Variation of the Fe/Mn ratio of ferromanganese crusts from the Central North Pacific: implication for paleoclimate changes[*]

LU Zunli[1][***], LING Hongfei[1][**], ZHOU Feng[1], JIANG Shaoyong[1],
CHEN Xiaoming[1] and ZHOU Huaiyang[2]

(1. State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing 210093, China;
2. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China)

Abstract   Contents of Fe, Mn and other elements in four ferromanganese crusts recovered from the central North Pacific are analyzed at high depth-resolution by electron microprobe for reconstructing factors controlling their deposition. Manganese (IV) in hydrogenetic ferromanganese crusts is mainly supplied as colloidal precipitates from the Oxygen Minimum Zone (OMZ), which concentrates high amounts of dissolved Mn (II). The iron is derived from carbonate dissolution and silicate particles of eolian dust. An increase in paleoproductivity during cooler climate would potentially lead to a decrease in Mn deposition due to enlargement of the OMZ which has a "temporary storage" effect for Mn. On the other hand, not affected by the OMZ, the iron entering the Fe-Mn crust would likely increase with the eolian dust input and surface productivity at glacial stages. As a result, the increasing Fe/Mn ratio should indicate a cooling climate. This is supported by the following observations. In the profile of the past 1Ma, the variations of Fe/Mn ratio coincide with benthic oxygen isotope fluctuation in glacial-interglacial cycles. Three episodes with high Fe/Mn ratios, approximately at 2.6, 1.8 and 0.8 Ma, are detected within the past 3 Ma and coincide with major climate transitions and cooling events. The secular evolution pattern of Fe/Mn ratio in the Cenozoic is similar to the Pb isotope evolution which is mainly controlled by eolian dust and related to climate. The Fe/Mn evolution pattern is also broadly consistent with the global deep-sea oxygen isotope records. Therefore, Fe/Mn ratio recorded in the ferromanganese crusts may be a new proxy for climate change.

Keywords: Fe/Mn ratio, ferromanganese crust, central North Pacific, paleoclimate.

Hydrogenetic ferromanganese crusts (Fe-Mn crusts hereafter), are inorganic colloid precipitates from seawater, which are believed to have recorded the evolution of elemental and isotopic compositions of seawater over time[1—7]. Studies on trace elements and isotopes have brought more insights than studies on iron and manganese contents. The Mn/Fe ratio has been considered to reflect water depth, deep-water oxygenation[8,9], and has also been suggested as a reliable criterion for distinguishing different genetic types of ferromanganese deposits[10]. A possible relationship between the Fe/Mn ratio of Fe-Mn crusts and the climate changes has, however, not been explored in detail yet, although the cyclicity of Sr concentration in crusts has been found to be correlated with the Quaternary glacial-interglacial cycles[11] and series of Mn, Fe, Al and Fe/Mn in Pacific Mn-nodules has been revealed to have cyclicity resembling Milankovitch orbital cycles[12].

In this paper we focus on the sources and deposition factors of Fe and Mn in Fe-Mn crusts collected in the North Pacific. We examine the variations of these sources and compare them with the changes in global or regional climate, bio-productivity in the ocean and continental input over time. By electron microprobe profiling, we find that variations of the Fe/Mn ratio recorded in the Fe-Mn crust layers have a close correlation to the cooling and warming trends of the global climate over the past up to 80 Ma. This is demonstrated by comparison of Fe/Mn ratio profiles with oceanic oxygen isotope evolution on different time scales and with secular Pb isotope evolution. The similarity between them suggests that the Fe/Mn ratio in the Fe-Mn crusts is a probable proxy for part of the global climate change.

1   Samples and analytical methods

Four ferromanganese crusts recovered from the Central North Pacific (Table 1, Fig. 1) were analyzed with electron microprobe. Three of them from

relatively shallow water depths ($<$ 2800 m) contain two growth generations, young un-phosphatized layers and older phosphatized layers. One crust (CJ-01) growing at the deepest water depth (3082 m) has no phosphatized layer. This is consistent with previous observations that phosphatization only occurred in the old parts of crusts from relatively shallow water depths ($<$ 3000 m)[5, 13, 14]. Element contents confirm that all these crusts are typical hydrogenetic precipitates[15, 16] with high enrichments of Co and Ni (0.3%—1.6%).
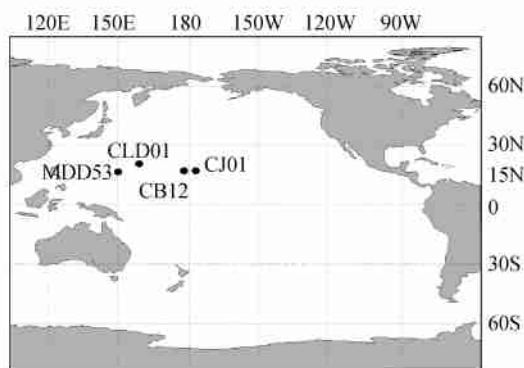

Fig. 1.   Sampling locations of the investigated ferromanganese crusts.

Table 1.   Sampling sites and thickness, age, and growth generations of seamount Fe-Mn crusts

Crust	Location	Water depth (m)	Thickness (mm)	Part 1[1] (mm)	Part 2[2] (mm)
CJ-01	177°43′W / 17°59′N	3082	70		
CB-12	178°40′E / 18°00′N	2381	69	38	31
CLD-01	161°12′E / 22°15′N	2310	77	52	25
MDD-53	150°28′E / 17°45′N	2800	104	60	44

1) Part 1, young un-phosphatized part; 2) part 2, old phosphatized part.

The crusts were cut into slabs from top to substrate rock. The slabs were molded in resin and polished for analysis with a high-resolution electron probe microscope analyzer (Super-probe JEOL JXA-8800M)[17]. Concentrations of 11 elements were determined at different depth resolutions with electron beam diameter of 2 μm. Measurement intervals of 0.01—0.04 mm within the top 5—8 mm of the crusts were carried out for investigations at middle (3 Ma-present) to short (1 Ma-present) time scales in three crusts. In all four crusts, points with intervals of 0.4—0.6 mm through the whole crust are for investigations of secular evolution. The points with Si content higher than 10%, Al higher than 5% or total amount less than 50% are deleted from the data sets, because they are thought to be aluminium-silicate de-

tritus or uneven surfaces with micro-notches. The in-run precision for the measurement is better than 10%. More than 1100 points in total were analyzed for the four crusts. It is difficult to present all the data by tables due to the space limitation of the paper, so only figures are presented here. The short interval results for the top 5—8 mm of crust CJ01 and the long interval results of crusts CJ01, CB12 and CLD01 will be found in the web Background Data Set of Ling et al.[6]. The short interval results for the top layers of crust CB12 and CJ01 and the long interval results of crust MDD53 are available on request to the authors.

2   Results

2.1   Growth generations and age estimate of crusts

The flux of Co incorporation into crusts has been suggested to be constant during the crust formation[18]. Thus, growth rates R (mm/Ma) and ages of crust layers can be estimated by using two empirical Co-chronometers[15, 18, 19].

$$R = 1.28/([Co] - 0.24), \qquad (1)$$
$$R = 0.68/[Co]^{1.67}, \qquad (2)$$

where [Co] is the Co concentration in crust in weight percent. Equation (1) is considered to be valid for Co-rich ($>$ 0.8%) Pacific seamount crusts and Eq. (2) is more reliable for Co-poor ($<$ 0.7%) crusts. A comparison of ^{10}Be/^{9}Be and Co-based dating supports the validity of this approach for crusts in the Pacific[5]. Equation (1) is applied to crust CJ01 since its average Co content is greater than 0.8. Except for the top 5—8 mm where Co contents vary from well above 0.8% to well below 0.7% so that both equations are used accordingly, the growth rates and ages of all parts of the other three crusts are calculated using Eq. (2), because their Co contents are mostly below 0.7, and Co contents in the phosphatized parts of the crusts have been corrected according to the method proposed by Puteanus & Halbach[15] before age calculation. The results show that crusts CJ01, CLD01 and MDD53 started to grow from 74 to 78 Ma ago. This is consistent with the Os isotope evolution curve of crust D11-1 (Burton, personal communication) and CD29-2 (Bolz et al., personal communication) from the North Pacific which shows a nadir of ^{187}Os/^{188}Os ratios corresponding to the Cretaceous/Tertiary boundary in the low part of the crusts. However, crust CB12 yielded much younger Co model age (49.7 Ma). Nevertheless, all four crusts of

this study and crusts D11-1 and CD29-2 have very similar Pb isotope variation patterns and thus they are believed to have similar ages[4, 6]. The younger age of crust CB12 may have been caused by growth hiatus in its upper part, while Co constant flux model cannot detect growth hiatus in crusts. Thus the ages of crust CB12 are adjusted according to the similarity of its Pb isotope variation pattern to those of the other crusts, and an age of 82.7 Ma for its bottom is yielded. In the crusts of this study, generally, average growth rates are lower in younger crust layers and higher in older layers, similar to previous observations for other Pacific crusts, which is possibly related to different ocean circulation conditions[20—23].

2.2　Variations of Fe/Mn ratio at different time scales

Within the top part of the crusts corresponding to the past 1 Ma, 54, 69 and 101 points were analyzed respectively in three crusts as fine-scale profiles. Fe/Mn ratios in top layers of the crusts show cyclic change similar to deep-water $\delta^{18}O$ variation[24], with high values during the glacial intervals and low values during the inter-glacial intervals, although detailed differences of Fe/Mn variations exist among the crusts (Fig. 2).
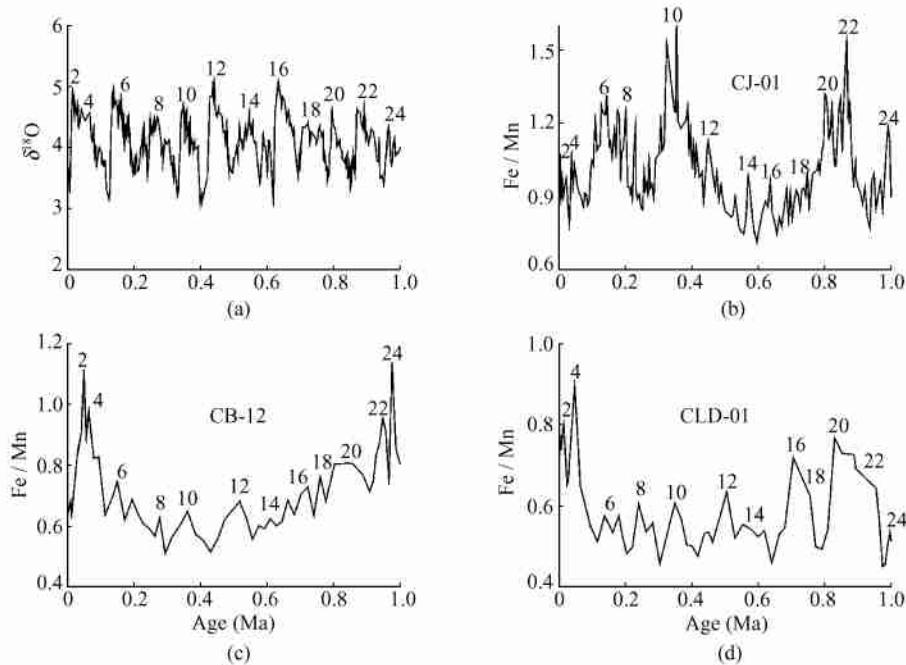

Fig. 2.　Fe/Mn ratios of the top part (within 1 Ma) of crusts CJ-01, CB-12 and CLD-01 analyzed by electron microprobe co-varying with the glacial-interglacial cycles corresponding to the oxygen isotope stages of 2 to 24.

When the Fe/Mn ratios are examined at a longer time scale, the most distinct common feature is three peaks appearing in each crust approximately at 2.6, 1.8 and 0.8 Ma, although there are two extra peaks in the uppermost part of crust CJ01 (Fig. 3). All four crusts studied have similar secular evolution patterns (Fig. 4): the Fe/Mn ratio decreases from the lower part or bottom of the crust to the middle part (~50 Ma), and then increases to the top layer.

3　Discussion

3.1　Fe/Mn ratios in the Fe-Mn crusts: a new proxy of paleoclimate changes

The chemical similarity between Fe and Mn is reflected geochemically in the close association in their marine deposits, but the sources of the two elements are different. For hydrogenetic Fe-Mn crusts, the Mn is mainly supplied from the Oxygen Minimum Zone (OMZ), at the bottom of which dissolved Mn (II) is oxidized to form colloidal Mn (IV) oxides or hydroxides and precipitates into Fe-Mn crusts and nodules[25]. There are two main contributors of Fe to Fe-Mn crusts, carbonate dissolution enabled by a sufficient bio-productivity, and disassociation of colloidal Al-Fe-silicate particle mainly from eolian input in the open oceans[8]. Thus the Fe/Mn ratio recorded in the Fe-Mn crusts should be influenced by the temporal fluctuations of these sources: changes in the intensity of the OMZ, the paleo-productivity, and the eolian

dust input. In the following sections, we will discuss how the deposition of Fe and Mn into the Fe-Mn crusts relates to these three sources and how these sources change correspondingly with the climate changes, and examine the reflection of those changes in the Fe/Mn ratio records in different time scales.

3.1.1 Mn deposition and its relation to paleoclimate

The reduced Mn^{2+} species dissolved and enriched in the OMZ[26] is oxidized when OMZ water is mixed with upwelling oxygen-rich deeper water forced by submarine topography, seamount slopes or by turbulent process, and so colloidal $\delta\text{-}MnO_x$ phases are formed[25]. Once $\delta\text{-}MnO_x$ formation starts it will trigger more autocatalytic oxidation of dissolved Mn^{2+}[27]. Manganese and other oxide- or hydroxide-metals form mixed colloids due to their surface charges and precipitate onto sediment-free substrate rocks on seamounts to form Fe-Mn crusts[25].

Formation of the manganese maximum in the OMZ has long been in debate[26,28,29]. Three factors were given to explain this maximum: (1) reduction of Mn (IV) oxides in continental margin sediments into dissolved Mn (II) and subsequent transport to the open ocean; (2) reduction of Mn (IV) oxides from water column entering the OMZ with low oxygen and low pH value; (3) release of soluble Mn (II) from organic matter decomposition. Some authors emphasized the offshore transport of Mn released from continental margin sediments[30]. Later study[31] confirmed that the Mn (II) flux across the sediment-water interface is much greater at the continental shelf than in the OMZ. However, based on model calculation, Johnson et al.[32] argued that the dissolved Mn in the OMZ was controlled by a balance between Mn (II) released from organic matter and the output from the system by oxidation to particulate Mn oxides, and other sources like horizontal mixing or reduction of Mn (IV) oxides were not necessary to account for the Mn maximum in the OMZ.

During the glacial stages, the maximum of surface productivity occurred in the North Pacific due to the influence of Subarctic water[33], which consequently caused the enlargement of the OMZ[34,35]. The enhanced OMZ would accumulate more dissolved Mn (II) before intensification process of the OMZ stopped[35]. Since the hydrothermal input of Mn does not fluctuate with climate, the riverine input of Mn is mainly trapped in the continental shelf sediments and

the eolian input of Mn is an order of magnitude lower than hydrothermal and riverine input[36], the change in overall input of Mn into the Pacific can be considered insignificant when compared with the change in Mn output caused by changing OMZ volume and intensity on a short time scale. The volume and intensity of the OMZ which was related to bioproductivity served as a "temporary storage" in the Mn budget of water column and might have considerable effects on the sink of Mn into Fe-Mn crusts. Consequently, an increase in productivity due to a cooling climate would lead to a decrease in Mn deposition and thus an increase in the Fe/Mn ratio in the Fe-Mn crusts, and vice versa, on the time scale of glacial-interglacial sequence. On a longer time scale, output and input of Mn would be in balance. If Mn input is relatively stable with small variation mainly resulting from variation of hydrothermal venting at seafloor, the variation of Fe/Mn ratio in crusts would be dominated by variation in Fe input.

3.1.2   Fe deposition and its relation to paleoclimate

Iron in Fe-Mn crusts is primarily contained in three solid phases: (1) amorphous FeOOH intergrown with Mn oxide ($\delta\text{-}MnO_2$); (2) oxalate-reducible amorphous $FeOOH \cdot xH_2O$; (3) silicates and aluminosilicates[23]. The common Fe sources of the first and second phase are the colloidal Fe hydroxides released in the water column from the dissolution of carbonate plankton skeletons. The input of these biogenic carbonates fluctuates with surface productivity and is controlled by sea surface temperature. Thus this Fe input to intermediate and deepwater column can be correlated with climate conditions. Similar to Mn, the increase in surface productivity in the North Pacific[33] will cause a discernable increase in Fe input to the deeper water column from carbonate dissolution. The eolian dust supplies the third phase[8], but unlike Mn, these Fe compounds do not undergo complex redox processes. They deposit into the crusts in the forms of amorphous hydroxides and silicates, similar to those entering the water column by carbonate dissolution and eolian input, respectively. Thus, the "temporary storage" effect of OMZ, which complicates the relation between the deposition of Mn and the climate, does not influence the deposition of Fe. Therefore, during glacial stages the iron entering the Fe-Mn crusts will increase with the increasing surface productivity and elevates eolian dust input into the North Pacific[33], meanwhile, Mn deposition will decrease. Consequently, Fe/Mn ratio in Fe-Mn crusts

will increase.

3.2　Climate changes recorded by the Fe/ Mn ratio

Following the above discussion, we conclude that the Fe/ Mn ratio will increase during the glacial stages as the paleoproductivity and eolian input increase. In the profiles representing the past 1 Ma of all the investigated crusts (Fig. 2), the Fe/Mn ratio apparently fluctuates with glacial cycles and roughly corresponds to 24 oxygen isotope stages, although the inception of some Fe/Mn fluctuation stages is not precisely consistent with their corresponding oxygen isotope stages. High Fe/Mn ratios are observed in stages 2, 4 in crusts CB-12, CLD-01 and stages 6, 8, 10 in CJ-01. This difference is probably a result of the difference in water-depth between CJ-01 (> 3000 m), CB-12 and CLD-01 (both < 3000 m), but further investigations are needed. Within the past 3 Ma records, all three crusts show peak Fe/Mn ratios for the following periods of time: 0.7—1 Ma, 1.5—1.8 Ma and 2.4—2.6 Ma (Fig. 3). These episodes coincide with major climate transitions during the past 3 Ma. Global ice volume variability[37] and Lake Baikal record[38] demonstrated that the

Earth's glacial-interglacial cyclicity changed from 41 ka cycles (the Earth's obliquity), to 100 ka cycles (the Earth's orbital eccentricity), at about 0.6—0.8 Ma. Between 1.8 and 0.6, the 41 ka obliquity cycle was particularly strong. Two major cooling episodes at 2.8—2.6 Ma and 1.8—1.6 Ma ago were also recorded in biogenic silica sediment of Lake Baikal[38]. The cooling episode from 1.8 to 1.6 Ma coincided with the Plio-Pleistocene boundary. Although these cooling episodes can be regional events, the increased physical erosion will lead to an enhanced eolian input into the North Pacific and be reflected in the increase of Fe/Mn ratio in the Fe/Mn crusts.

In the case of the secular evolution pattern of Fe/Mn ratio of each crust studied, the decrease from the bottom (75—80 Ma) to the part of about 50 Ma, and then increase to the present time (Fig. 4(a), (b), (c), (d)) imply a general trend of warming and then cooling climate. The secular Fe/Mn evolution pattern of the un-phosphatized crust (CJ01) is surprisingly similar to its Pb isotope evolution curve (Fig. 4(e))[6]. As most of Pb with radiogenic isotope signature in the Pacific has been controlled by eolian input, this similarity is not a coincidence only. Pb-Pb isotope correlations also suggest a warmest period with the least eolian dust input at 50—60 Ma and strong eolian input at late Cretaceous and Pleistocene[6]. The secular climate pattern suggested by Fe/Mn ratio of the crusts is also consistent with other studies of sedimentary archives. Zachos et al.[39] presented global deep-sea oxygen isotope records based on data compiled from more than 40 DSDP and ODP sites (Fig. 4(f)). During much of the last 70 Ma, the Earth climate system experienced continuous change, warmed up to extremes of expansive warmth with ice-free poles and then cooled to extremes of cold with massive continental ice-sheets and polar ice caps. The evolution patterns of Fe/Mn ratio of the crusts (Fig. 4(a), (b), (c), (d)) broadly resemble the oxygen isotope evolution curve (Fig. 4(f)). What has to be pointed out is that the Fe/Mn ratios in the phosphatized older part of crusts CLD01, CB12 and MDD53 are much lower than those in the coeval part of the un-phosphatized crust (CJ-01). The decrease trend of Fe/Mn ratio from bottom to middle part in the phosphatized crusts is much less evident than that in the un-phosphatized crust. These could be a result of the effect of phosphatization. During post-depositional phosphatization in the old part of Fe-Mn crusts in the North Pacific much more iron than manganese
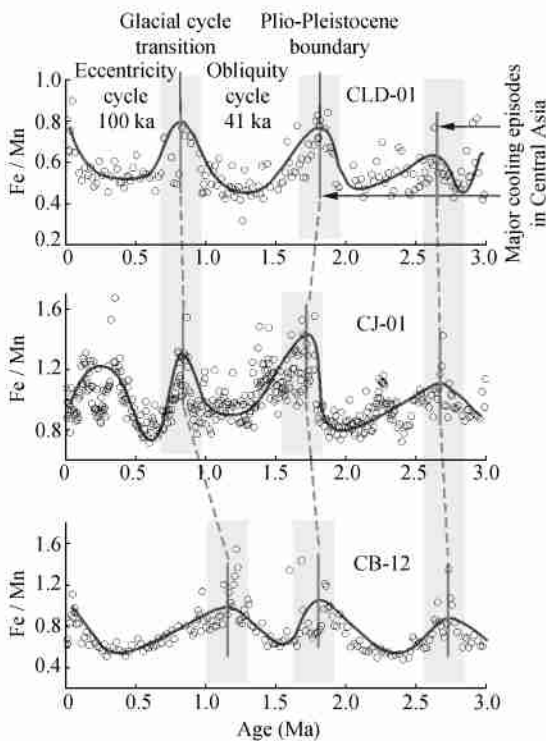

Fig. 3.　Profiles of Fe/Mn ratio in the past 3 Ma showing correspondence to the transition of glacial cyclicity from 41 kyr-cycles to 100 kyr-cycles at approximately 0.6—0.8 Ma and to two major cooling episodes recorded in Asia lake sediments at 1.6—1.8 and 2.6—2.8 Ma.

is believed to be removed from the crusts,[40] causing a decrease in Fe/Mn ratios. The highest average P concentration of the phosphatized old generation of CB-12 (4.21%) supports that it underwent a stronger phosphatization event than the other two phosphatized crusts (3.09% of P for MDD-53 and 2.65% of P for CLD-01), which is consistent with the most apparently altered Fe/Mn ratios in the phosphatized layers. However, in crust MDD53 there is

an abrupt small but clear increase in Fe/Mn at the transition from un-phosphatized part to phosohatized part (Fig. 4(c)), suggesting the effect of phosphatization on Fe/Mn ratio is more complicated than that stated above. Nevertheless, the large variation or decrease of Fe/Mn ratios from the bottom upward as shown by the un-phosphatized crust CJ01 is vanished in crust MDD53, which is similar to the features in other phosphatized crusts (Fig. 4).
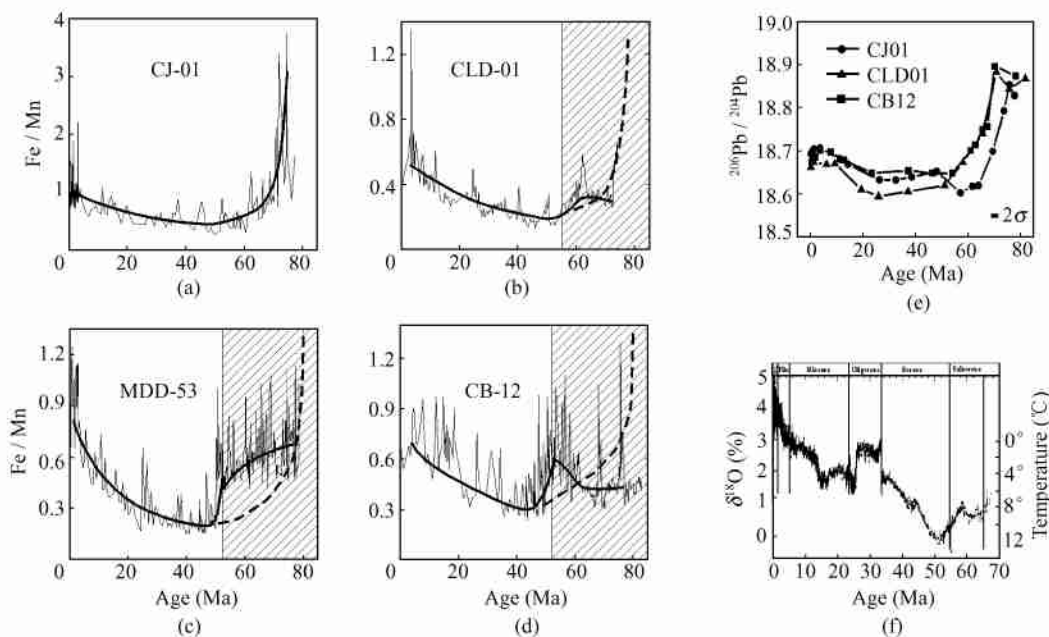

Fig. 4.   Secular evolutions of Fe/Mn ratios in four Fe-Mn crusts showing a similar pattern. (a), (b), (c) and (d) Fe/Mn evolution of the crusts. Note that the Fe/Mn ratios of the phosphatized lower parts (hatched) of the crusts are lower than the coeval ratios in the un-phosphatized crusts (CJ-01). The evolution of Fe/Mn ratio in the phosphatized part of each crust would have been the dashed curve if there were no post-depositional modification by phosphatization. (e) evolution of $^{206}Pb/^{204}Pb$ in crusts CJ01, CLD01 and CB12[6]; (f) variation trend of global deep-sea oxygen isotope records compiled by Zachos et al.[36]. Note that there is certain similarity between Fe/Mn, $^{206}Pb/^{204}Pb$ of crusts and global oceanic $\delta^{18}O$. This is probably because oceanic $\delta^{18}O$ is a reflection of climate, while Fe/Mn and $^{206}Pb/^{204}Pb$ of crusts are mainly related to eolian dust input to the oceans which is also controlled by climate.

4   Conclusions

In this paper, the sources and deposition of Fe and Mn in North Pacific Fe-Mn crusts and variations of these sources with past climate change have been discussed. During the glacial stages, the maximum surface productivity likely caused enlargement of the OMZ, which accumulated more dissolved Mn (II) until its intensification stopped. Since the overall input of Mn into the OMZ can be considered nearly constant, the volume and intensity of OMZ will influence the amount of Mn depositing to Fe-Mn crusts. As a result, the increase in paleoproductivity due to a cooling climate likely led to a decrease in Mn deposition and thus an increase in the Fe/Mn ratio in the

Fe-Mn crusts. But the "temporary storage effect" of OMZ, which complicates the relation between the deposition of Mn and the climate changes, does not influence the deposition of Fe. The iron entering Fe-Mn crusts increases with eolian dust input and surface productivity[33] during glacial stages and consequently causes increased Fe/Mn ratios.

In the 1 Ma profiles, the Fe/Mn ratio fluctuates with glacial cycles and corresponds to 24 oxygen isotope stages. The common feature of the Fe/Mn ratio of the studied crusts over the past 3 Ma is the high values at about 2.6, 1.8, and 0.8 Ma. They apparently coincide with three major climate transitions in the past 3 Ma: (1) the change of glacial-interglacial

cycles from the 41 ka to the 100 ka at about 0.6—0.8 Ma; (2) a major cooling episode at Plio-Pleistocene boundary (1.6—1.8 Ma)[41]; (3) another major cooling episode in Central Asia[38] at 2.8—2.6 Ma ago. The secular evolution pattern of the Fe/Mn ratio is broadly consistent with global deep-sea oxygen and Pb isotope records, supporting that, during the last at least 70 Ma, the Earth climate system has experienced warming to expansive warmth and then cooling to extreme cold. Therefore, Fe/Mn ratios recorded in the Fe-Mn crusts would likely be used as a new proxy for global climates and have its wide applications in different time scales. However, further investigation is needed to fully unravel the effect of phosphatization in the older generation of crusts on the Fe/Mn ratio and Co empirical chronometer and the cause for the higher ratios that occurred at different times in the crusts.

References

1　De Carlo E. H. Paleoceanographic implications of rare earth element variability within a Fe-Mn crust from the central Pacific Ocean. Mar. Geol., 1991, 98: 449—467.

2　von Blanckenburg F., O' Nions R. K., Belshaw N. S. et al. Global distribution of beryllium isotopes in deep ocean water as derived from Fe-Mn crusts. Earth Planet. Sci. Lett., 1996, 141: 213—226.

3　Burton K. W., Ling H. F., O' Nions R. K. et al. Closure of the Central American Isthmus and its impact on North Atlantic Deep water circulation. Nature, 1997, 386: 382—385.

4　Ling H. F., Burton K. W., O' Nions R. K. et al. Evolution of Nd and Pb isotopes in Central Pacific seawater from ferromanganese crusts. Earth Planet. Sci. Lett., 1997, 146: 1—12.

5　Frank M., O' Nions R. K., Hein J. R. et al. 60 Myr records of major elements and Pb-Nd isotopes from hydrogenous ferromanganese crusts: reconstruction of seawater paleochemistry. Geochim. Cosmochim. Acta, 1999, 63: 1689—1708.

6　Ling H. F., Jiang S. Y., Martin F. et al. Differing controls over the Cenozoic Pb and Nd isotope evolution of deepwater in the central North Pacific Ocean. Earth Planet. Sci. Lett. (accepted)

7　Zhou F., Ling H. F., Lu Z. L. et al. Research of lead isotope of ferromanganese crusts from Centrtal Pacific Ocean. Mar. Geol. Quatern. Geol. (in Chinese), (in press).

8　Halbach P. and Puteanus D. The influence of the carbonate dissolution rate on the growth and composition of Co-rich ferromanganese crusts from Central Pacific seamount areas. Earth Planet. Sci. Lett., 1984, 68: 73—87.

9　von Stackelberg U., Kunzendorf H., Marchig V. et al. Growth history of a large ferromanganese crust from the Equatorial North Pacific Nodule Belt. Geol. Jahrb, 1984, A75, 213—235.

10　Halbach P., Friedrich G., von Stackelberg U. et al. Transport and accumulation processes. In: The Manganese Nodulebelt of the Pacific Ocean. Ferdinand Enke, Stuttgart, 1988, 151—158.

11　Zhang Z. Y., Ling H. F., Jiang S. Y. et al. Variation of Sr contents in ferromanganese crusts from the Pacific: A possible paleoclimate proxy. Progress in Natural Science (in Chinese), 2002, 12 (4): 387—391.

12　Han X. Q., Jing X. L., Yang S. F. et al. Rhythmic growth of Pacific ferromanganese nodules and their Milankovitch climatic origin. Earth Planet. Sci. Lett., 2003, 211: 143—157.

13　Halbach P., Kriete C., Prause B. et al. Mechanism to explain the platinum concentration in ferromanganese seamount crusts. Chem. Geol., 1989, 76: 95—106.

14　Hein J. R., Yeh H. W., Gunn S. H. et al. Two major Cenozoic episodes of phosphogenesis recorded in equatorial Pacific seamount deposits. Paleoceanography, 1993, 8: 293—311.

15　Puteanus D. and Halbach P. Correlation of Co concentration and growth rate- a method for age determination of ferromanganese crusts. Chem. Geol., 1988, 69: 73—85.

16　Manheim F. T. Marine cobalt resources. Science, 1986, 232: 600—608.

17　Manheim F. T. and Lane-Bostwick C. M. Cobalt in ferromanganese crusts as a monitor of hydrothermal discharge on the Pacific sea floor. Nature, 1988, 335: 59—62.

18　Futa K., Peterman Z. E., Hein J. R. et al. Strontium and neodymium isotope variations in the ferromanganese crusts from the Central Pacific: Implications for age and source provenance. Geochim. Cosmochim. Acta, 1988, 52, 2229—2233.

19　Jeong K. S., Jung H. S., Kang J. K. et al. Formation of ferromanganese crusts on northwest intertropical Pacific seamounts: electron photomicrography and microprobe chemistry. Mar. Geol., 2000, 162: 541—559.

20　Halbach P., Segl M., Puteanus D. et al. Co-fluxes and growth rates in ferromanganese deposits from central Pacific seamount areas. Nature, 1983, 304: 716—719.

21　Segl M., Mangini J., Beer G. et al. Growth rate variations of manganese nodules and crusts induced by paleoceanographic events. Paleoceanography, 1989, 4(5): 511—530.

22　Ingram B. L., Hein J. R., Farmer G. L. et al. Age determination and growth rates of Pacific ferromanganese deposits using strontium isotopes. Geochim. Cosmochim. Acta, 1990, 54: 1709—1721.

23　Hein J. R., Bohrson W. A. and Schulz M. S. Variations in the fine-scale composition of a central Pacific ferromanganese crust: paleoceanographic implications. Paleoceanography, 1992, 7 (1): 63—77.

24　Mix A. C. Benthic foraminifera stable isotope record from Site 849 (0—5 Ma): Local and global climate changes. In: Proceedings of the Ocean Drilling Program, Scientific Result, 1995, 138: 371.

25　Koschinsky, A. and Halbach P. Sequential leaching of marine ferromanganese precipitates: Genetic implications. Geochim. Cosmochim. Acta, 1995, 59: 5113—5132.

26　Klinkhammer G. P. and Bender M. L. The distribution of manganese in the Pacific Ocean. Earth Planet. Sci. Lett., 1980, 46: 361—384.

27　Stumm W. and Morgan J. J. Aquatic Chemistry. New York: Wiley, 1981.

28　Martin J. H. and Knauer G. A. VERTEX: manganese transport through oxygen minima. Earth Planet. Sci. Lett., 1984, 67: 35—47.

29　Landing W. M. and Bruland K. W. The contrast biogeochemistry of iron and manganese in the Pacific Ocean. Geochim. Cosmochim. Acta, 1987, 51: 29—43.

30　Martin J. H. and Knauer G. A. Lateral transport of manganese within the north-east Pacific Gyre oxygen minimum. Nature, 1985, 314: 524—526.

31　Johnson K. S., Berelson W. M., Coale K. H. et al. Manganese flux from continental margin sediments in a transect through the oxygen minimum. Science, 1992, 257: 1242—1245.

32　Johnson K. S., Coale K. H., Berelson W. M. et al. On the formation of the manganese maximum in the oxygen minimum. Geochim. Cosmochim. Acta, 1996, 60: 1291—1299.

33　Maeda L.，Kawahata H.，Nohara M. et al. Fluctuation of biogenic and abiogenic sedimentation on the Shatsky Rise in the western North Pacific during the late Quaternary. Mar. Geol., 2002, 189: 197—214.

34　Duplessy J. C. and Shackleton N. J. Response of global deep-water circulation to earth's climate change 135, 000—107, 000 years ago. Nature, 1985, 316: 500—507.

35　Kuhn T. and Halbach P. Formation of ferromanganese microcrusts in relation to glacial/ interglacial stages in Pleistocence sediments from Ampere Semount (Subtropical NE Atlantic). Chem. Geol., 1996, 130: 217—232.

36　Chester R. Marine Geochemistry. London: Uwin Hyman, 1990.

37　Rutherford S. and D' Hondt S. Early onset and tropical forcing of 100, 000-year Pleistocene glacial cycles. Nature, 2000, 408: 72—75.

38　Williams D.，Peck J.，Karabanov E.B. et al. Lake Baikal record of continental climate response to orbital insolation during the past 5 million years. Science, 1997, 278: 1114—1117.

39　Zachos J. C.，Pagani M.，Sloan L. et al. Trends rhythms and aberrations in global climate 65 Ma to present. Science, 2001, 292: 686—693.

40　Koschinsky A.，Stascheit A.，Bau M. et al. Effects of phosphatization on the geochemical and mineralogical composition of marine ferromanganese crusts. Geochim. Cosmochim. Acta, 1997, 61: 4079—4094.

41　Van Couvering J. The Pleistocene Boundary and the Beginning of the Quaternary. Cambridge: Cambridge Univ. Press, 1997.