

Letter Section

# RADIOMETRIC AGES OF PHOSPHORITES FROM THE WEST COAST OF INDIA

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## Abstract

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Four algal carbonate nodules with ~1 mm thick phosphorite coatings were dated, by the <sup>230</sup>Th/<sup>234</sup>U and three of the carbonates by <sup>14</sup>C methods. All ages (5.8-13.9 k.y.) are in satisfactory agreement indicating that phosphorite deposition started soon after the carbonate nodule formation.

The U, Th concentrations and isotopic ratios as well as the U/P weight ratios of the phosphorite coatings are in good agreement with those from other regions of the world.

## Introduction

Phosphogenesis, though episodic has been an ongoing process since Cambrian and is indicative of a number of factors such as oceanographic, geographic, climatic, etc., which were operative during its existence (Sheldon, 1981). A study of various marine phosphorite deposits widely distributed in space and time will hopefully yield a better understanding of this important process and the associated paleofactors. For a detailed account on marine phosphorites reference is made to Baturin and Bezrukov (1972), Burnett (1977), Kolodny (1981), Sheldon (1981) and Baturin (1982). U-Th decay series nuclides have been successfully employed to date late Pleistocene to very recent phosphorites from different geographic

locations (Kolodny and Kaplan, 1970; Baturin et al., 1972; Veeh et al., 1973; Kress and Veeh, 1980; Burnett et al., 1982; Veeh, 1982; Thomson et al., 1984; Kim and Burnett, 1985).

Holocene phosphorite coatings on algal limestones have been reported from the western continental shelf off Goa, India (Nair, 1985). It was thought worthwhile to date these phosphorites and add age data from the Indian region to the growing pool from several other locations. We report here the <sup>14</sup>C and <sup>230</sup>Th/<sup>234</sup>U ages of the algal limestones and their phosphorite coatings.

## Materials and methods

The locations of the nodular type of algal limestones (usually 5-10 cm diameter) coated

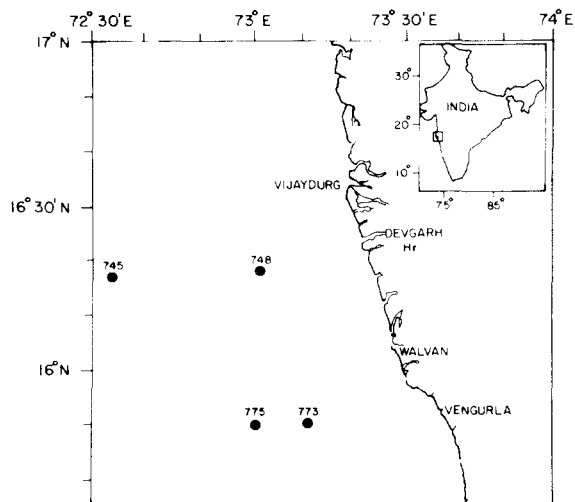


Fig. 1. Location of the phosphorite nodules from the western continental shelf of India.

with up to ~1 mm layer of phosphorite are shown in Fig. 1. A complete account of these nodules is given by Nair (1985) according to whom the principal mineral phase is carbonate flourapatite. The bulk of the nodule is  $\text{CaCO}_3$ .

Four nodules (Nos. 745, 748, 773 and 775 collected from water depths of 126, 55, 59 and 90 m, respectively; Fig. 1), were taken for dating. The phosphorite coating (< 1 mm) was shaved off from each nodule using a dental drill and the shavings were dated by the  $^{230}\text{Th}/^{234}\text{U}$  method (Ku, 1976; Ivanovich and Harmon, 1982). About 0.5 g sample was brought into complete solution in the presence of  $^{232}\text{U}$ - $^{228}\text{Th}$  spike. U-Th isotope measurements were carried out following standard procedures (Krishnaswami and Sarin, 1976; Borole, 1980). The carbonate material was dated by  $^{14}\text{C}$  (Rajagopalan and Vishnu-Mittre, 1977).

## Results and discussions

The Th and U isotopic concentrations and relevant activity ratios of the four phosphorite coatings and two of their carbonate nodules are given in Tables 1 and 2. Three  $^{14}\text{C}$  ages for the carbonate nodules 748 C, 773 C and 775 C are also given in Table 2.

The  $^{230}\text{Th}/^{234}\text{U}$  ages for the four phosphorite coatings (samples denoted by P) are calculated taking the initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio to be that of seawater viz. 1.14 (Koide and Goldberg, 1965; Krishnaswami et al., 1970). In fact all the analyzed phosphorite coatings have the  $^{234}\text{U}/^{238}\text{U}$  activity ratio ranging from 1.13 to 1.15 averaging 1.14. Relevant details of the age calculations using the  $^{230}\text{Th}/^{234}\text{U}$  activity ratio can be found in Broecker (1963), Ku (1976) and Ivanovich and Harmon (1982). The calculated ages for the four phosphorite coatings are also given in Table 2. Two of the carbonate nodules have also been dated by the  $^{230}\text{Th}/^{234}\text{U}$  method.

The U concentrations of the phosphorite coatings from the western continental shelf of India range from 22.3 to 124.2 ppm which is about the same as that reported for phosphorites from other regions (Kolodny and Kaplan, 1970). The  $^{232}\text{Th}$  concentrations of phosphorite coatings varied from 2.8 to 13.24 ppm and are higher than the  $^{232}\text{Th}$  of carbonates. These ranges are also in agreement with those reported for phosphorites and carbonates respectively (Kim and Burnett, 1985; Somayajulu et al., 1985). The  $\text{P}_2\text{O}_5$  concentrations of phosphorites from the western continental shelf of India were reported to be ranging from 0.8 to 10.8% (Nair, 1985). Since the U contents are measured, we compute the U/P weight ratio to be ranging from  $4.2 \times 10^{-4}$  to  $1.7 \times 10^{-2}$ . The U/P ratios of phosphorites from the Namibian shelf and Chile and Peru regions range from  $1.3 \times 10^{-4}$  to  $4.6 \times 10^{-3}$  (Thomson et al., 1984; Kim and Burnett, 1985).

## Ages of phosphorite coatings

The ages of the four phosphorite coatings investigated range from 5.8 to 13.9 k.y. These are in very good agreement with the  $^{14}\text{C}$  ages of the algal carbonate nodules which mean that soon after formation of the carbonates the phosphoritization started taking place. Only in sample 775 there is a discrepancy by about a factor of two in the ages. The carbonate is 7.5 k.y. whereas the phosphorite coating, which should

TABLE 1

U, Th isotope systematics in limestones and their phosphorite coatings

Sample code	Material	<sup>238</sup> U (ppm)	<sup>232</sup> Th (ppm)	<sup>230</sup> Th (dpm g <sup>-1</sup> )	Activity ratio	
					<sup>234</sup> U/ <sup>238</sup> U	<sup>230</sup> Th/ <sup>232</sup> Th
745 P	Phosphorite crust	124.2 ± 4.2	13.24 ± 0.56	5.50 ± 0.22	1.13 ± 0.01	1.7 ± 0.1
748 P	Phosphorite crust	28.7 ± 1.1	2.8 ± 0.3	1.97 ± 0.12	1.15 ± 0.02	2.8 ± 0.3
775 P	Phosphorite crust	22.3 ± 0.5	4.3 ± 0.6	2.34 ± 0.22	1.13 ± 0.02	2.2 ± 0.7
775 C	Carbonate	47.2 ± 4.9	0.68 ± 0.07	1.29 ± 0.09	1.10 ± 0.02	7.6 ± 0.7
773 P	Phosphorite crust	36.4 ± 1.3	3.7 ± 0.4	2.29 ± 0.16	1.14 ± 0.02	2.5 ± 0.3
773 C	Carbonate	18.3 ± 0.7	1.00 ± 0.06	1.18 ± 0.05	1.13 ± 0.02	4.9 ± 0.3

Errors indicated are due to 1 sigma counting statistics only.

TABLE 2

<sup>230</sup>Th/<sup>234</sup>U and <sup>14</sup>C ages of limestones and their phosphorite coatings

Sample	<sup>230</sup> Th/ <sup>234</sup> U (activity ratio)	<sup>230</sup> Th/ <sup>234</sup> U (× 10 <sup>3</sup> years)	<sup>14</sup> C age (× 10 <sup>3</sup> years)
745 P	0.052 ± 0.003	5.8 ± 0.03	—
748 P	0.080 ± 0.007	9.2 ± 0.8	—
748 C	—	—	8.9 ± 0.2
775 P	0.12 ± 0.01	13.9 ± 1.3	—
775 C	0.033 ± 0.004	3.6 ± 0.2	7.5 ± 0.2
773 P	0.074 ± 0.007	8.5 ± 0.8	—
773 C	0.076 ± 0.007	8.6 ± 0.8	8.3 ± 0.1

Errors indicated are based on 1 sigma counting statistics only.

be contemporary if not younger, is older by a factor of ~2. At present there is no good explanation if the ages obtained are taken on their face value. Considering the fact that bomb <sup>14</sup>C has contaminated the ocean during the past 3–4 decades (Nydal et al., 1984), one can argue that <sup>14</sup>C ages of the limestones could have been older but for contamination with post bomb <sup>14</sup>C activities that prevailed in the ocean water. As far as the <sup>230</sup>Th/<sup>234</sup>U ages are concerned the dates are on a firmer footing. The <sup>230</sup>Th/<sup>234</sup>U ages of the two carbonate nodules 775 C and 773 C are 3.6 ± 0.2 and 8.6 ± 0.8 k.y. respectively (Table 2). Because of the very high U content of these carbonates, 47.2 and 18.3 ppm respectively for 775 C and 773 C (compared to the expected values of few ppm) which are due to contamination of the carbonates with phosphorite, the deduced ages can be expected to be lower limits. Sample 775 C indeed shows this effect. How-

ever, in the case of sample 773 C the <sup>230</sup>Th/<sup>234</sup>U ages of phosphorite and carbonate as well as the <sup>14</sup>C age of carbonate are in excellent agreement which can be fortuitous.

The <sup>234</sup>U/<sup>238</sup>U activity ratios of the phosphorite coatings are within errors identical with that of seawater indicating that they are very recent. Thus the <sup>234</sup>U/<sup>238</sup>U activity ratios support the <sup>230</sup>Th/<sup>234</sup>U and <sup>14</sup>C ages. All these imply that phosphogenesis has been an ongoing process during the Holocene in at least a portion of the western continental shelf on India. Other such areas are the sea floor off Chile/Peru (Veeh et al., 1973; Kim and Burnett, 1985) and the Namibian Shelf (Thomson et al., 1984). Since phosphorite formation would have occurred immediately after the formation of the carbonate nodules, post-depositional introduction of U in the apatite lattice does not appear to be the mechanism. Uranium uptake from seawater during phosphogenesis looks more reasonable in this region. The source of phosphorus is most likely due to upwelling which is known to be taking place in the region of study (Wyrтки, 1973).

### Phosphorite growth rates

Assuming on an average ~1 mm to be the phosphorite thickness and 10 k.y. age we estimate 0.1 mm per 10<sup>3</sup> years as the average growth rate for the coatings from the Indian region; these rates are one to two orders of magnitude

slower than those found from the Peru/Chile seafloor (Kim and Burnett, 1985). The low rate of phosphorite formation in the western continental margin of India is most likely due to weak upwelling in this region (Wyrтки, 1973).

### Climatic changes

Nair and Hashimi (1980), based on their study of the western continental shelf sediments, concluded that during the Holocene (10 k.y. ago) climate changes occurred which resulted in warmer conditions and low terrestrial runoff whereas Borole et al. (1982) found a major environmental change from cold to warm that could have been responsible for a faunal change in the sediments off the western continental margin at about 13,000 years B.P. Corals of 6–7 k.y. have also been found in the Saurashtra coast (Gupta and Amin, 1974; Somayajulu et al., 1985) which are contemporaneous with the formation of the algal limestones from the region of the present study. These conditions appear to have been congenial to phosphorite formation in the western Indian continental shelf region.

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