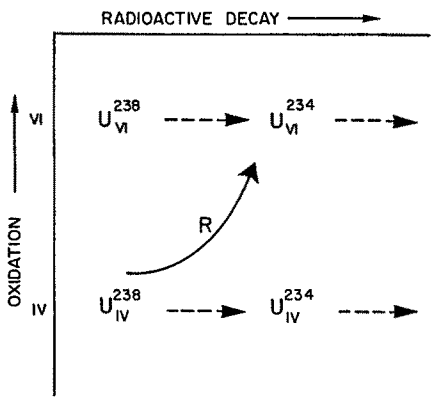


Figure 12: Diagrammatic representation of the partial oxidation of ^{234}U as a result of radioactive decay. After Kolodny and Kaplan (1970)

O'Brien et al. (1987) have applied a similar approach to the analysis of East Australian phosphorites. They demonstrate

convincingly that these nodules underwent at least two distinct stages in their history: (1) an initial stage in which phosphate diffuses interstitially into a slowly growing layer of phosphorite and incorporates U only as $U_{(IV)}$ and (2) a subsequent exposure at the sediment water interface during which the layer is broken up into nodules, which are periodically reworked and exposed. Whereas in the first stage conditions might be mildly oxic or sub-oxic, clearly oxidizing conditions prevail during the weathering stage, as evidenced by a strong ferruginous impregnation of the phosphorites, oxidation of organic matter and oxidation of U to $U_{(VI)}$. Both the differences in $\%U_{(IV)}$ and "R" values of exposed and buried nodules are related to the length of time that the nodules have been exposed to oxic conditions at the sediment-water interface. Thus the isotopic analysis of U in its two oxidation states leads one to adopt a two-stage phosphogenic model, which is also required from numerous petrographic, geochemical and field evidences (Baturin, 1971 a,b; Kolodny, 1981): a suboxic (or anoxic) stage in which initial apatitic layers and concretions are formed, and an oxidizing winnowing stage in which apatite is mechanically enriched and concentrated.

SUMMARY

Figure 13 is a graphic summary of the different isotopic species which can be analyzed in apatite and of their structural location. Isotopic studies of phosphatic rocks (as of any other rock) are not a substitute for field, petrographic, elementary geochemical, and mineralogical studies. The isotopic analysis of apatites does however shed light on many aspects of their environment of deposition and diagenesis that cannot be understood without the application of such methods. The third column in table 1 summarizes these aspects.

Our understanding of phosphogenesis can be enormously increased by identifying the environments in which phosphorites are forming today, or where they were forming in the recent **past,**

but ceased to form due to change of conditions. Studying radioactive disequilibrium in the U series, possibly in combination with ^{14}C analysis leads to the recognition of such environments. In addition to dating phosphatic sediments these studies also lead us to an understanding of the geometry and rate of phosphatic nodule growth, and to a more precise grasp of the alternating stages of apatite precipitation and winnowing.

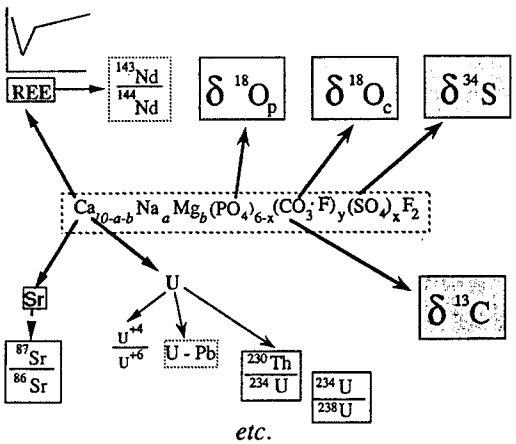


Figure 13: Scheme of location of the different isotopes in the carbonate fluor apatite structure. Note that the stable isotopes of the light elements are constituents of major anions in CFA, whereas the radiogenic isotopes of the heavy elements are trace substitutions for the Ca cation

It is still a matter of dispute whether the sites of Recent phosphorite deposition are indeed modern analogs of the large, economic phosphorite deposits of the geologic past (see Bentor, 1980). Nevertheless, data from phosphatic sediments forming off Peru-Chile, Namibia and Australia combined with the geological record lead to the conclusion that phosphorite pellets and nodules must be forming from interstitial solutions and that every phosphorite must be the end product of numerous cycles of deposition and reworking.

Phosphorites being essentially a diagenetic product, it is this environment that is monitored by both $\delta^{13}C$ in the structural CO_2 of apatite and $\delta^{34}S$ in sulfate. Both of these are strongly

sensitive to redox conditions in the interstitial environment, and reflect such factors as sediment redox, degree and mode of organic matter oxidation, carbonate alkalinity, and degree of sulfate reduction. It appears that the site of CFA formation, a few centimeters below the sediment-water interface, is usually suboxic to anoxic. The broad range of $\delta^{13}C$ in apatite of different phosphorites supports the conclusion of Froelich et al. (1988), that CFA precipitation "is interface-linked, rather than driven by organic diagenesis of phosphorus deeper in the sediment". Froelich et al. (1988) have also suggested that the formation of CFA may be preceded by the precipitation of a metastable precursor, often referred to as amorphous Ca phosphate (ACP). The isotopic analysis of O in its two crystallographic sites (δ_p and δ_c) suggests that the formation of a phosphorite may involve dissolution-precipitation at considerably deeper burial conditions, resulting in isotopic re-equilibration.

The last column of table 1 summarizes that information which isotopic analysis of phosphorites (and phosphatic fossils) yields about the world in which they were deposited. $\delta^{18}O$ of phosphate oxygen is probably a very strong paleoclimatic indicator. In fact, for Paleozoic sediments it may be *the* paleoclimatic indicator. The paleoclimatic application of fossils of fresh-water and warm-blooded animals is only in its infancy. Whereas most isotopic studies of oxygen in sediments leave the temperature-water dilemma unsolved, the analysis of δ_p in mammal bones and teeth holds promise for separating these variables. $^{87}Sr/^{86}Sr$ and εNd values in phosphorites and phosphatic fossils carry information about the major paleoceanographic connections during those times. The distribution of land and sea, the opening and closure of land bridges and ocean passages have traditionally been subjects addressable mainly by faunistic analysis; geochemistry now extends its influence into these new territories.

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