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RESEARCH ARTICLE

Geochemical characteristics and metal element enrichment in crusts from seamounts of the Western Pacific

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Abstract Elemental geochemistry is an essential part of understanding mineralization mechanisms. In this paper, a data set of 544 cobalt crust samples from seamounts of the Western Pacific are used to study the enrichment characteristics of metal elements. REE normalization is utilized to reveal the origin of the crusts; effects of water depth on Co enrichment and impacts of phosphatization on mineral quality are discussed to obtain the evolution of these marine mineral deposits, which gives support to further resource assessment. Conclusions are reached as follows: 1) Elemental abundances, inter-element relationships, and shale-normalized REE patterns for phosphate-poor crusts from different locations reflect hydrogenetic origin of the crusts. EFs (enrichment coefficients) of REE exhibit exponential increase from surface sediments to phosphorite to polymetallic nodules to crusts, suggesting that the improved degree of hydrogeneous origin induces the enrichment of REE. 2) The crusts in the Western Pacific, formed through hotspot produced guyots trails, have relatively lower REE than those in the Mid-Pacific. The latter could be attributed to the peculiar submarine topography of seamounts formed by intraplate volcanism. 3) The non-phosphatized younger crust layers have 40% higher Co than the phosphatized older layers. This indicates the modification of the elemental composition in these crusts by phosphatization. A general depletion of hydroxide-dominated elements such as Co, Ni, and Mn and enrichment of P, Ca, Ba, and Sr is evident in phosphatized crusts, whereas non-phosphatized younger generation crusts are rich in terrigenous aluminosilicate detrital matter. 4) Co increases above the carbonate compensation depth (CCD) from less than 0.53% to over 0.65% in seamount regions with water depth of less than 2,500 m, suggesting the significance of the dissolution of carbonate in the sea water column to the growth and composition of crusts.

Keywords cobalt-rich crust, seamounts, Western Pacific, geochemical characteristics

1 Introduction

The cobalt crusts from oceanic submarine seamounts are potential resources for common economic metals such as Mn, Cu, Co and Ni, for noble metals such as Pt, and for dispersive metals such as REE (Rare Earth Elements) (Wen et al., 1997; Hein and Morgan, 1999; Zhang et al., 2012). Previous studies have shown that cobalt-rich crusts are also significant carriers of paleoceanographic records for the last 60–100 million years or more (e.g., Halbach et al., 1983; McMurtry et al., 1994; Koschinsky et al., 1997; Banakar et al., 2003; Klemm et al., 2007; Meynadier et al., 2008). Interest in cobalt crusts emerged in 1981–1982 and has continued. During the past two decades, China has sponsored a series of surveys covering more than 20 seamounts in 5 seamount regions over the Western Pacific to enhance knowledge of cobalt rich crusts. Research results have included both the causes and mechanism of element enrichment of Co-rich crust. Based on the surveying data from dredge hauling on seamounts in the Pacific, Zhang et al. (2011) established a system for Co-rich crust resources appraisal. Each seamount is assigned a crust thickness based on its height and the age of ocean crust. The amount of dry crust resources is then calculated to be 5.07×10^{10} t to10.14×10^{10} t, and the distribution area of crust on seamounts in the Pacific is 2,062,862 km^2.

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To further obtain accurate amounts of the recoverable resources of Co-rich crusts and accumulated metal elements in seamounts from areas of the Western Pacific, it is necessary to study: 1) the origin of Co-rich crusts, which is demonstrated to be very important for the enrichment degree of metal elements; 2) the impacts of later phosphatization on the enrichment and depletion of metal elements in new and old generation crusts; 3) the impacts of water depth on the growth of crusts.

In this study, 544 cobalt crust samples from 5 seamounts of the Western Pacific between 150°E–165°W, 5°N–25°N (Yao et al., 1996; Zhang et al., 2001a; He et al., 2005; Zhang et al., 2008a, b) are used to conduct the following analysis. First, the geochemical characterization of metal elements distribution in Co-rich crusts is analyzed, the enrichment of metal elements is compared with other geological deposits, and the significance of Co-rich crusts as potential economically valuable resources is examined. Second, fractionation of REE, the origin of Co-rich crusts, and its effects on the enrichment of elements is discussed through the interelemental correlation. Third, the relationships between elements and water depth are analyzed to understand the effects of water depth on the enrichment of elements in Co-rich crust. Finally, distribution characterization of elements along the profile of crusts is investigated to evaluate the effects of phosphatization on the enrichment or depletion of elements in the younger or older layers.

2 The study area

The study area is located in the Western Pacific, bordered to the west by the Mariana Island Arc, the Western Pacific plate convergent boundary-subduction zones and to the east by the central uplift of the Pacific ocean. The crust of the Western Pacific is much older than that of the Eastern Pacific and due to multiple volcanic activities; it is topographically and tectonically complex, distributed with seamounts and deep basins. Figure 1 shows the main seamount chains and bathymetry.

The Clarion-Clipperton (CC) zone formed with EW-trending Orozco giant fault zones traversing between the two. Smaller scale transform faults occur parallel to the CC faults. These faults are a passageway for volcanic activities, creating large-scale volcano chains and intermontane basin tectonic areas.

It is widely accepted that the seamounts in the study area are closely related to the localized upwelling of volcanic material, or “hotspots”. They display a linear age sequence from the Marcus Seamounts, to the Magellan Seamount, the Marshall Seamounts, and to the Line Islands, indicating the profound impacts by hotspots. Nonlinear arrangement of seamounts in the Mid-Pacific reflects the effects of intraplate volcanism besides hotspots (Morgan, 1972; Koppers et al., 2001; Koppers and Staudigel, 2005).

Aided by the improved availability of high-quality sediment cores recovered by the Deep Sea Drilling Project (DSDP), Ocean Drilling Program (ODP) and single tracing seismic data, features of the shallow stratum of seamounts are recovered. Different types of sediment including shallow-water carbonates, atolls carbonatite formation, ferromanganese oxide crusts on the submerged carbonate sedimentary platform and pelagic carbonate caps are developed on Jurassic alkali-basalts topped with tholeiitic basalt. The sediment layer increases from seamount slope to the summit platform. Both the maxima of deposit and penetration depth occur on the summit platform of guyots.

The basaltic basement rock of the Line Islands Ridge and the Mid-Pacific Mountains is older than 70 Myr BP. A main mineral phase of δ-MnO_2 intimately intergrown with X-ray amorphous $FeOOH \cdot H_2O$ has been precipitated immediately on the solid substrate rocks without an intervening sediment layer (Halbach et al., 1983). The ocean currents in the study region are far away from continental coast and hydrothermal sources, which suggests that the mechanism for Co enrichment in crusts could be simply the result of hydrogenetic co-precipitation of dissolved metals and colloids.

3 Results and discussion

3.1 Enrichment of metal elements in Cobalt-Crusts

Calculated from reference material, enrichment factors (EFs) have proven to be efficient in quantifying enrichment in different geological deposits. Here, EFs are defined as the average concentration of an element in crusts divided by that in Earth’s crust (Rosler and Lange, 1972). The formula used was:

$$\mathrm{EFs} = [E]_{\mathrm{sample}}/[E]_{\mathrm{earthcrust}}. \tag{1}$$

Five grades were divided based on the order of magnitude of EFs as shown in Table 1. The highly enriched metals (EFs values higher than 100) such as Mn, Co, Ni and noble metal (including Pt, Ir, and Au) make the crusts a potentially great economic resource.

It is notable that the medium enriched metals, especially REE, are very close to the grades of land-based REE deposits in southern China. Table 2 presents enriched REE content in seamount crusts. The lowest REE content is found in crusts from the Marshall Seamounts with $1{,}657\times10^{-6}$, while seamounts in the Mid-Pacific have the highest REE of $2{,}052\times10^{-6}$. Some of the seamounts in the Mid-Pacific are formed through intraplate volcanism; the peculiar submarine topography of clustered seamounts makes it possible to capture precipitating sediments. It is demonstrated that relatively higher clayey sediment was also observed in the crusts from the Mid-Pacific, thus resulting in higher REE.

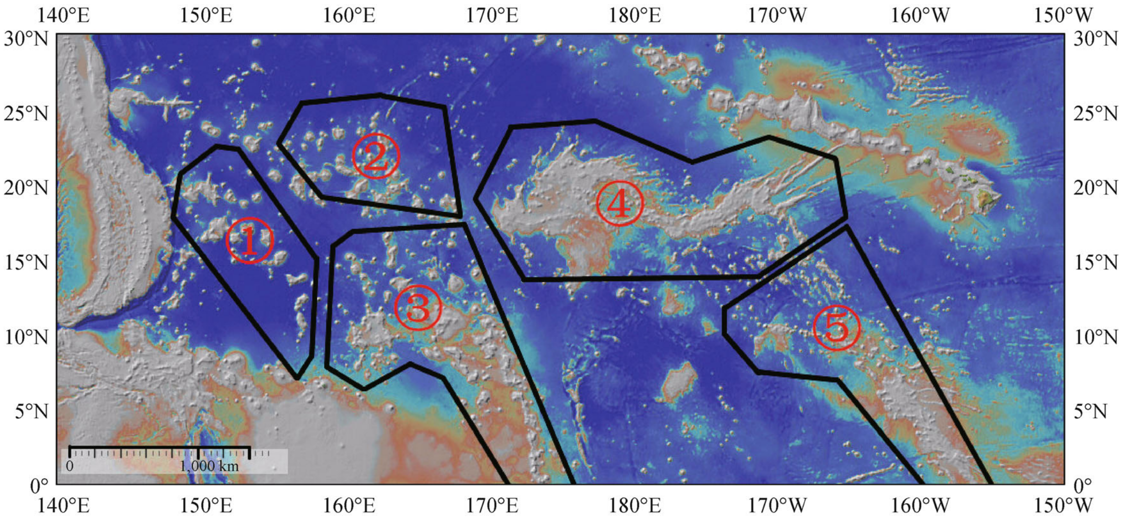

Fig. 1 Schematic diagram showing survey area (Zhang et al., 2008b). ① Magellan Seamount; ② Marcus; ③ Marshall; ④ seamounts in Central Pacific; ⑤ Line Islands.

Table 1 Elemental enrichment coefficients in crusts from Pacific seamounts ($n = 238$)

Elements	EFs	Elements	EFs	Elements	EFs	Elements	EFs	Elements	EFs
Al	0.09	Ca	1.10	Pr	5.26	P	12.89	Pb	106.08
Rb	0.09	Ti	1.73	Sm	6.17	Dy	13.5	As	114.97
Si	0.11	Fe	2.39	Y	6.31	Rh	14.59	Au	142.11
Pd	0.11	Hf	3.77	Nd	6.57	Ce	17.55	Bi	172.11
Cr	0.23	U	3.82	Lu	6.89	Cu	20.20	Mn	236.14
K	0.24	Zr	3.86	Ho	7.34	Cd	21.08	Co	268.53
Sc	0.32	Sr	3.93	Er	7.70	W	36.96	Mo	351.63
Mg	0.48	Ba	4.03	Eu	7.72	Ni	68.31	Ir	420.00
Th	0.64	V	4.46	Tb	7.91	Pt	99.96		
Na	0.67			Tm	7.96				
				La	8.02				
				Yb	8.23				
				Gd	8.81				
				Zn	9.13				

EFs of REE exhibit an exponential growth from surface sediments of the Pacific, to phosphorites, to polymetallic nodules to crusts (Fig. 2). Material source and genesis could be the reasonable explanation for this phenomenon. Surface sediments of the Pacific are mainly from terrigenous detrital sediments, submarine volcanic eruptions and bio-chemical deposition. Usually 75% of abiotic components are continental in origin (aeolian) with particle diameters in the 2.4–2.8 μm range, and are basically composed of Si, Fe, Al, Na, Ca, Mg, and Ti. Geochemical analyses of column sediments in the Pacific indicate 95.9% are of terrigenous aeolian origin and 1.3% are of hydrogeneous deposition since 1.8 Mya. The formation of phosphorites is suggested to be the accumulation of great amount of terrigenous chemically weathered material with rich phosphorus in deep sea (Hein et al., 1993), although the REEs normalization pattern suggested seawater genesis of REE in phosphorites. The relatively lower content of terrigenous materials in sediments and phosphorites result directly in the lower EFs of REE compared to nodules and crusts.

Table 3 shows the composition of near shore muddy sediments, sediments on the shelf of the East China Sea, sediments from the central South China Sea (SCS), hydrogenetic nodules from the eastern SCS, hydrogenetic nodules from the Clarion-Clipperton Fracture Zone in the Mid-Pacific, and cobalt crusts in Pacific. Their comparison results reveal the following:

Table 2 REE data for Co-rich crust collected in different seamounts (10^{-6})

Region	Sample (number)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	ΣLREE	ΣHREE	ΣLREE/ΣHREE
Marcus Seamounts	Crusts (3)	261.7	985.3	51.1	221.7	46.3	11.6	49.5	7.7	46.8	9.6	27.8	3.8	25.3	3.9	1752.1	1577.7	174.4	9.0
Magellan Seamounts	Crusts (12)	266.6	976.6	46.6	162.7	39.7	9.9	48.5	7.2	43.4	9.2	23.2	3.6	23	3.6	1663.8	1502.1	161.7	9.3
Marshall Seamounts	Crusts (7)	288.3	924.4	48.6	170.3	40.2	10	50.7	7.6	46.9	10.4	23.2	4.3	27.6	4.4	1656.9	1481.8	175.1	8.5
Seamounts in Mid-Pacific	Crusts (10)	293.9	1206.1	57.5	247.4	50.7	12.4	53.1	8.3	49.7	10.2	29	4.0	26	3.9	2052.2	1868.0	184.2	10.1
Line Islands	Crusts (31)	320.7	974.2	57.9	219.2	45.5	11.4	54.9	8.4	50.3	10.6	23.9	4.3	27.7	4.2	1813.2	1628.9	184.3	8.8
Magellan Seamounts	Sediments (4)	49.23	74.68	12.38	42.73	11.13	2.68	11.83	1.93	11.6	2.45	6.28	0.93	5.73	0.83	234.4	192.8	41.6	4.6
South China Sea (Bao and Li, 1993)	Crusts	165.8	917	41	132.6	44	12.76	48	9.74	53	7.3	22.12	5.44	19.6	4.98	1483.3	1313.2	170.2	7.7
Pacific (Xu et al., 1994)	Polymetallic nodules	160	530	60	160	35	9	32	5.4	23	4.2	15	2	18	2	1055.6	954.0	101.6	9.4
Pacific (Xu et al., 1994)	Deep sea sediments	42	90	11	54	12.6	3.2	10	1.5	9	2.4	7.3	1.4	6.5	1.9	252.8	212.8	40.0	5.3
South China Sea (Gu et al., 1989)	Sediments	28.63	55.8	6.31	22.65	4.71	1.09	4.27	0.68	4	0.82	2.43	0.34	2.18	0.43	134.3	119.2	15.2	7.9
North Atlantic	Deep water	3.4	1.2	0.64	2.8	0.45	0.13	0.7	0.14	0.91	0.22	0.87	0.17	0.82	0.15	12.6	8.6	4.0	2.2
Earth Crust (Xu et al., 1994)		30	60	8.2	28	6	1.2	5.4	0.9	3	1.2	2.8	0.46	3	0.5	150.7	133.4	17.3	7.7
North American Shale Composite (Taylor and McLennan, 1985)		32	73	7.9	33	5.7	1.24	5.2	0.85	5.8	1.04	3.4	0.5	3.1	0.48	173.2	152.8	20.4	7.5

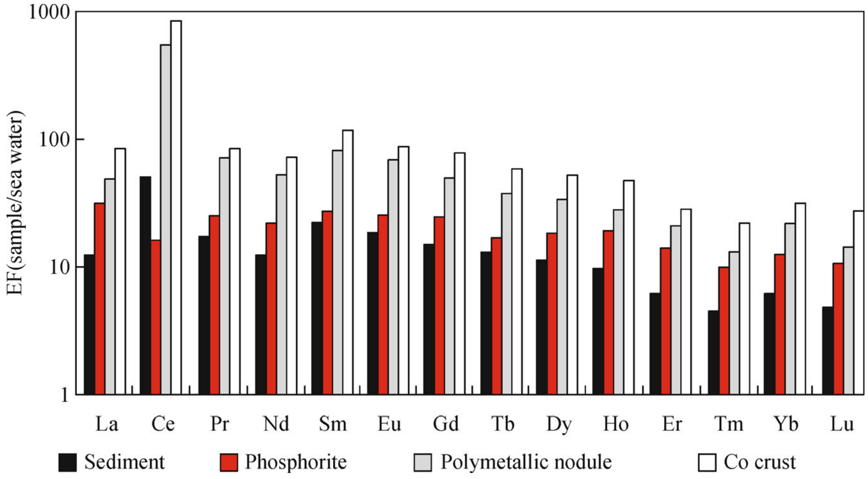

Fig. 2 EFs of REE in deep sea sediment, phosphorites, polymetallic nodules and Co crusts.

Table 3 Elemental enrichment coefficients in Co-crusts, polymetallic nodules and sediments

Enrichment Coefficient	Al	Si	K	Mg	Ca	Ti	Fe	Sr	Ba	Zn	P	Cu	Ni	Pb	Mn	Co
Nearshore muddy (Bao, 1990)	0.87	0.60	/	0.70	0.75	/	1.19	/	/	1.36	/	0.87	0.73	/	0.85	0.52
Continental shelf sediments of ESC (Zhang et al., 1991)	0.58	1.08	0.72	0.43	1.25	0.56	0.49	0.80	0.90	0.87	0.45	0.20	0.28	/	0.45	0.52
Sediments of central SCS(Zhang, 1991)	0.83	0.75	1.00	0.68	1.72	0.46	0.58	0.83	1.43	1.91	0.35	1.11	1.03	1.76	8.16	0.68
Sediments of Mid-Pacific (Zhang and Chen, 1991)	0.69	0.71	1.01	0.68	1.9	0.49	0.62	0.72	/	1.79	/	5.64	2.47	2.16	7.30	4.16
Hydrogenetic nodules of Eastern SCS (Lin et al.,1991)	/	/	0.33	/	0.23	0.44	1.27	0.11	0.70	2.93	/	7.09	19.35	42.48	77.10	13.68
Hydrogenetic nodules of CC zone in Pacific (Zhang et al., 2001a)	0.34	0.26	0.44	0.82	0.42	1.16	1.65	2.02	4.37	15.00	2.17	154.55	149.33	/	256.70	100.00
Co crusts in Pacific	0.09	0.11	0.24	0.48	1.10	1.73	2.39	3.93	4.03	9.13	12.89	20.20	68.31	106.08	236.14	268.53

1) EFs of Fe are higher in clay fractions of sediments from nearshore than those from continental shelf, deep sea and ocean sediments. EFs increase from hydrogenetic nodules of the eastern SCS (1.27) to hydrogeneous nodules, to crusts from the Eastern Pacific (2.39).

2) Mn is depleted in nearshore and continental shelves sediments, displaying a different enrichment pathway than Fe and indicating that Fe precedes Mn during littoral sedimentation, while EFs of Mn increase drastically from deep sea sediment (8.16) to nodules and crusts (256.7).

The behaviors of Fe and Mn suggest that the two elements coexist with similar geochemical characteristics, but separate under varied sedimentary environments. Mn is more active than Fe and apt to deposit in environments with high pH and Eh. This is why Fe usually deposits before Mn under natural environmental conditions. For example, FeS or FeS_2 form under hypoxic conditions, thus the deposit flux of Fe is greater than that of Mn. In contrast to Fe, Mn^{2+} is active to release to upper water, and could be transported long distances to ocean by ocean currents in MnO_2 colloids.

The high EFs of Fe and Mn also imply that they are the principal mineral phases in crusts, vernadite (&MnO_2), which scavenges elements such as Co, Ni, Ce, Pt, and REE more effectively than do clay minerals (e.g., Murray, 1975; Koeppenkastrop and de Carlo, 1992, 1993).

3.2 Origin of cobalt-crusts

3.2.1 Proofs from bulk composition and interelement correlation

Crusts (or nodules) are usually categorized into diagenetic, hydrogenetic, and hydrothermal deposits based on their forming mechanisms (Wen et al., 1997). Diagenetic nodules grow when the fallen organic materials on the sea floor are sufficiently concentrated; organically bound elements then are released into sediments interstitial waters and thence to the nodules. Diagenetic nodules which form in the upper oxic sediments are therefore enriched in Mn, Cu, and Ni (Dymond et al., 1984; Takematsu et al., 1989). Cu and Ni are particularly enriched in nodules with

Table 4 Comparison of main elements between hydrogeneous and hydrothermal Co crusts

Samples	Water depth/m	Fe/%	Mn/%	Cu/10^{-6}	Co/10^{-6}	Ni/10^{-6}	Samples number	Data sources
Hydrogenetic Co crusts	2,249	16.48	21.87	1,300	5,900	4,400	544	*
Hydrogenetic Co crusts in Pacific	2,411	15.83	21.29	1,200	6,600	4,400	1,900	http://www.ngdc.noaa.gov
Hydrogenetic Co crusts in Indian Ocean	/	16.46	18.04	1,300	3,800	3,900	/	Manheim, 1986
Hydrogenetic Co crusts in Atlantic	/	18.56	20.07	1,100	5,300	4,000	/	Manheim, 1986
Hydrothermal Co crusts in Pitcairn Islands in southeastern Pacific	/	0.54	39.05	29	49	128	22	Hodkinson et al., 1994

* The data are collected from five seamounts Western Pacific between 150°E–165°W, 5°N–25°N (Yao et al., 1996; Zhang et al., 2001b; He et al., 2005; Zhang et al., 2008a, b)

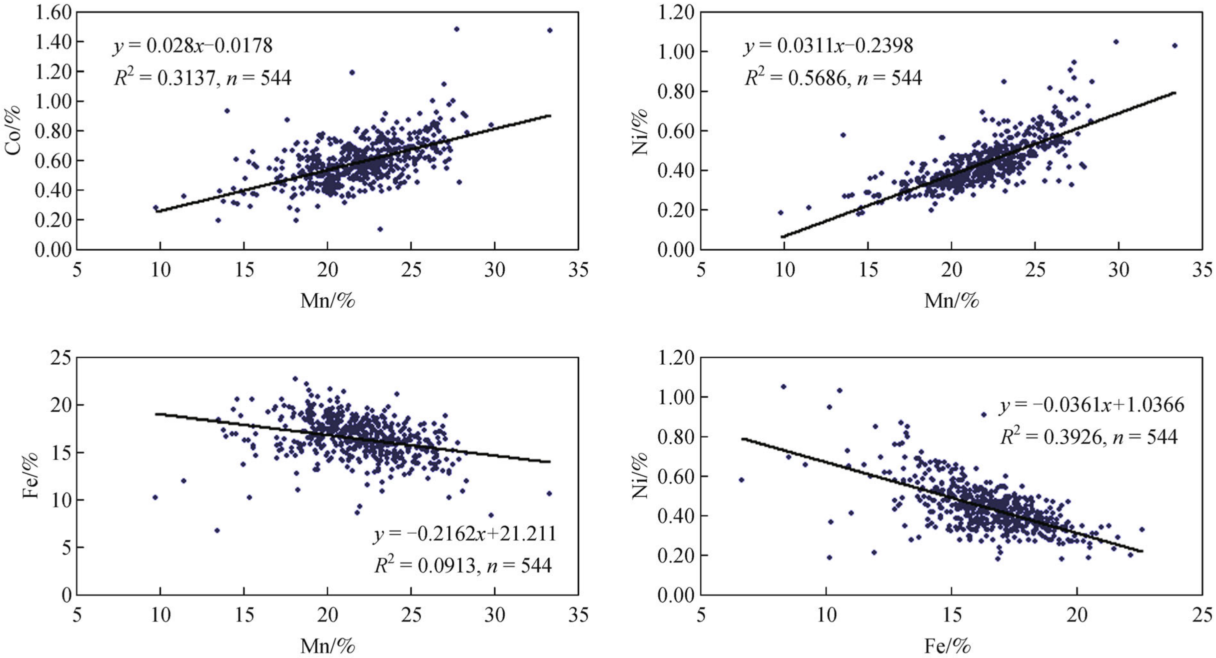

Fig. 3 Correlation analysis among Fe, Mn, Co and Ni in Co crusts in Western Pacific.

$2 < \mathrm{Mn/Fe} < 5$. Ni and Cu decrease with a Mn/Fe ratio of over 5, the so-called ‘‘point of reversal’’ (Halbach et al., 1981; Halbach, 1986). Hydrogenetic nodules formed by direct precipitation of elements out of well-oxygenated bottom seawater or metal-poor interstitial waters where sediments accumulate slowly (or very rarely) on sediment-free hard rock surfaces. Hydrogenetic nodules typically have a Mn/Fe ratio of less than 2.5 (Halbach et al., 1981), Co enrichment (Calvert and Price, 1970), and low levels of Ni and Cu (Dymond et al., 1984). Hydrothermal Fe-Mn deposits have lower trace metal contents and widely varied Fe/Mn ratios compared to their hydrogeneous counterparts (Hein et al., 1997; Mills et al., 2001). Of these, the hydrogenetic crusts are by far the most important deposits on seamounts of the Western and Central Pacific.

The general features of elemental composition in this study could be summarized as: 1) high content of Cu, Co, and Ni, they are respectively 45, 120, and 34 times than those in hydrothermal origin crusts from Pitcairn Islands of the southeastern Pacific; 2) low Mn with regional average Mn/Fe ratio of 1.33, as shown in Table 4, thus is classified as hydrogenetic Co crust.

The ore-forming metal elements could be classified into two types: Mn group and Fe group elements. Usually Fe, Mn, Cu, Co, and Ni have positive correlations with each other in deep sea sediments (Fig. 3). Mn group elements diverge from Fe group elements in polymetallic nodules. Co, Ni, and Cu have a positive correlation with Fe, but are negatively correlated with Mn in polymetallic nodules.

Over the full data set from crusts in this study, Mn has a negative correlation with Fe, but a positive correlation with Co. These relations are consistent with those of deep sea sediments, but differ greatly from those of polymetallic nodules. This suggests that crusts in the Western Pacific are basically hydrogeneous in origin. However, polymetallic nodules have a mixed origin: both hydrogenetic and diagenetic.

The crusts in this study are principally hydrogenetic. The different behaviors of the Mn group and Fe group could be further illustrated as follows: Mn hydrous oxide has a high surface energy and thus adsorbs effectively dissolved transitional metal ions from the water column, especially to Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, they are positively charged with a small ion diameter. Co^{2+} is oxidized on the surface of MnO_2, which produces undissolved stable Co^{3+} and causes the enrichment of Co rather than Ni, Zn, and Cd. Although water depth and phosphorization have important impacts on Co, mineral phase is the key factor affecting the distribution of elements in crusts. Co, Ni, Pt, Pb, Ce, As, Mo, Cd, and Zn have positive correlations with manganese minerals, while Cu, B, K, Al, Ba, and Si have positive correlations with ferrous minerals.

3.2.2 Fractionation of REE in Cobalt Crust

The results of NASC normalization REE pattern, as shown in Fig. 4, suggest that: 1) Crusts have REE enrichment several orders of magnitude higher than those in seawater and sediments; 2) The enrichment of Ce and its strong positive abnormality show that the key factors controlling fractionation of REE in crusts are basically consistent with

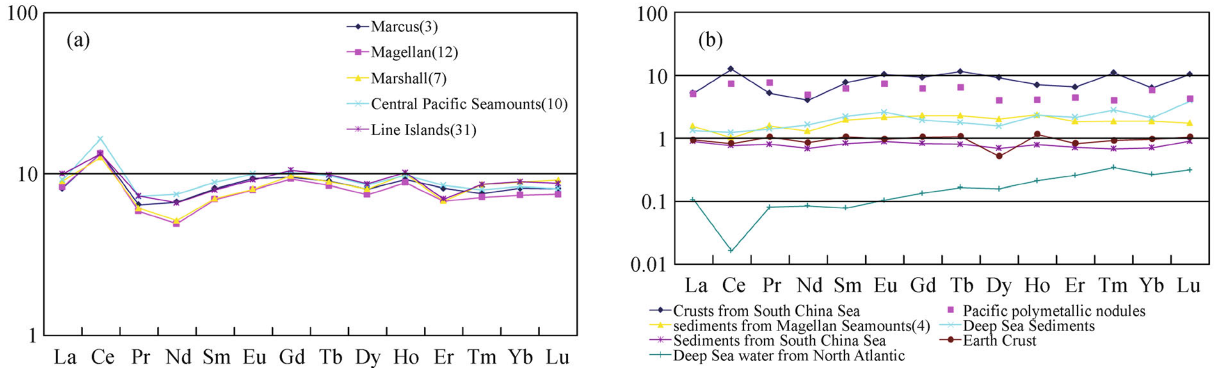

Fig. 4 NASC normalization plot of REE ((a) crusts from seamounts region of the Western Pacific; (b) different geological deposits).

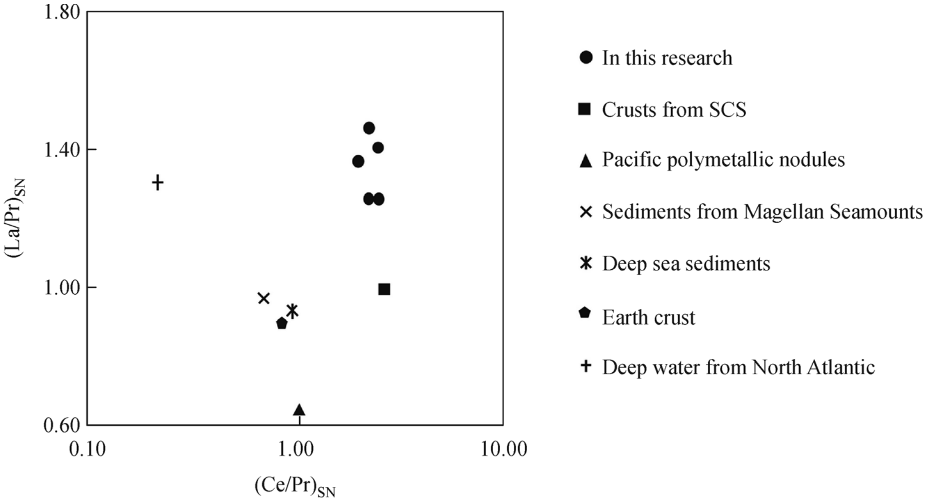

Fig. 5 Plot of $(La/Pr)_{SN}$ *vs.* $(Ce/Pr)_{SN}$.

those from the Central Pacific (Hein et al., 1988). 3) Fractionation is observed between LREE and HREE with depleted HREE. All suggests the hydrogeneous origin of the Co crusts in the study area.

Usually Fe and Mn oxyhydroxides sweep quantities of elements (e.g., Co, Ni, Pb, Ce, Tl, Te, Pt) from seawater. Thus the elements in seawater are actually controlled by their incorporation into those oxyhydroxides (Goldberg, 1963; Piper, 1974), which leads to a great difference in element composition between seawater and crusts.

Unlike the other REE, Ce^{3+} is apt to oxide to Ce^{4+} and then be fixed in the iron, manganese, and phosphate phases in crusts, which induce the separation from other REE and a large positive anomaly on a shale normalized plot. The fractionation between LREE and HREE is related to the major element composition and mineralogy. The separation occurs during adsorption. Usually LREE are highly enriched in iron oxide whereas vernadite is the principle carrier of HREE (Carlo, 1991). HREE form more stable complexes in seawater than LREE and are consequently more difficult to fix in the crust mineral phases than the LREE (Hein et al., 1988).

$(La/Pr)_{SN}$ varied from 1.26 in crusts from the Mid-Pacific to 1.46 in crusts from the Marshall Seamounts, displaying positive La_{SN} anomalies as shown in Fig. 5. These values are consistent with ratios of 1.33 for crusts from the South Central Pacific and the North Central Pacific with a mean $(La/Pr)_{SN}$ of 1.46 (Aplin, 1984; Hein et al., 1990, 1992a, b; De Carlo et al., 1992; Michael, 1996). Crusts from the SCS have relatively small ratios with a mean $(La/Pr)_{SN}$ of 1.00, which is similar to crusts from the Mariana Island Arc with a mean $(La/Pr)_{SN}$ of 1.09. However, these crusts are known to have been deposited in areas with hydrothermal activity (Hein et al., 1988), and low $(La/Pr)_{SN}$ ratios might be typical of Fe-Mn crusts with a hydrothermal genesis. La_{SN} anomalies in hydrogenetic Fe-Mn crusts may be inherited and reflect the La_{SN} anomaly of seawater which is known to have variable $(La/Pr)_{SN}$ ratios depending on the sampling site (De Baar et al., 1991). A plot of $(La/Pr)_{SN}$ ratios *vs.* $(Ce/Pr)_{SN}$ suggests that the La_{SN} anomaly in this case may be generated during precipitation.

3.3 Impacts from water depth

We observe an increase in Mn, Co, and Ni but a decrease in Fe with decreasing water depth. Co increases above the carbonate compensation depth (CCD) from 0.53% at depths of over 4,000 m, to 0.65% with a narrow range in seamount regions of 1,000–2,500 m water depths, as shown in Fig. 6. A distinct increase tendency of Co occurs in water depths of around 2,500 m, a discrepancy with result from Halbach, who suggested 2,000 m as the turning point (Halbach et al., 1983).

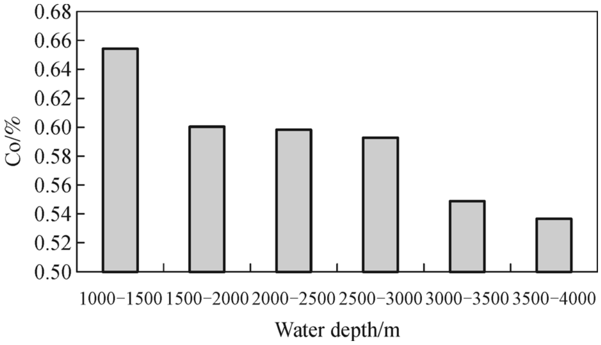

Fig. 6 Co content in crusts *vs.* water depth in seamounts from Western Pacific (with samples number $n = 544$).

Previous studies suggested that carbonate dissolution in the water column might have an important impact on the elemental composition of hydrogenetic precipitation. In the water column below the oxygen minimum zone, a mixture of colloidal particles of Mn Fe-oxyhydroxide and Al-Fe-silicate precipitate together on the surface of substratum rocks. The mixing ratio of these colloidal phases which controls the metal composition of the ferromanganese precipitation is a function of depth and time. In general, Mn/Fe ratios, Ni, and Co contents decrease with depth downward to the calcite compensation depth. Fe-Mn crusts are formed by slow precipitation reactions from seawater. The main mineral phase that precipitates from this colloid fraction is Fe-bearing vernadite (δ-MnO_2), which is also the main carrier of enriched minor metals like Co, Ni, Zn, and Cu in hydrogenetic crusts. $Fe(OH)_3$ colloids precipitate as an amorphous FeOOH-$x$$H_2O$ phase form, the second most important metal-bearing crust phase, and incorporate mainly neutral and anionic metal species like $[MOO]^-$.

Experiments show that the main Fe source for the hydrogenetic crust formation is colloidal Fe-hydroxide particles being released in the water column from the dissolution of calcareous plankton skeletons (Halbach and Puteanus, 1984). Recent analyses of cleaned calcite skeletons from the MidPac 81 areas have shown that the Fe content is particularly high ($(400–500)\times10^{-6}$) and is mainly present as amorphous iron hydroxide. Therefore, an increasing supply of iron hydroxide from calcite dissolution might have a diluting effect on Co, Ni, and Mn; the concentration of these metals may decrease with increasing water depth downward to the CCD (Halbach et al., 1983).

Manganese is mainly supplied from the oxygen-minimum-zone in a depth range of around 1,000 m, where the Antarctic Bottom Water (AABW) delivers oxygen-rich deep water. Enriched Mn^{2+} is oxidized to MnO_2 in deeper water layers. Depending on their surface charges in the water column, Mn and Fe may form mixed colloids and adsorb dissolved metal species (Koschinsky and Halbach, 1995; Koschinsky et al., 1997). δ-MnO_2 is especially able to absorb hydrous Co^{2+}, Ni^{2+}, because of enrichment of Co on the surface and the strong electrical field of the Mn^{4+}, a subsequent oxidation of Co^{2+} to Co^{3+} leads to the higher enrichment of Co in comparison with Ni. The most important factor governing Co enrichment is the growth rate of crust: the slower the growth rate, the higher the Co concentration (Halbach et al., 1983). Maximum values of up to 2% Co occurring in samples from water depths of 1,500 to 1,100 m are related to lower carbonate dissolution rates and corresponding lower Fe supply (Halbach and Puteanus, 1984). Titanium forms another hydrogenetic phase, probably $TiO_2\cdot2H_2O$ and A1 and Si are distributed between an amorphous Fe-Al-silicate and a detrital aluminosilicate fraction. The ratio of these colloidal phases that controls the metal composition of the hydrogenetic ferromanganese crusts depends on the metal supply and the physicochemical conditions in the water column, which themselves are affected by spatial and temporal parameters like water depth, geographic location, and bioproductivity (Koschinsky and Halbach, 1995; Koschinsky et al., 1997).

3.4 Impacts of phosphatization

Fe-Mn crusts can be divided into a younger and an older growth generation based on the phosphatization (e.g., Halbach and Scattler, 1989). Phosphatization is suggested to be the main cause inducing the depletion of ore-forming minor elements such as Co, Ni, and Mn, but of enrichment of non-mineral elements such as P and Ca.

In this study, measurements of trace metal elements for 16 crusts with subsamples suggested that younger layers have higher content of Si, Al, Fe, Co, Ti, Mg, Ni, and lower abundance of P, Ca, Ba, Sr, Cu, Zn, Pb, Mn, V, as shown in Fig. 7. The younger layers are characterized by enrichment of terrigenous aluminum silicates , whereas the older layers have abundant carbonate compositions such as P, Ca, Ba and Sr. Co in the younger layer is 40% higher than in the older layer, thus it is necessary to give clear indications of layers (or crust depth) when elemental abundance is discussed.

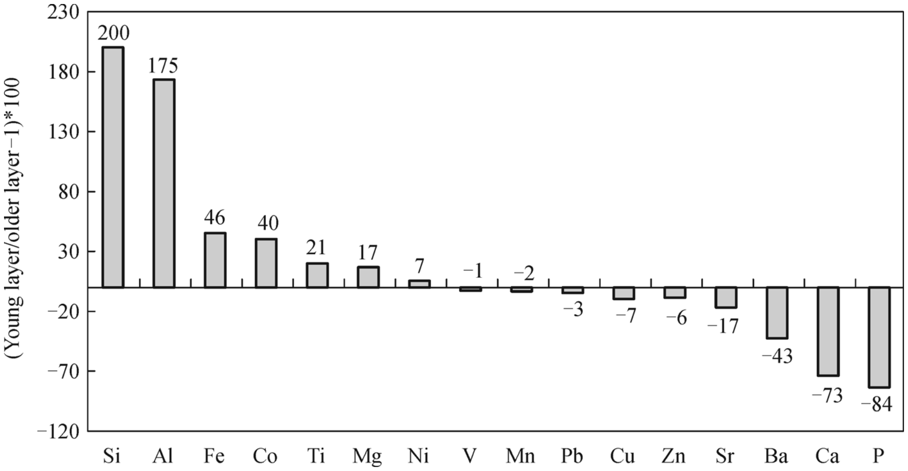

Fig. 7 EFs of elements in crusts from Western Pacific.

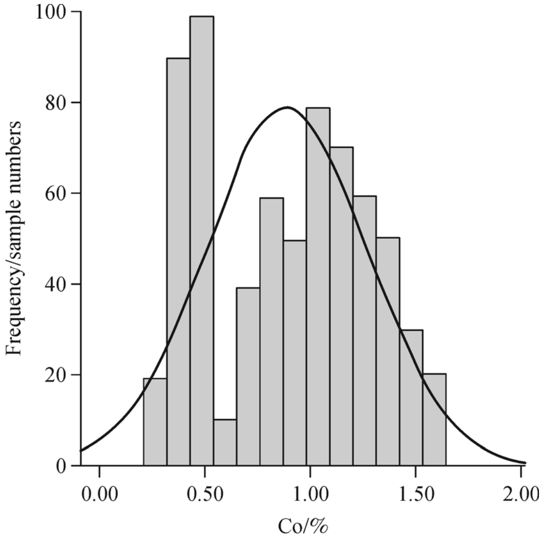

Fig. 8 Distribution of Co frequency in crusts from Johnston Island of Central Pacific.

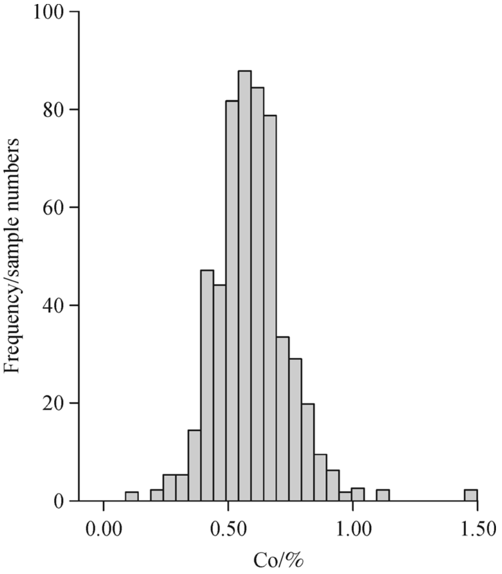

Fig. 9 Distribution of Co frequency in crusts from seamounts of Western Pacific.

Co data vary greatly in different studies. Co contents in subsamples taken from vertical profile of crusts from Johnston Island in the Central Pacific distributed with a bimodal pattern (Fig. 8), which shows the maximum Co content in upper 0.5 cm, but a relatively lower value in bottom of older layer. Co displays a unimodal style in whole samples (Fig. 9). The variation of Co is observed in crusts from the Magellan Seamounts. Co varies from 0.14%–1.09% in sample CHA06. The mean value is 0.46%. The crust has two distinct generations of growth, the average value of Co in younger layer is 0.66%, whereas older layers have a mean value of 0.26%. Almost all samples with Co content higher than 1.0% are from younger top layer of crusts of 0.5 cm. More detailed studies need be carried out further on elemental content in subsamples with high resolution sampling.

Phosphatization of older crust layers has been widely reported (e.g., de Carlo et al., 1987; Halbach and Scattler, 1989; McMurtry et al.,1994). These authors all describe the occurrence of older phosphatized crust generations with P concentrations up to 5.5 wt% and decreasing influence of phosphatization below the water depth of 2,500 m. Crusts from the Tuamotu Archipelago are phosphatized as well in the lower crust parts (Pichocki and Hoffert, 1987; Neumann and Sttiben, 1991). Only a minor degree of phosphatization found in crusts from the Tasman Rise (Bolton et al., 1988) may be related to the greater water depth of sample recovery (2,800–4,000 m).

Terrigenous dissolved phosphorus accumulated in the deep sea during relatively stable climatic conditions with sluggish oceanic circulations. As a result of major global cooling, Antarctic glaciation expanded and AABW upwelling intensified. The expansion and intensification of the oxygen minimum zone (which would be related to increased surface-water bioproductivity) may have increased the midwater storage capacity of phosphorus supplied by dynamic upwelling around seamounts. Fe-Mn crust precipitation took place below the oxygen-minimum-zone, where Mn^{2+}-rich and O^{2-}-poor water was mixed with O^{2-}-rich deep water. This suboxic and phosphate-rich water layer reached down the crust-covered slopes, inhibiting further crust precipitation and impregnating the older crust generation with CFA. Phosphatization of the older ferromanganese crust layers has been shown to cause differences in the chemistry of two crust generations (Puteanus and Halbach, 1988). Besides a dilution of the primary crust concentrations, a partial dissolution of the hydrogenetic oxide phases in suboxic microenvironments can be assumed.

4 Conclusions

In this study, based on an elemental geochemical data set of 544 cobalt crusts in seamounts from the Western Pacific, the geochemical characteristics and enrichment of metal elements in Co crusts are analyzed. The interelement correlation, REE NASC normalization pattern are utilized to obtain the origin of the cobalt crust in the study area. Impacts on the enrichment of metal elements from the genesis of cobalt crusts, water depth where these crusts grow, and phosphatization of older layers are then discussed. The major results include the following:

1) Mn, Cu, Co, Ni and noble metals such as Pt, Ir and Au are highly enriched in these crusts. The REE (except Ce) and carbonate (Ca and Sr) are moderately enriched. The highest abundance of REE in the Line Islands is $2{,}052\times10^{-6}$, due to the strong sediment capture ability for fascicular distributed seamounts of the middle Pacific formed by intraplate volcanism. Compared to the chemical composition of deep sediment, polymetallic nodules and phosphorites, Cu, Co and Ni here are respectively 45, 120, and 34 times higher than those in hydrothermally formed crusts from the Pitcairn Islands of the southeastern Pacific with Mn/Fe value of 1.33. The enrichment of metallic elements suggests the potential economic value of these crusts.

2) The low value of Mn/Fe, REE NASC normalization pattern, fractionation of REE with depleted HREE and interelement relationship analyses among Fe, Mn, Cu, Co, and Ni all suggest that the crusts in the study area are of an aqueous origin, are analogous to deep sea sediments, but differ greatly from the polymetallic nodules. This indicates the similar hydrogenetic origins of metal elements in both the crusts and sediments. The polymetallic nodules show both a diagenetic and hydrogenetic genesis. Ce^{3+} is oxidized to Ce^{4+} then adsorbed onto the surface of MnO_2, producing Ce enrichment in crusts with distinctly positive abnormal. Ce in sediments and seawater is relatively depleted and exhibit negative abnormal.

3) Phosphatization induces dilution for ore-forming elements (Co, Ni, Mn), but enrichment of P, Ca, Ba, and Si. The 40% higher Co content in upper younger layers than that in lower older layers is actually mainly determined on contents of Ca and P along the crust depth. Alumino-silicate component of Si and Al from land source is rich in the upper layers.

4) We observe an increase in metal concentration with decreasing water depth. In general, Co is higher in water depth of less than 2,500 m than that in water depth of over 2,500 m, and thus the turning point of water depth for Co content is 2,500 m. Variation of content of metal elements with water depth may be attributed to the dissolution of carbonate.

It follows that for the further detailed evaluation of metal ore-forming resource, it is necessary that the above factors impacting the enrichment of metal elements should be included to obtain accurate amounts of recoverable resources.

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