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The distribution of iodine and effects of phosphatization on it in the ferromanganese crusts from the Mid-Pacific Ocean

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Abstract

In the present paper, iodine (I), iron (Fe), manganese (Mn), cobalt (Co), phosphorus (P) and calcium (Ca) contents in three ferromanganese crusts from the Pacific Ocean are measured by spectrophotometric method and inductively coupled plasma atomic emission spectrometers (ICP-AES) to investigate the contents and distribution of iodine in ferromanganese crusts. The results show that iodine contents in three crusts vary between 27.1 and 836 mg/kg, with an average of 172 mg/kg, and the profile of iodine in the three crusts all exhibits a two-stage distribution zone: a young non-phosphatized zone and an old phosphatized zone that is rich in I, P and Ca. The iodine content ratios of old to young zone in MP5D44, CXD62–1 and CXD08–1 are 2.3, 3.4 and 13.7, respectively. The boundary depths of two-stage zone in MP5D44, CXD62–1 and CXD08–1 locate at 4.0 cm, 2.5 cm and 3.75 cm, respectively, and the time of iodine mutation in three crusts ranges from 17–37 Ma derived from ^{129}I dating and Co empirical formula, which is consistent with the times of Cenozoic phosphatization events. The present study shows that the intensity of phosphatization is the main responsible for the distribution pattern of iodine in the crusts on the basis of the correlation analysis. Consequently, iodine is a sensitive indicator for phosphatization.

Key words: ferromanganese crust, iodine, phosphatization, Mid-Pacific Ocean, two-stage distribution

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1 Introduction

The geochemical behavior of iodine is great importance for two reasons. Firstly, iodine is an essential element for humans and other biological species, and the diseases in some regions of world caused by iodine deficiency are occurring. Secondly, radioactive iodine (^{129}I), a cosmogenic radioisotope, can be a useful tool for age dating in geochemical studies (Fehn et al. 2000; Tomaru et al., 2009; Fehn, 2012). The half-life of ^{129}I (15.7 Ma) is an order of magnitude longer than that of ^{10}Be, which allows age determinations up to 80 Ma, i.e., the Tertiary dating.

Iodine is mainly dominated by the marine system. Iodine in seawater exists predominantly as iodate (IO_3^-), iodide (I^-) and dissolved organic iodine. Although the concentration of total dissolved iodine is at around 0.45 μmol/L, those of I^- and IO_3^- are more spatially variable. The deep water in all major ocean basins is high in iodate but low in iodide (Campos et al., 1996; Farrenkopf et al., 1997). Iodide is mainly found in the surface water of the oxic ocean, and at deep water in anoxic basin (Truesdale et al., 2001; Waite et al., 2006). Iodine inventory in the marine sediment, estimated by Muramatsu and Wedepohl (1998) is about 70% of the crustal iodine. Many researchers have significative studies on iodine enrichment mechanism from different angles (Price et al., 1970; Harvey, 1980; Ullman and Aller, 1983; Ullman and Aller, 1985; Wakefield and Elderfield, 1985; Gao et al., 2003; Tomaru and Fehn, 2013). Some scholars think that the iodine enrichment mechanism is associated with organic matter. However, according to different contents of iodine in different redox environments and low iodine in iron-poor sediments, some scientists consider that the distribution of iodine is affected by metal oxides in sediments. Kodama et al. (2006) studied the iodine in solid samples through K-edge XANES, showing iodate was the predominant species of iodine in ferromanganese crust.

Hydrogenetic ferromanganese crusts (hereafter called Fe-Mn crusts or crusts) are formed by direct precipitation of colloidal hydrated metal oxides, which are known to reflect oceanographic conditions by textures and chemical and isotopic compositions (Koschinsky et al., 1996; Claude et al., 2005; Klemm et al., 2005) during their growth. The crusts are characterized by slow growth rates and generation of an extremely high specific-surface area, which promotes the enrichment of trace elements through the scavenging by the major metal oxides (Hein et al., 1997). Crusts have been shown to concentrate cobalt (Co), and Co content has been used to derive an empirical relation for estimating their growth rates (Halbach et al., 1983; Manheim and Lane-Bostwick, 1988; Frank et al., 1999). Most hydrogenetic crusts in the Pacific Ocean are divided into two growth generations with different chemical compositions: a phosphatized old generation and a non-phosphatized young generation. The phosphatized old generation is rich in calcium (Ca) and phosphorus (P), and it depletes iron (Fe), manganese (Mn) and cobalt (Co) (Koschinsky et al., 1997; Hein et al., 2000; Wang, 2005; Cui et al., 2008). However, at present, iodine contents have rarely been measured in the Fe-Mn crusts.

In this paper, the contents of iodine and other major elements (Ca, P, Fe, Mn and Co) in three Fe-Mn crusts collected from the Pacific Ocean are measured by spectrophotometric

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method and plasma atomic emission spectrometers (ICP-AES). The aims of this study are to address the poorly studied distribution and geochemistry of iodine in the crusts, and build a foundation for the preparation of samples for ^{129}iodine/iodine (^{129}I/^{127}I) ratio determination.

2 Methods and materials

2.1 *Study area*

In the Mid-Pacific Ocean, a large number of seamounts and islands form chains including Line Islands Chain and Mid-Pacific Mountains. The Line Islands are a complex with the NW-trending chain of atolls, submarine ridges, and seamounts in the central Pacific Ocean and southwest of Hawaii. The Line Islands Chain is located on the ocean floor that was formed the Cretaceous, lasting from 119 Ma to 83 Ma (Davis et al., 2002). The Mid-Pacific Mountains are located at the west of Hawaii-Emperor Island Line and the north of the Mid-Pacific Mountains fault zone. It extends about 3 000 km in east-west direction. The Mid-Pacific Mountains originate in today French Polynesia Mountains during 120–90 Ma. The age of the Mid-Pacific Mountain increases from east to west (Chu, 2005).

2.2 *Sampling*

Three Fe-Mn crusts were collected from the Mid-Pacific Ocean in the present study, named as MP5D44, CXD62–1 and CXD08–1, respectively (Fig. 1).

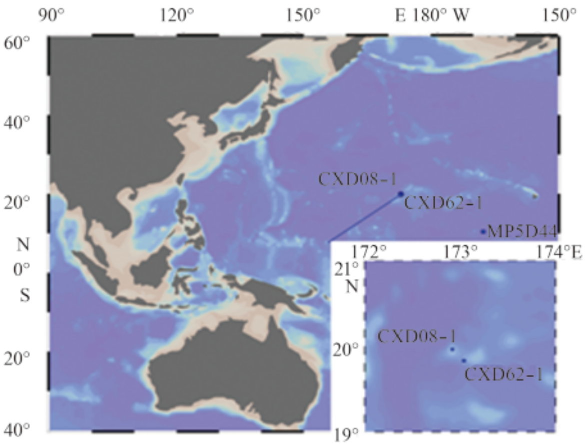

Fig. 1. Sampling locations of ferromanganese crusts.

All the samples used in this study are plate-like ones, and their thicknesses range from 5 cm to 8 cm (Table 1). MP5D44 was sampled from Line Islands, and the color of the crust gradually changes from black to gray with the depth increasing (Fig. 2a). The crust was sliced to thirteen subsamples including one of 1.0 cm thick and twelve of 0.5 cm thick.

CXD62–1 and CXD08–1 were collected from the Mid-Pacific Mountains. For the CXD62–1, stratification could be easily identified from surface to bottom layer. The upper layer is compact with the thickness of about 2 cm, while the middle layer is loose and its thickness is about 1.5 cm. The bottom layer is also compact with the thickness of about 1.5 cm and contains some white substance in the layer (Fig. 2b). The CXD62–1 was divided into five subsamples at 1.0 cm interval.

Fig. 2. The appearance of the three crusts. a. Sample MP5D44, b. Sample CXD62–1 and c. Sample CXD08–1.

From the vertical section, obvious layering structure is found in the CXD08–1 crust. The dense upper crust of 4 cm is black color, and dense bottom zone of 2.5 cm thick is grayish white, but middle pore zone of 1.5 cm contains yellow material (Fig. 2c). It was sliced to fifteen subsamples that include one of 1.0 cm thick and fourteen of 0.5 cm thick.

Table 1. The information of crust samples stations

Sample	Latitude	Longitude	Depth/m	Thickness/cm
CXD08–1	19°57.9'N	172°55.1'E	1 908	8.0
CXD62–1	19°49.8'N	173°02.5'E	2 618	5.0
MP5D44	10°24.2'N	167°36.5'W	3 100	7.0

2.3 *Analyses*

Based on the sequential leaching procedure of Koschinsky and Halbach (1995) and a method of iodine separation reported by Hou et al. (2001), the measurement method of iodine in Fe-Mn crusts was developed as following shown.

First, the mixture of 8 mL of 1mol/L Na_2SO_3, 25 mL of 1 mol/L $H_2C_2O_4$ and 10 mL of 1 mol/L $NH_2OH{\cdot}HCl$ was applied to leach iodine from the Fe-Mn crust powder in water bath (45°C) for 12 h. The excessive $NaNO_2$ solution was added to oxidize the iodide to molecular iodine (I_2), followed by the extraction of chloroform and back-extraction of $NaHSO_3$. Then, the solution of iodine was purified and separated through anion exchange column. For the measurement of iodine after the purification, under acidic conditions, the saturated bromine water oxidized the iodine to iodate. When the mixed solution of starch-potassium iodide was added as color reagent, the iodate in solution will react with excessive iodide to form iodine. Finally, the iodine solution was measured by spectrophotometer with the reagent blank as the reference.

In addition, the experimental conditions were studied in the present study, including the leaching temperature and time, the amount of $NH_2OH{\cdot}HCl$, $H_2C_2O_4$ and Na_2SO_3, the volume of elution for the exchange column. The results showed that the leaching temperature of 25–95°C was suitable. For leaching time, 12 to 20 h was needed to obtain constant iodine concentrations. For 2 g crust sample, 10–25 mL of 1 mol/L $NH_2OH{\cdot}HCl$ and 25–40 mL of 1 mol/L $H_2C_2O_4$ were suitable for the sample leaching. During the back-extraction, when 8 mL to 16 mL of 6 mol/L Na_2SO_3 solution was added, the extracted iodine concentration remained constant. For anion exchange, it was found that 120 mL of 2 mol/L KNO_3 solution could completely elute the iodine when using 4.59 mg potassium iodide solution as the test.

The recovery of the method was evaluated through the addition of a certain amount of KIO_3 into the Fe-Mn crusts. After the procedure as mentioned above, the recovery was obtained and ranged from 83.1% to 98.9%, with an average of 90.3% in the present study. The reproducibility of the method was assessed by measuring eleven subsamples, and the relative standard deviation was 2.6% in the present study. The iodine standard crust was not purchased, thus the iodine reference sediment (171 mg/kg) was used, and the relative standard deviation was 4.8% by measuring six subsamples and the recovery ranged from 82.8% to 93.5%, with an average of 86.4%.

Chemical analysis of five elements (P, Ca, Fe, Mn and Co) in three Fe-Mn crusts was performed by ICP-AES according to the method from Cai (2002). Subsamples of 0.05 g were accurately weight into Teflon vessels and wet with few deionized water. The samples were digested at 180°C to near dryness, using a mixture of concentrated HCl, HF and HNO_3 in a ratio of 3:2:1. After cooling, residues were taken up with 5 mL concentrated $HClO_4$ and evaporated to near dryness. Then, the hot residues were carefully dissolved with 4 mL concentrated HNO_3. The resulting clear solutions were filled into volumetric flasks, and diluted to 50 mL with deionized water. Finally, the solution was measured by ICP-AES with the reagent blank as the reference.

The profiles of ^{129}I in MP5D44 and CXD08–1 crusts are measured using Acclerator Mass Spectrometer (AMS) in China Institute of Atomic Energy Acclerator Mass Spectrometer (Xie, 2013).

The enrichment factor is defined as the ratio of the elemental concentration in the Fe-Mn crust to that in seawater. The enrichment factor of iodine in three crusts (E_I) is calculated by $E_I = C_{crust}/C_{sw}$ (Wen et al., 1997), where C_{crust} is the iodine content in the crust and C_{sw} is the iodine content of sea water (55×10^{-9}; Behrens, 2006).

3 Results and discussion

3.1 *The contents and distribution of iodine in Fe-Mn crusts*

For all samples, the iodine contents range from 27.1 to 836 mg/kg, with an average of 172 mg/kg. The iodine contents of three Fe-Mn crusts MP5D44, CXD08–1 and CXD62–1 fall ranges of 36.4–116.0 mg/kg, 27.1–836.0 mg/kg and 51.8–272.0 mg/kg, respectively, with averages of 69.3 mg/kg, 280 mg/kg and 113 mg/kg, respectively. The iodine contents of three crusts exist significant difference, following the order of MP5D44 < CXD62–1 < CXD08–1. The iodine enrichment factors fall in a range of 492–15 196, with an average of 3 073, indicating that marine Fe-Mn crusts are enriched in iodine.

The profiles of iodine in three crusts are shown in Fig. 3. In the MP5D44 crust, iodine content is relatively constant throughout the top 4 cm of the crust, but increases sharply from 4.0 to 4.75 cm, and then becomes constant again toward bottom. For the section between 0 and 3.75 cm, the iodine content in the CXD08–1 crust is relatively constant, while the iodine content increases sharply at the depth of 3.75 and 5.75 cm, and then iodine increases slightly from the depth to the bottom. In CXD62–1, iodine content is relatively constant for the upper 2.50 cm, and then iodine increases sharply toward the bottom. The results show that MP5D44, CXD08–1 and CXD62–1 crusts have two generation zones with different iodine contents: a young generation and an old generation, with a boundary depth locating at 4.0 cm, 3.75 cm and 2.50 cm, respectively (Fig. 3). Iodine is enriched in the old generaion compared to the young generation. The average iodine contents in the young generations of MP5D44, CXD62–1 and CXD08–1 are 45.9 mg/kg, 57.9 mg/kg and 40.3 mg/kg, respectively, while the average iodine contents in the old generations for three crusts are 107 mg/kg, 196 mg/kg and 553 mg/kg, respectively. The iodine content ratios of old to young generations are 2.3, 3.4 and 13.7, respectively, consistent with previous report showing that a thicker crust consisted of two generations, containing different element levels (Hein et al., 2000).

One and six values of iodine content in Fe-Mn crust and nodules were found in previous researches. Only one value of iodine content in CD25 crust (16.3°N, 169.3°W, 2 320 m) found in a literature is 1 520 mg/kg (Kodama et al., 2006). The six groups of data about the iodine in Fe-Mn nodules include 24.8 and 34.6 mg/kg (She and Fang, 1997), 2 500 mg/kg, 510 mg/kg and 27 mg/kg (Wang et al., 1999), and 1 370 mg/kg (Kodama et al., 2006). It is evident that these data are scattered. Among the environmental and geological samples, igneous rock has relatively lower iodine contents of <1 mg/kg, while the sedimentary rock contains more iodine, but it is still lower than 10 mg/kg (Whitehead, 1984). The iodine contents in marine sediments show a wide variation range, ranging from 3 to 2 000 mg/kg (Wong, 1991), but the iodine contents in many oceanic regions are lower than 1 000 mg/kg. Algae samples are found to have high iodine contents falling in a wide range of 90–2 500 mg/kg. For particulate matter, the concentration of particulate iodine ranged from less than 50 to over 1 200 mg/kg. In the paper, the iodine contents in Fe-Mn crusts fall on the similar magnitude order with those of marine sediments and particulate matter, and iodine contents show higher values compared to those in sediments from the China seas and estuaries (Zhao and Yan, 1994; Ji et al., 2013).

3.2 *The contents and distribution of other elements in crusts*

The measured elements in crusts included Fe, Mn, Co, P and Ca. P and Ca mainly come from carbonate fluorapatite (Wang, 2005). The contents of P, Ca, Fe, Mn and Co in three crusts fall in range of 0.11%–9.28%, 1.64%–25.14%, 4.99%–21.07%, 0.20%–19.52% and 0%–0.70%, respectively.

The transitions between phosphatized and non-phosphatized sections are resolved in the abundances of the P element. Pan et al. (2002) considered phosphatization occur in crusts when P weight percentage (w(P)) is more than 1%, otherwise not occur. The content and vertical distribution of P (Fig. 4) in three crusts show that the P content in old crust layer ranges from 1.36% to 9.28%. According to the standard of Pan, the old crust layers of three crusts have undergone phosphatization, which could be named as old phosphatized generation. The boundaries of phosphatized and non-phosphatized layer in MP5D44, CXD08–1 and CXD62–1 crusts locate at 4.0 cm, 3.75 cm and 2.50 cm, which are the same depths as those of iodine mutation in crusts. The Mn/Fe ratios in three crusts range from 0.02 to 1.88, showing that three crusts in the present study are hydrogenetic. Halbach et al. (1981) reported that Mn/Fe ratio in the hydrogenetic crusts was generally less than 2.5.

In general, significant differences in the elements composition between the young and the old generations are evident for three crusts. Figure 4 shows that P and Ca in the three crusts have similar distribution pattern to that of iodine, which are

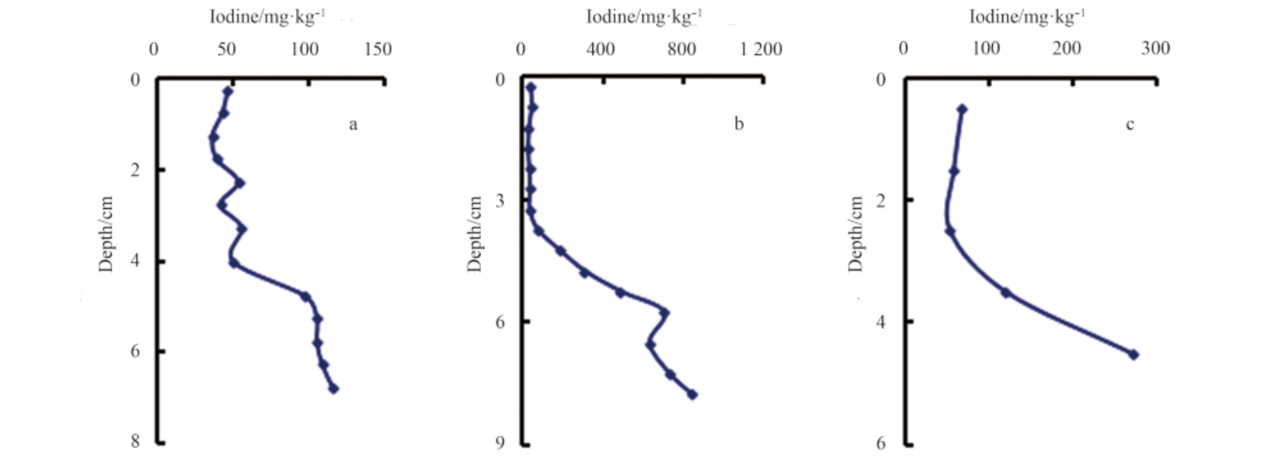

Fig. 3. The distribution of iodine in three ferromanganese crusts. a. Sample MP5D44, b. Sample CXD08–1 and c. Sample CXD62–1.

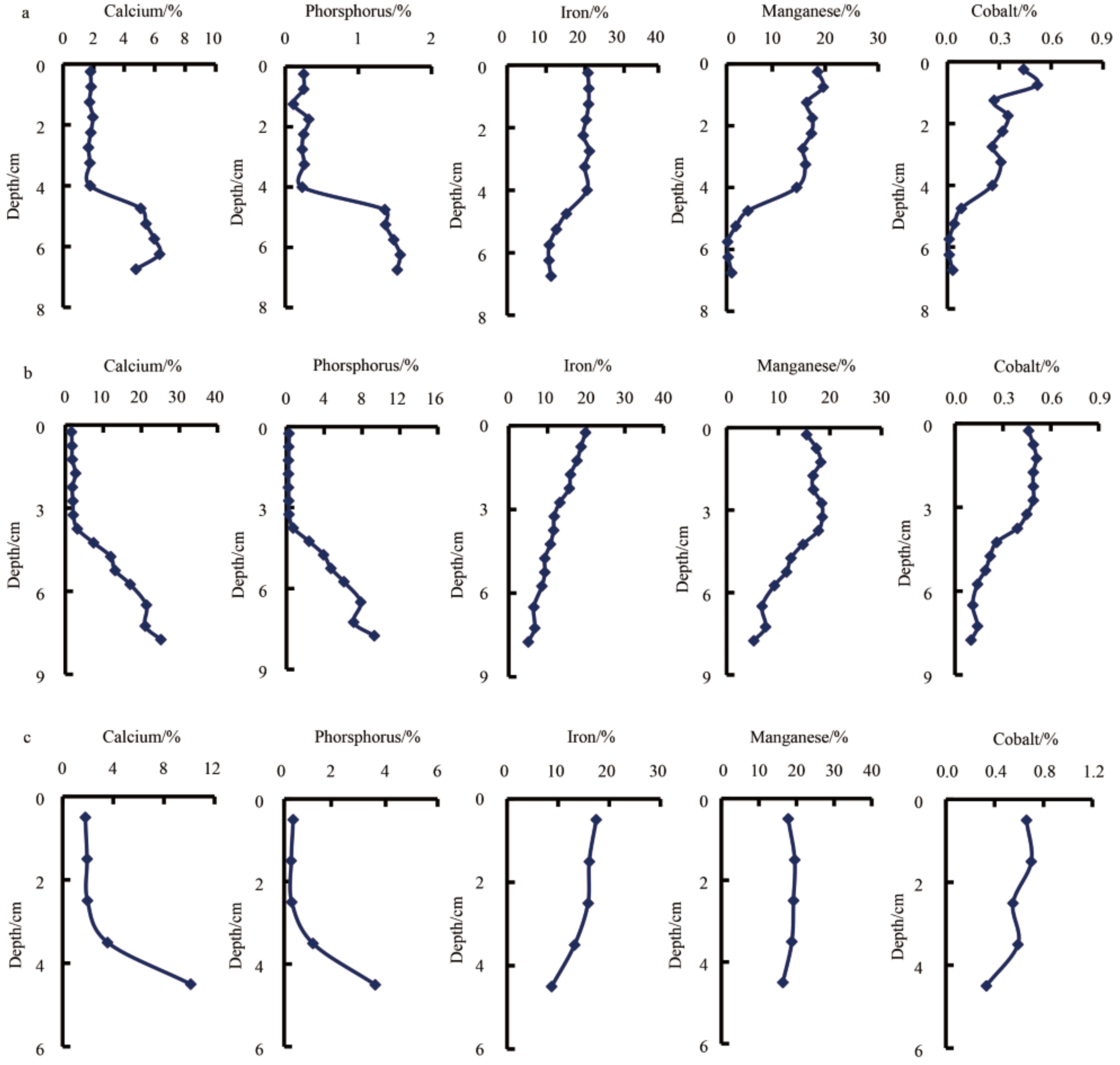

Fig. 4. The depth distribution of Ca, P, Fe, Mn and Co in ferromanganese crusts. a. Sample MP5D44, b. Sample CXD08–1 and c. Sample CXD62–1.

consistently enriched in the old generations compared to the young generations. However, Fe, Mn and Co contents are depleted in the old generations. Phosphatization commonly affected the older parts of crusts from water depths less than about 3 000 m and involves the enrichment of P and Ca (Frank et al., 1999). The phosphatized sections of three crusts are rich I, P and Ca relative to the unphosphatized sections.

3.3 *The factors affecting the iodine distribution in the crusts*

In order to examine the factors affecting iodine distribution in crusts collected from the Pacific Ocean, some factors are considered, such as Fe, Mn, Co, P, Ca. The correlation analysis of elements in crusts may reflect some association between iodine and other elements. As shown in Fig. 5, for three crusts, I is positively correlated with P and Ca, but it is negatively correlated with Fe, Mn and Co, demonstrating that iodine content is usually higher in the old generation with high P and Ca content than that of young generation crust. In addition to δ-MnO_2 and FeOOH·$x$$H_2O$, the phosphorite is the third main component in the old generation of Fe-Mn crusts (Hein et al., 1993; Koschinsky et al., 1997; Jeong et al., 2000). Some studies have shown that carbonate fluorapatite has higher iodine content, which exists in the apatite lattice skeleton, which may be isomorphous replacement of fluorine (Liu, 1984; Sun et al., 2008). Zhao and Yan (1994) reported that phosphates collected from seafloor are rich in iodine. These researches illustrated phosphatized Fe-Mn crust enriching iodine. In summary, the intensity of phosphatization is the main factor responsible for the distribution pattern of iodine in the crusts.

3.4 *The time of the iodine mutation*

In order to obtain the information about the time of iodine mutation, the crusts was dated with I-isotope ratios and Co element.

The profiles of ^{129}I/^{127}I ratio show an exponential decay. The paper gets the exponential decay equation (A=A_0e$^{-(L/V)}$, where A and A_0 are the ^{129}I/^{127}I ratio at any depth L and at L=0, is decay constant, V is the growth rate) from Fig. 6. According to the equation, the average growth rates of MP5D44 are 3.88 mm/Ma and 0.92 mm/Ma for the depth above and below 4.0 cm, respectively, with an average of 1.8 mm/Ma. The average growth rates of CXD08–1 are 1.99 mm/Ma and 0.82 mm/Ma for the the section between 0 and 3.75 cm and between 3.75 and 8.00 cm, respectively, with an average growth rate of 1.1 mm/Ma.

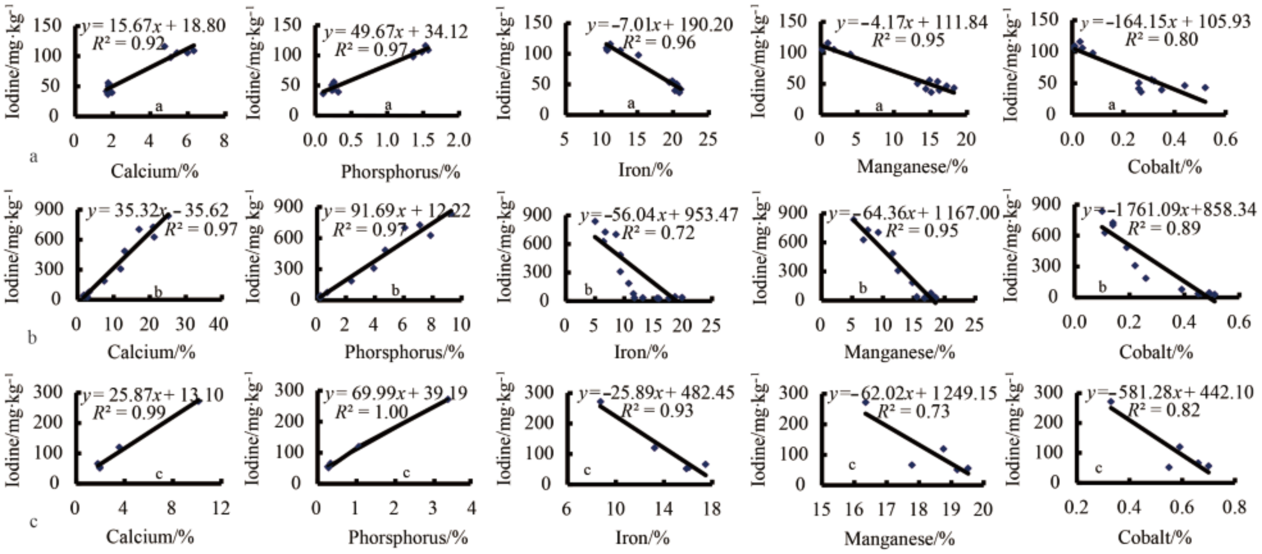

Fig. 5. Correlation between iodine and other elements (Ca, P, Fe, Mn and Co). a. Sample MP5D44, b. Sample CXD08–1 and c. Sample CXD62–1.

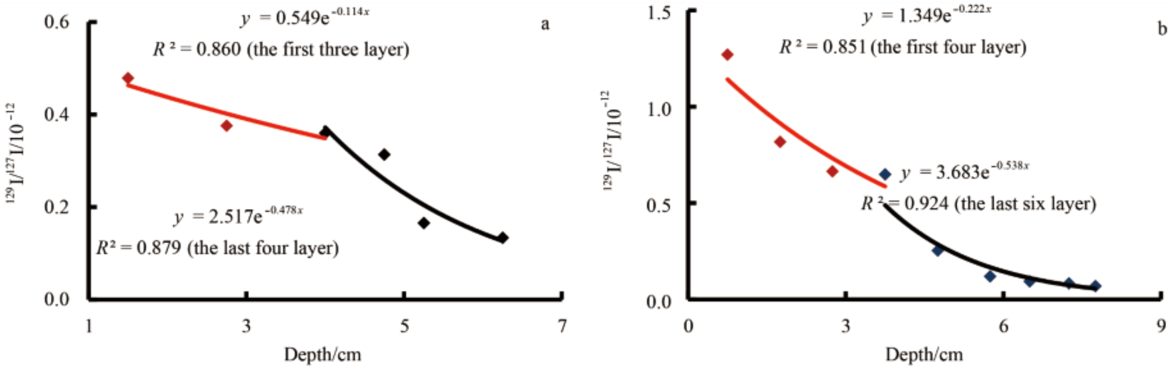

Fig. 6. The distribution of ^{129}I/^{127}I ratio in grade. a. Sample MP5D44 and b. Sample CXD08–1.

Co is used to calculate the growth rate of the CXD62–1 crust. The method is based on the inverse relationship between the Co contents of the crusts and their rate of accumulation. The Co-chronology method of Manheim and Lane-Bostwick (1988) was applied for samples with Co contents less than 0.7%. The growth rate of CXD62–1 is derived by applying empirical formula (Table 2).

Table 2. The growth rate and age of CXD62–1

Depth/cm	Co/mg·kg^{-1}	The growth rate	Age/Ma
0.5	0.66	1.36	3.67
1.5	0.70	1.23	11.78
2.5	0.55	1.85	17.20
3.5	0.59	1.64	23.29
4.5	0.33	4.33	25.60

Based on the growth rates, we estimate that the time of I, P and Ca mutation in three crusts is within the range from 17 Ma to 37 Ma. Hyeong et al. (2013) reported that phosphatization on mid-Pacific seamounts took place only between 36 and 12 Ma. Hein et al. (1993) found that two major episodes of Cenozoic phosphatization in crusts. One episode took place between about 39 Ma and 34 Ma, and second one occurred between about 27 Ma and 21 Ma. There were two major episodes occurring at times of climate transition: the first was from a nonglacial to glacial earth; and the second was from a predominantly glacial to warm earth (Hein et al., 1993). Phosphatization is the combined result of expansion of the suboxic oxygen minimum zone, increase of water productivity and Antarctic bottom current (Halbach and Puteanus, 1984; Halbach et al., 1989; Koschinsky et al., 1997; Jones et al., 2002). Namely, P and Ca in the crusts which are from the water column are strongly related to the oxygen minimum zone, water productivity and antarctic bottom current. Thus, the mutation of iodine contents in crusts was developed during the time when phoshpatization took place, showing the information about the paleoceanography and climate change.

4 Conclusions

The distributions of iodine in Fe-Mn crusts collected from the Pacific Ocean are determined in this study. Iodine contents in three crusts vary from 27.1 to 836 mg/kg, with an average of 172 mg/kg, which are in the range of those in marine sediments, demonstrating that the Fe-Mn crusts are rich in iodine. It is a foundation for ^{129}I dating of the crusts.

The distribution of iodine has a similar pattern in three Fe-Mn crusts. The increasing trend of iodine contents from the young generation to the old generation shows the characteristics of two-stage distribution, with the boundary depth locating at 2.5–4.0 cm. ^{129}I dating of CXD08–1 and MP5D44, as well as Co-dating of CXD62–1 confirm the mutation of iodine between 17 and 37 Ma.

Correlation analysis results show that iodine has well positive correlation with P and Ca, but it is negatively correlated with Fe, Mn and Co. The result indicates that the iodine enrichment of the crust is governed mainly by the intensity of phosphatization. I, P and Ca from the water column are strongly related to the oxygen minimum zone, water productivity and Antarctic bottom current. In other word, the iodine composition of crusts is controlled by changes in oceanographic conditions, and could reflect the information about the paleoceanography and environmental conditions.

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