

## Note on the Late Cenozoic marine phosphatic rocks in Japan

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**Abstract:** The occurrence of Late Cenozoic marine phosphatic rocks in Japan was reviewed, especially in respect of the depositional environments of their host sediments. Though there has been only a little description, it can be pointed out that (1) phosphate is precipitated, often together with carbonate, commonly forming concretions in late Early to early Middle Miocene and Late Miocene to Pleistocene, continental shelf to slope sediments, (2) most of phosphatic rocks contain  $P_2O_5$  less than 15-20% with some terrigenous contribution, and (3) late Early to Middle Miocene phosphatic rocks are found around the boundary between warm and cold ocean currents of that time. The occurrence of phosphatic rocks seems to be closely related to the depositional environments of their host sediments.

### Introduction

The purpose of this paper is to briefly review the occurrence of Late Cenozoic marine phosphatic rocks in Japan. Because of the scarcity or misinterpretation of them as carbonate rocks, there has been only a little description of marine phosphatic rocks in Japan. However, marine phosphatic rocks are important as a potential paleoenvironmental and geochemical indicator of their host sediments. Recent progress in the world-wide research of marine phosphatic rocks has disclosed that phosphatic rocks are diagenetic in origin but occur in specific marine environments (BENTON, 1980; BATURIN, 1982).

### Occurrence

Late Cenozoic phosphatic rocks have been reported from the Miyazaki district (TSUNETO, 1987; OTSUKA, 1900; MINERAL-FERTILIZER SURVEY of JAPAN, 1903a, 1904), the Kakegawa district (MINERAL-FERTILIZER SURVEY of JAPAN, 1902), the Fujigawa district (MINERAL-FERTILIZER SUR-

VEY of JAPAN, 1903b, 1904), and Joban Coal Field (MINERAL-FERTILIZER SURVEY of JAPAN, 1902, 1904; KANO, 1986) on the Pacific Ocean side, and from the Noto Peninsula (IMAI and YAMADERA, 1952; MORITANI, 1967; MURANAKA and SHIMADA, 1987), the Nagano district (MINERAL-FERTILIZER SURVEY of JAPAN, 1902, 1903a, b, 1904), the Niigata district (MINERAL-FERTILIZER SURVEY of JAPAN, 1903b, 1904), the Akita and Yamagata districts (KAMOSHITA, 1899; MINERAL-FERTILIZER SURVEY of JAPAN, 1902, 1904; OGIWARA and TAGUCHI, 1986) and the Tsugaru district (MINERAL-FERTILIZER SURVEY of JAPAN, 1902, 1904) on the Japan Sea side (Fig. 1)

Most of the reports were made in early times, and all of the stratigraphic positions of those phosphatic rocks are not always clear in light of the present knowledge of Late Cenozoic stratigraphy of Japan. Nevertheless, the phosphatic rocks seem to occur specifically in the continental shelf to upper continental slope sediments of late Early to early Middle Miocene time and of Late Miocene of Pleistocene time (Fig. 2). The late Early to early Middle Miocene phosphate-bearing facies includes carbonate concretions, carbonate bioclasts and diatomaceous sediments with

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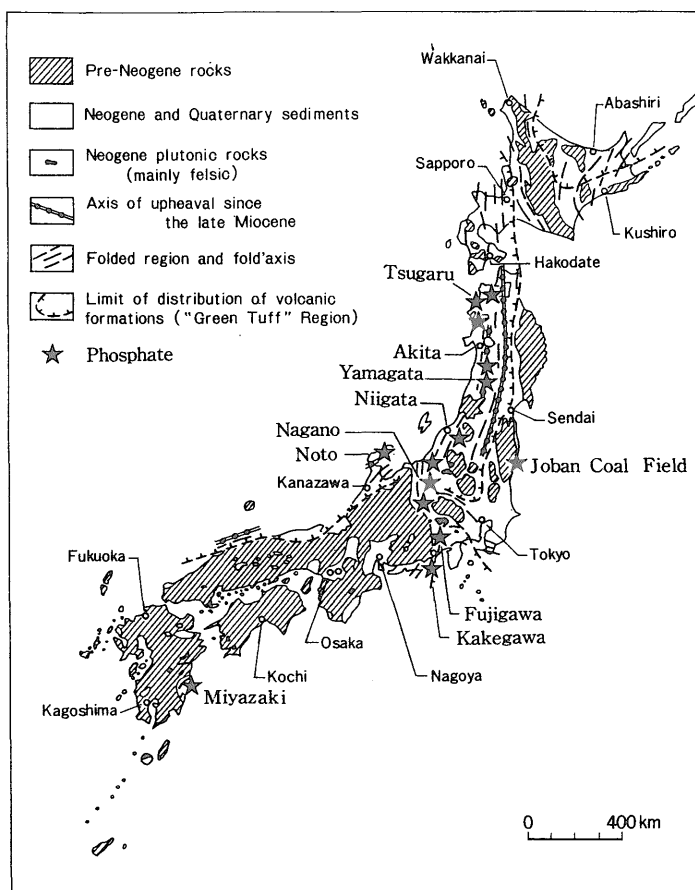


Fig. 1 Known localities of Late Cenozoic marine phosphatic rocks. Base map adopted from SAKAMOTO (1977).

some contribution of terrigenous materials. On the other hand, the Late Miocene to Pleistocene phosphate-bearing facies also includes carbonate concretions and carbonate bioclasts, but with larger terrigenous contribution.

Phosphatic rocks in these facies occur as nodular or lenticular concretions in arenaceous, argillaceous, diatomaceous or tuffaceous sediments, and are closely associated with carbonate concretions (Figs. 3, 4 and 5). Sometimes they are chemically zoned (Figs. 5 and 6) and are transitional to their host rocks (Fig. 5). Plastically-deformed but fragmented phosphatic clasts (Fig. 7) are rarely found suggesting that they were diagenetically formed in soft sediments and were reworked into the present host sediment.

### Chemistry and Mineralogy

569 analyses of Late Cenozoic marine phosphatic rocks, reported by TSUNETO (1897), OTSUKA (1900), KAMOSHITA (1899), MINERAL-FERTILIZER SURVEY OF JAPAN (1902, 1903a, b, 1904), IMAI and YAMADERA (1952), HAMACHI (1962) and KANO (1986), show the rarity of phosphorites (more than 15-20 wt%  $P_2O_5$ ; BENTOR, 1980) (Fig. 8). The maximum  $P_2O_5$  content of those phosphatic rocks is 31% in late Early to Middle Miocene sediments while 21% in Late Miocene to Pleistocene sediments, probably reflecting the difference of terrigenous contribution.

Some detailed analyses of those phosphatic

Late Cenozoic marine phosphatic rocks in Japan (K. Kano)

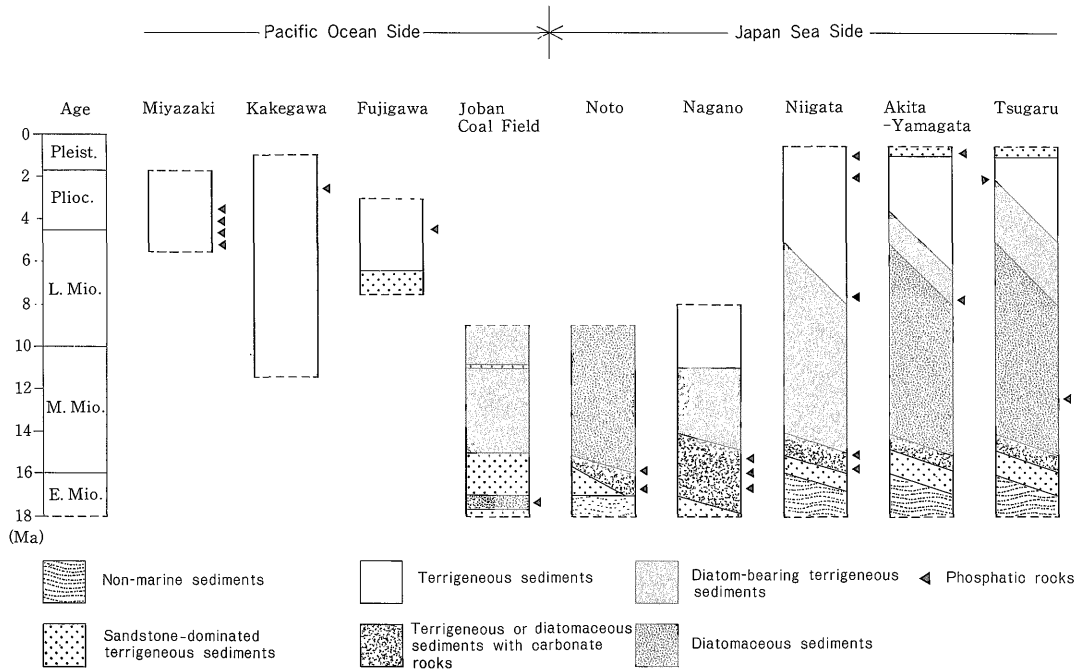


Fig. 2 Stratigraphic distribution of Late Cenozoic marine phosphatic rocks.

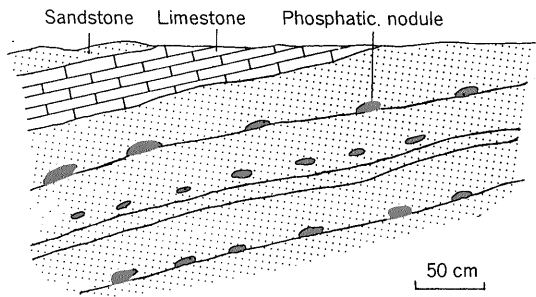


Fig. 3 Phosphatic nodules in the Pliocene sandstone, Miyazaki district (modified after OTSUKA, 1900).

this suggestion. Excess Ca and CO<sub>2</sub> relative to apatite (Figs. 9 and 10) suggest replacement of carbonate by phosphate or co-precipitation of phosphate and carbonate. Several cases are, in fact, known that carbonate shells in sandstone have been replaced by phosphate (e.g. OTSUKA, 1900). On the other hand, phosphate in the Miocene diatomaceous rocks of the Kamenoo Formation, Joban Coal Field occur as nodules replacing silica (KANO, 1986). Apatite in phosphatic nodules often forms aggregates of minute grains 2-10 μm in diameter (HAMACHI, 1962; KANO, 1986).

rocks from the Miyazaki district (TSUNETO, 1897) and the Akita and Yamagata districts (KAMOSHITA, 1899) suggest that major constituent phosphate is fluorocarbonate apatite and is associated with variable amounts of carbonate as implied in Figures 8, 9, 10 and 11. XRD analyses combined with chemical analyses of phosphatic rocks from the Noto Peninsula (IMAI and YAMADERA, 1952), the Niigata district (HAMACHI, 1962) and Joban Coal Field (KANO, 1986) confirm

Vivianite is suggested to be present in phosphatic rocks of the Miyazaki Group, Miyazaki district, based on the bulk rock chemistry and optical observation (OTSUKA, 1900). However, this mineral is common in reducing-prevalled nonmarine sediments (e.g. SHIMADA and KONNO, 1971) but not common in marine sediments. Its occurrence in the marine Miyazaki Group is specific, and should be confirmed by more appropriate methods.

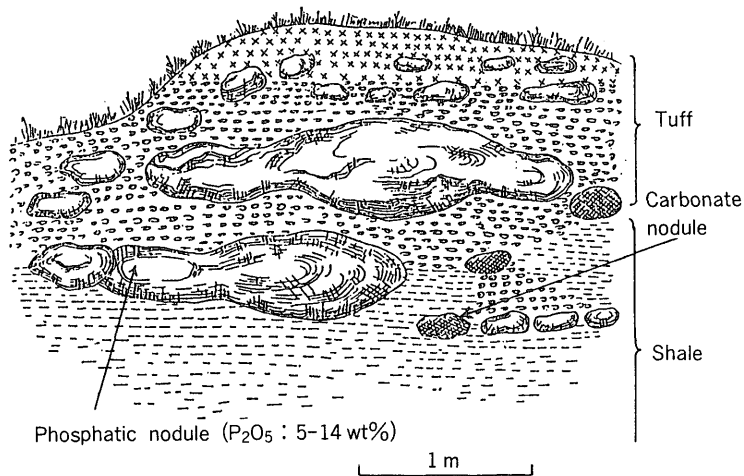


Fig. 4 Noular and lenticular phosphatic concretions in the Miocene shale (Nanatani Formation), Niigata district (modified after MINERAL-FERTILIZER SURVEY of JAPAN, 1901).

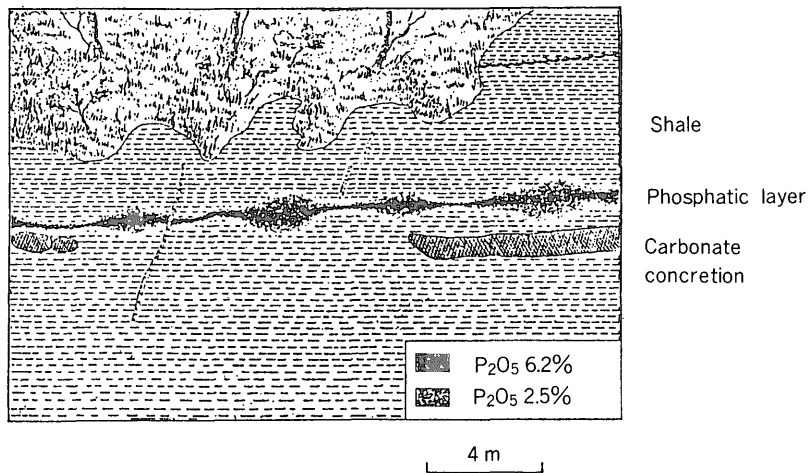


Fig. 5 Phosphatic layers transitional to shale in the Miocene Nanatani Formation, Niigata district (modified after MINERAL-FERTILIZER SURVEY of JAPAN, 1901).

Uraniferous phosphatic rocks are locally found in the Miocene phosphate deposits of the Noto Peninsula (MORITANI, 1967), and highly uraniferous phosphatic nodules ( $P_2O_5=4-17\%$  and  $U_3O_8=0.018-0.11\%$ ) are found in the Miocene Tsugawa Formation, Niigata district (HAMACHI, 1962).

#### Geologic factors relevant to phosphate genesis

Marine phosphate commonly occurs in organic

matter-rich argillaceous, siliceous or carbonate sediments on modern and ancient continental shelves and upper continental slopes that face the oxygen-minimum zone, especially its upper and lower boundary (BURNETT, 1977; BATURIN and BEZRUKOW, 1979; BENTOR, 1980; BATURIN, 1982; LOUGHMAN, 1984). This extraordinary concentration of a biophile element, phosphorous in marine sediments likely occurs through (1) high production of organism and active uptake of phosphorous by organism from nutrient-rich sea-

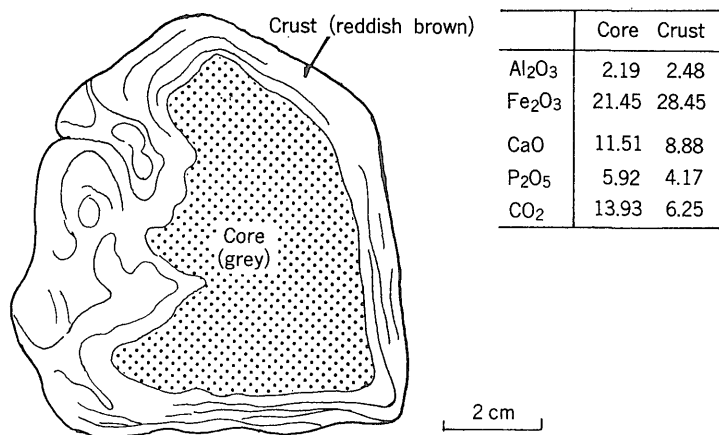


Fig. 6 Chemically zoned phosphatic carbonate nodule from the Pliocene, Miyazaki district (modified after TSUNETO, 1897).

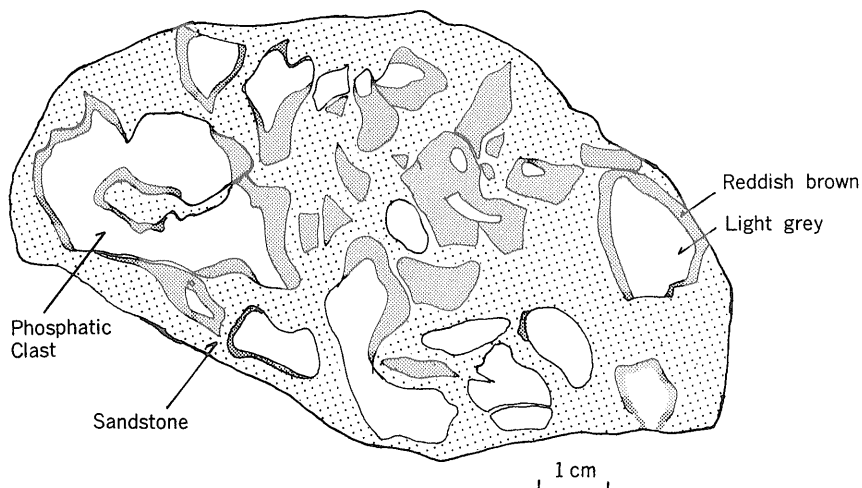


Fig. 7 Plastically deformed but fragmented phosphatic clasts in the Pliocene sandstone, Miyazaki district (modified after TSUNETO, 1897).

water actively upwelling in offshore areas, (2) accumulation of a large amount of organic remains sinking through a short water column and (3) decomposition of organic remains and precipitation of released phosphorous as apatite or Ca-phosphate in the sediments under a slightly alkaline (pH=7.0-7.4) and mildly reducing condition (BENTON, 1980; LOUGHMAN, 1984), as observed for modern marine phosphatic nodules (BURNETT, 1977; BATURIN and BEZRUKOW, 1979;

VEEH *et al.*, 1979; BATURIN, 1982; BURNETT *et al.*, 1980).

The above theory for the origin of marine phosphate has been widely accepted in recent years, and seems conformable with the occurrence of Late Cenozoic phosphatic rocks in Japan in respect of the depositional environments. In addition phosphatic nodule-bearing beds of the Noto Peninsula sparsely include glauconite and is underlain by glauconite beds (MORITANI, 1967),

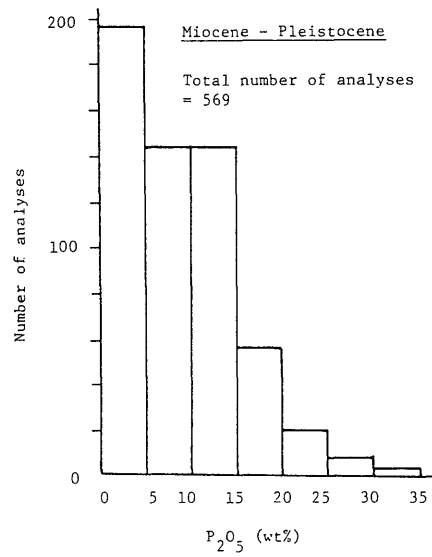


Fig. 8 P<sub>2</sub>O<sub>5</sub> content histogram for Late Cenozoic marine phosphatic rocks.

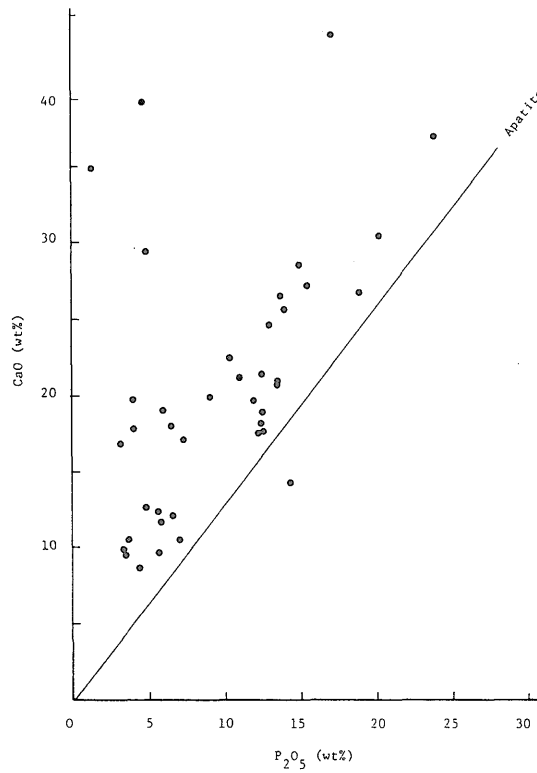


Fig. 9 CaO-P<sub>2</sub>O<sub>5</sub> relation of Late Cenozoic marine phosphatic rocks from Miyazaki, Yamagata and Akita districts.

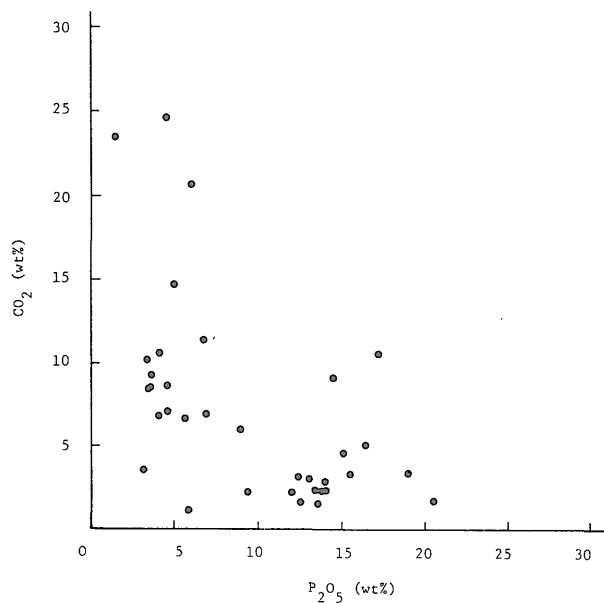


Fig. 10 CO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> relation of Late Cenozoic marine phosphatic rocks from Miyazaki, Yamagata and Akita districts.

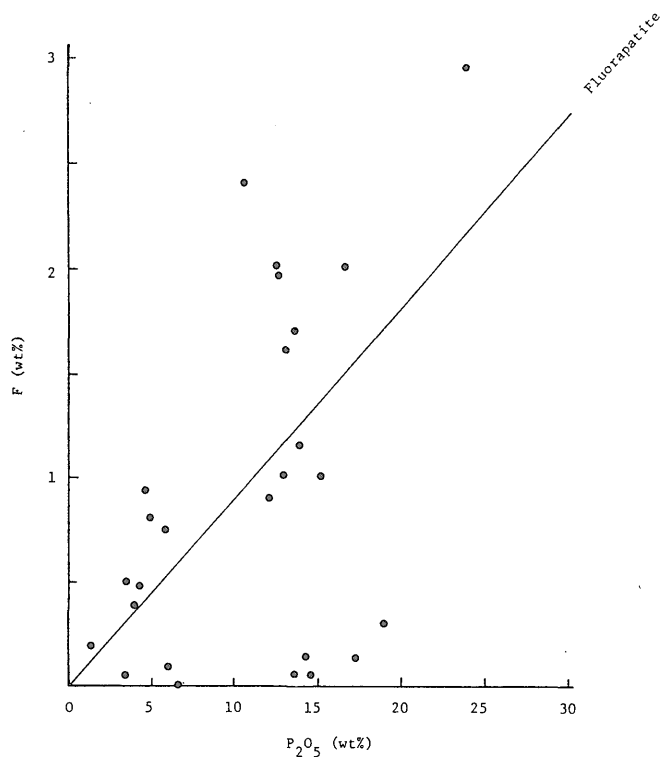


Fig. 11 F-P<sub>2</sub>O<sub>5</sub> relation of Late Cenozoic marine phosphatic rocks from Miyazaki, Yamagata and Akita districts.

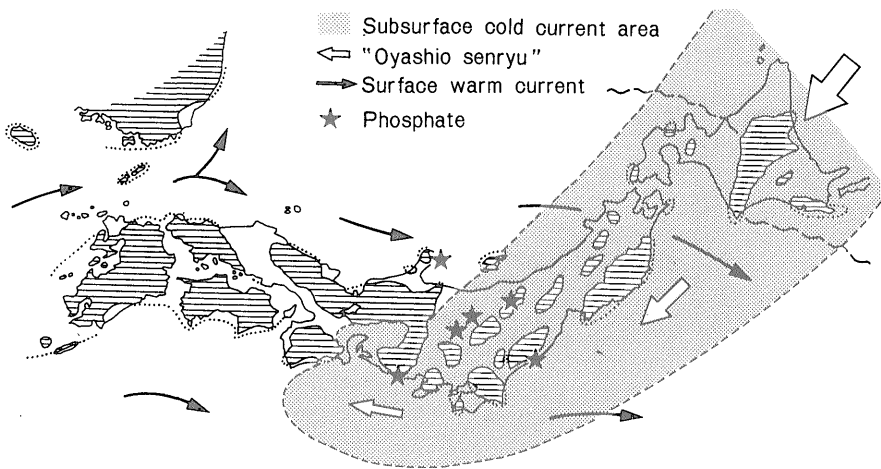


Fig. 12 Paleocurrents and phosphate occurrence of late Early to early Middle Miocene time (16-13 Ma). Paleogeographic map adopted from TSUCHI (1981).

suggesting a mildly reducing condition for phosphate-precipitation. Glauconite is common in late Early to early Middle Miocene shallow marine sediments (SHIMADA, 1986). Late Cenozoic phosphatic rocks in Japan occur in continental shelf to slope sediments which include variable amounts of carbonate and/or siliceous bioclasts. Especially late Early to early Middle Miocene phosphatic rocks are found in the mixing zone of cold and warm currents of that time (Fig. 12), i. e. in a potentially active upwelling zone.

It is known that bottom water currents in the equatorial Pacific Ocean became abruptly active about 15 Ma (VAN ANDEL *et al.*, 1976) coincident with the growth of Antarctic ice-sheet that intermittently lasted since 36 Ma (MILLER *et al.*, 1987). This has made upwelling active in the northern Pacific rim (BARRON and KELLER, 1983), and raised the biological productivity especially at the onset of upwelling of fairly nutrient-rich old bottom water. Therefore, phosphate precipitation was active not only in Japan Arcs but also in the continental margin of California (GARRISON *et al.*, 1986) during late Early to early Middle Miocene time. Phosphate of that time is less abundant in Japan, possibly due to higher contribution of terrigenous materials, lower

biological productivity or poor preservation of organic matter (poor development of oxygen-minimum zone).

Upwelling in the northern Pacific rim has been active since Middle Miocene (BARRON and KELLER, 1983), and probably enhanced the development of oxygen minimum zone. On the other hand, Late Cenozoic basins in the Pacific rim rapidly deepened in Middle Miocene time, and rapidly shallowed in Late Miocene to Pleistocene time with increasing terrigenous contribution (e. g. INGLE, 1981). Therefore, the sediments in those basins were presumably deposited below the oxygen-minimum zone during the most period of Middle Miocene time with little phosphate, but could have been deposited within the oxygen-minimum zone and possibly had a chance to form phosphatic rocks two times, i. e. in late Early to early Middle Miocene time and Late Miocene to Pleistocene time. However, increasing terrigenous contribution to the sediments of Late Miocene to Pleistocene time lowered the organic matter content (cf. HONZA *et al.*, 1982), so probably lowered the phosphorous content.

Late Cenozoic marine phosphatic rocks in Japan have not been yet studied in detail, and there are only a few data. However, I render to speculate a close relation of their occurrence to



the depositional environments and more common occurrence of phosphatic rocks in the late Cenozoic of Japan.

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## 日本の後期新生代海成磷酸塩岩に関する覚え書き

鹿野和彦

### 要旨

我国に産する後期新生代海成磷酸塩の産状とその母岩の堆積環境などについて文献を基にまとめた。後期新生代海成磷酸塩の多くは前期中新世後期-中期中新世及び後期中新世-更新世の大陸期-大陸斜面堆積物中に炭酸塩と共に団塊をなして産し、 $P_2O_5$  15-20 wt%以下である。前期中新世後期-中期中新世のものは当時の暖流と寒流の潮境付近に産する。磷酸塩のこのような産状は母岩の堆積環境と密接に関係しているように見える。

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