



# Cenozoic history of phosphogenesis recorded in the ferromanganese crusts of central and western Pacific seamounts: Implications for deepwater circulation and phosphorus budgets

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## ABSTRACT

Ages of seamount phosphatization episodes have been revised for 14 mid-plate seamounts in the western and central Pacific using the most up-to-date marine Sr isotope curve and <sup>87</sup>Sr/<sup>86</sup>Sr data from the literature. The new ages provide a composite geologic history of phosphatization consistent with Cenozoic climate history. Phosphatization on mid-Pacific seamounts took place only between 36 and 12 Ma, and it peaked at the Eocene/Oligocene (E/O) transition (~34 Ma). The unprecedented appearance of prominent amounts of phosphorites at the E/O transition, and frequent recurrences of it afterwards, suggests that a new mechanism came into play at that time, namely the intensification of the advective flow of bottom water, which accelerated the phosphorus cycle. In contrast, the absence of phosphorites younger than 12 Ma suggests another fundamental change in process, associated with the shift to a dry and cold climate that probably resulted in a decrease in the riverine input of labile phosphorus. The drastic decrease in the frequency of hiatuses in ocean-floor depositional records also indicates weakened bottom currents as a possible explanation for the absence of seamount phosphorite since 12 Ma. A phosphorus flux is a critical variable in modeling the response of the Earth system to climate forcing in the geologic past. Thus, the changes in phosphorus flux across the E/O boundary and around 12 Ma justify further study.

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## 1. Introduction

Phosphorus is a key element for understanding long-term feedback mechanisms between climate, environment, and ecology because its availability governs ocean productivity on long time-scales (Smith, 1984; Follmi, 1996; Delaney, 1998; Tyrrell, 1999). The variations in phosphorus burial rates in the geological past are probably associated with changes of ocean productivity and continental weathering rates, both of which are important mechanisms for the drawdown of atmospheric CO<sub>2</sub> (Raymo and Ruddiman, 1992). For this reason, quantifying sizable marine sedimentary phosphate deposits, and understanding their stratigraphy, can be informative with regards to climate change and its causal relationship with the phosphorus cycle in the geologic past.

Phosphorite on mid-plate seamounts is one of four major types of marine phosphorite deposits, the others being 1) continental shelf; 2) submarine plateau, ridge, and bank; and 3) island atoll, and within atoll lagoon (Hein et al., 1993). Seamount phosphate deposits have been reported in the Pacific, Atlantic, and Indian oceans and adjacent

seas (Hein et al., 1993; Koschinsky et al., 1997; Jones et al., 2002; Glasby et al., 2007; Ren et al., 2007), and they occur within layers of hydrogenetic ferromanganese crust (hereafter called Fe–Mn crust) that have grown on the flanks of seamounts for as long as 70 million years at very slow growth rates (1–15 mm/my) (Segl et al., 1984; Puteanus and Halbach, 1988; Ingram et al., 1990; Kim et al., 2006; Ren et al., 2007). The association of seamount phosphorite with long-grown Fe–Mn crusts is very meaningful from a paleoclimatic and paleoceanographic point of view because the deposits may provide a record of fertile ocean conditions. A growing number of researchers have used Fe–Mn crusts for reconstructions of paleoclimatic and paleoceanographic conditions in the Pacific and Southern Oceans using their radiogenic Nd and Pb isotope compositions (Christensen et al., 1997; Frank, 2002; Klemm et al., 2007; Ling et al., 2005; Meynadier et al., 2008; van de Flierdt et al., 2003, 2004).

There is general agreement on the mechanism of phosphorite precipitation on the flanks of seamounts: it involves an expansion of the suboxic oxygen minimum zone (OMZ), the result of increased productivity of surface waters (Halbach and Puteanus, 1984; Halbach et al., 1989; Koschinsky et al., 1997; Jones et al., 2002). The Fe–Mn crust formation takes place below the OMZ where Mn<sup>2+</sup>-rich and O<sub>2</sub>-poor water is mixed with O<sub>2</sub>-rich deep water (Halbach and Puteanus, 1984). When the OMZ expands due to increased surface water productivity

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and consumption of O<sub>2</sub> during the decay of sinking particles, the suboxic and phosphate-rich water is brought down to the crust-covered slopes of seamounts and promotes the precipitation of phosphorite (Halbach et al., 1989). Thus, the proposed mechanism for the formation of seamount phosphorite has the prerequisite of high surface water productivity.

The connection between seamount phosphorite precipitation and global climate change was first demonstrated by Hein et al. (1993). They found that 87% of phosphorites collected from nine seamounts in the central and western Pacific were formed mainly during two periods of time, the Late Eocene (39–34 Ma, peak at 37 Ma) and the Late Oligocene/Early Miocene (27–21 Ma, peak at 25 Ma). The wide spatial distribution of their sampling sites, with a latitudinal span from 8°N to 22°N, led them to conclude that global climate transitions were triggering mechanisms for phosphate precipitation. Their findings suggested that the history of seamount phosphorite precipitation could be used to reconstruct the paleoclimatic and paleoceanographic conditions of the Pacific in terms of global ocean fertility. However, their data do not provide any direct correlations with global climatic events that might have been responsible for fertile ocean conditions, and this inconsistency may reflect the differences in age models between marine Sr isotope curves and other methods used to date global climate events. Such inconsistencies are also found among the sources of data on the ages of seamount phosphorites (Hein et al., 1993; McMurtry et al., 1994; Yoo et al., 2001; Hyeong et al., 2008), partly because these workers have used different marine Sr isotope curves for the projection of phosphorite ages from their <sup>87</sup>Sr/<sup>86</sup>Sr ratios.

In order to reconstruct a history of seamount phosphatization that is consistent with the available data (Hein et al., 1993; McMurtry et al., 1994; Yoo et al., 2001; Hyeong et al., 2008) and with model dates of climate change, we have calculated new phosphorite ages using <sup>87</sup>Sr/<sup>86</sup>Sr data from the literature and the Sr LOWESS fit (McArthur et al., 2001). The new age data allow us to address the connections between phosphatization and global climate change and the implications for global phosphorus budgets during the Cenozoic. We have also used Co-chronology to determine the ages of Fe–Mn crusts from four Magellan seamounts studied by Yoo et al. (2001) and Hyeong et al. (2008). The data help us understand the growth history of the Fe–Mn crusts that host phosphorite precipitates, and to single out the correct phosphatization age from the multiple possibilities provided by Sr isotope ratios.

## 2. Study area and methods

The seamounts that provided the Fe–Mn crust samples for this study, as well as the phosphorite age data in the literature, are located in the western and central Pacific (Fig. 1). The seamounts were formed

by hot spot activities south of the equator during the Cretaceous, and the seamounts have been carried to their present positions by the movement of the Pacific plate (Hein et al., 1993; McMurtry et al., 1994; Kim et al., 2006). Eight representative Fe–Mn crust samples from four seamounts, Lemkein (166°05'E, 9°18'N), Lomilik (161°37'E, 11°42'N), OSM2 (157°35'E, 13°55'N), and OSM7 (152°00'E, 17°00'N), located among the Magellan seamounts (Fig. 1), were analyzed for their chronology and phosphorus contents. Phosphorite samples from these seamounts have previously been dated by Yoo et al. (2001) and Hyeong et al. (2008). The Fe–Mn crust samples consist of 3 or 4 well-defined layers (labeled layers 1–4 from top to bottom) with distinct textural and geochemical compositions (Kim et al., 2006). The top three layers are found in all samples examined, but bottom layer 4 is observed only in OSM2 and OSM7, the two northernmost seamounts. The visible phosphorite precipitates are present only in the two inner layers.

Bulk Fe–Mn crusts were sampled for elemental chemical analysis using a dental drill at 4–10 mm intervals along a specimen slab. A split of oven-dried bulk powder sample was dissolved in a mixture of HCl and HF at 150 °C. After evaporation, the residue was dissolved in 0.1 M HCl. The elemental contents (Co, Mn, Fe, and P) were determined on a Perkin–Elmer DV3300 ICP-OES at the Korea Ocean Research and Development Institute. The external precision for the analyses was within ±5%. Some of the chemical data, for layers 1 and 2, was published in Kim et al. (2006) in connection with age determinations.

The ages of the Fe–Mn crusts were determined using Co-chronology, a method that is based on the inverse relationship between the Co content of the crusts and their rate of accumulation (Manheim, 1986; Puteanus and Halbach, 1988; McMurtry et al., 1994; Frank et al., 1999). Based on the results of Frank et al. (1999), we applied the Co-chronology of Puteanus and Halbach (1988) to estimate the growth rate of crusts with Co contents greater than 0.7%, and the Co-chronology of McMurtry et al. (1994) for samples with Co contents less than 0.7%.

## 3. Results and discussion

### 3.1. Ages of the Fe–Mn crusts

The age of an Fe–Mn crust helps us understand how long it has been recording phosphogenetic events, and it can also be used to single out the correct age of the phosphorite from the multiple possibilities provided by the <sup>87</sup>Sr/<sup>86</sup>Sr ratios (as discussed in the next section). The average growth rates of the studied crusts varied from 1.7 to 2.5 mm/Myr, giving maximum crust ages of 38 to 64 million years, depending on the thickness of the crust and the seamount where the particular sample was taken (Table 1, Fig. 2). The data indicate that the Fe–Mn crusts on

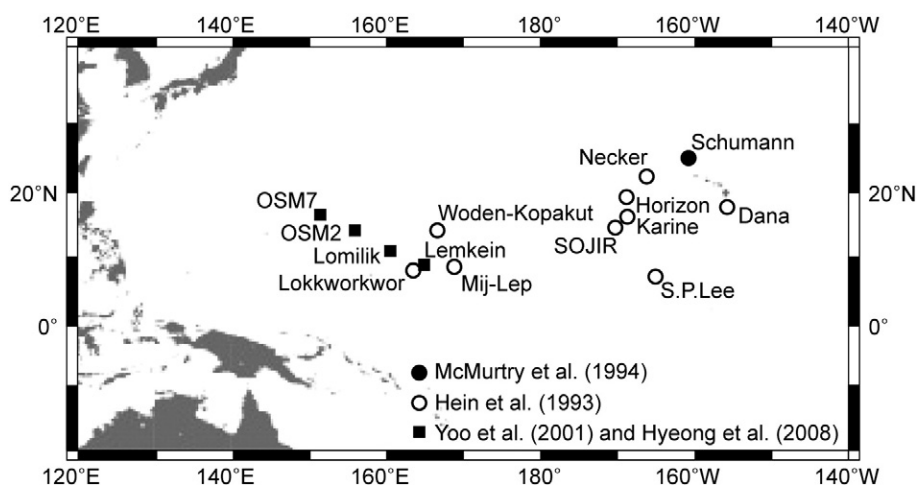


Fig. 1. Locations of seamounts discussed in this study.

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