

Geochemical characteristics of platinum-group elements in polymetallic nodules from the Northwest Pacific Ocean

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Abstract

Polymetallic nodules and cobalt (Co)-rich crusts are enriched in platinum-group elements (PGEs), especially platinum (Pt) and may be important sinks of PGEs. At present, little information is available on PGEs in polymetallic nodules, and their geochemical characteristics and the causes of PGEs enrichment are unclear. Here, PGEs of polymetallic nodules from abyssal basin in the Marcus-Wake Seamount area of the Northwest Pacific Ocean are reported and compared with the published PGEs data of polymetallic nodules and Co-rich crusts in the Pacific. The total PGEs (Σ PGE) content of polymetallic nodules in study area is 258×10^{-9} in average, markedly higher than that of Clarion-Clipperton Zone (CCZ) nodules (Σ PGE= 127×10^{-9}) and lower than that of Co-rich crusts in the Marcus-Wake Seamount (Σ PGE= 653×10^{-9}), similar to that of Co-rich crusts in the South China Sea (Σ PGE= 252×10^{-9}). The CI chondrite-normalized PGEs patterns in different regions of polymetallic nodules and cobalt-rich crusts are highly consistent, with all being characterized by positive Pt and negative Pd anomalies. These results, together with those of previous studies, indicate that PGEs in polymetallic nodules and Co-rich crusts are mainly derived directly from seawater. Pt contents of polymetallic nodules from the study area are negatively correlated with water depth, and Pt/ Σ PGE ratios in nodules there are also lower than those of the Co-rich crusts in the adjacent area, indicating that sedimentary water depth and oxygen fugacity of ambient seawater are the possible important controlling factors for Pt accumulation in crusts and nodules.

Key words: platinum-group elements, polymetallic nodules, Co-rich crusts, Marcus-Wake Seamount

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1 Introduction

Hydrogenetic polymetallic nodules and cobalt (Co)-rich crusts enriched in useful metal elements such as Cu, Ni, Co, and rare earth elements including yttrium (REY) have very important economic value (Hein et al., 2013; Manheim, 1986), and serve as sinks of some trace elements in seawater. Platinum-group elements (PGEs), particularly Pt, are also relatively enriched in nodules and crusts, and are receiving increasing research attention (Astakhova, 2017; Cabral et al., 2009; Halbach et al., 1989).

Sources and enrichment mechanisms of PGEs in polymetallic nodules and Co-rich crusts are still debated. Halbach et al. (1989) suggested that PGEs in crusts are derived mainly from seawater and extraterrestrial materials, and Pt^{2+} in seawater co-precipitated with MnO_2 through redox reaction, which lead to enrichment of PGEs in crusts. Stüben et al. (1999) and Le Suave et al. (1989) found significant Pd negative anomalies in the CI chondrite-normalized PGEs patterns of hydrogenetic ferromanganese nodules and crusts, and suggested that meteorite spheroids were not the main source of PGEs for these deposits. Ren et al. (2016) and Hodge et al. (1985) suggested that PGEs in nodules and crust should be derived directly from seawater, and selective adsorption of PGEs by seawater in nodules and crusts resulted in positive Pt anomalies. Sun et al. (2006) and He et al. (2006) suggested

that PGEs in nodules and crusts are perhaps derived mainly from submarine seawater-basalt interactions, partly from extraterrestrial materials. They explained the greater enrichment of PGEs in crusts than in nodules as being due to the crusts being located near the Oxygen Minimum Zone (OMZ), which gave a more advantageous marine chemical environment for PGEs precipitation.

To improve our understanding of possible sources and enrichment mechanisms of PGEs in polymetallic nodules and Co-rich crust, and to increase the available data on PGEs in polymetallic nodules. Here, we report PGEs contents of 23 hydrogenetic polymetallic nodule samples from the abyssal basin in the Marcus-Wake Seamount area of the Northwest Pacific Ocean and compare PGEs characteristics of polymetallic nodules and Co-rich crusts in different regions of the Pacific Ocean.

2 Geological setting

The study area is located in the Marcus-Wake Seamount area, Northwest Pacific, ~1 200 km from the eastern Mariana Trench (Fig. 1). There are NE-trending and EW-trending secondary structures in the area and the water depth at the top of the seamount is 1 200–1 800 m (Ren et al., 2016). The seamounts in study area are formed on the ancient oceanic crusts, and their

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Table 1. PGEs, Fe and Mn contents in polymetallic nodules from the Northwest Pacific Ocean

Sample No.	Pt/10 ⁻⁹	Pd/10 ⁻⁹	Rh/10 ⁻⁹	Ru/10 ⁻⁹	Ir/10 ⁻⁹	Os/10 ⁻⁹	ΣPGE/10 ⁻⁹	Pt/Pt*	Pt/Pd	Fe ₂ O ₃ /%	MnO/%
S01	164	1.87	13.4	15.5	3.69	0.86	199	8.67	87.7	24.2	25.0
S02	183	3.76	15.4	18.6	5.04	2.39	228	6.37	48.7	22.6	23.9
S03	240	3.33	19.3	20.4	5.22	1.27	290	7.93	72.1	22.4	25.6
S04	278	7.28	22.8	22.1	6.11	1.60	338	5.71	38.2	22.3	26.0
S05	254	4.69	21.7	16.9	4.90	0.93	303	6.67	54.2	20.3	25.0
S06	230	3.14	16.4	19.3	4.52	1.13	274	8.49	73.2	22.5	27.4
S07	271	11.50	19.6	20.4	5.41	1.16	329	4.78	23.6	18.4	23.5
S08	222	2.50	18.5	18.8	4.93	1.34	268	8.64	88.8	23.6	25.6
S09	228	2.90	19.3	19.5	5.21	1.24	276	8.07	78.6	24.4	26.2
S10	236	3.22	17.7	19.8	5.01	1.21	283	8.28	73.3	24.6	26.0
S11	194	2.43	17.5	18.1	5.13	1.54	239	7.88	79.8	24.2	26.1
S12	262	2.53	20.6	21.3	5.58	0.89	313	9.61	104	24.5	26.0
S13	192	2.24	15.4	16.6	4.75	1.76	233	8.65	85.7	23.2	25.0
S14	183	4.58	16.1	17.4	4.38	0.95	226	5.64	40.0	21.9	22.0
S15	189	2.17	15.8	19.0	4.79	1.70	232	8.55	87.1	24.4	25.6
S16	240	2.48	20.0	18.9	4.77	0.72	287	9.02	96.8	21.7	25.5
S17	206	13.50	16.9	14.7	5.08	1.54	258	3.61	15.3	22.4	25.3
S18	183	2.33	15.0	15.9	3.85	1.16	221	8.20	78.5	22.7	25.1
S19	196	1.95	15.9	16.9	4.17	1.02	236	9.32	101	23.6	25.6
S20	173	4.46	14.4	14.9	3.88	0.89	212	5.72	38.8	23.6	25.2
S21	226	4.40	18.7	18.4	4.67	0.96	273	6.60	51.4	20.5	24.3
S22	197	3.62	16.6	16.0	4.20	0.88	238	6.73	54.4	22.8	25.4
S23	156	1.65	12.3	14.0	3.51	1.24	189	9.17	94.5	23.1	26.9
Mean	213	4.02	17.4	18.0	4.73	1.23	258	7.49	68.0	22.8	25.3
Maximum value	278	13.50	22.8	22.1	6.11	2.39	338	9.61	104	24.6	27.4
Minimum value	156	1.65	12.3	14.0	3.51	0.72	189	3.61	23.6	18.4	22.0
CI chondrite	1 010	550	130	710	455	490	3 345	1.00	1.84	-	-
Primitive mantle	7.10	3.90	0.90	5.00	3.20	3.40	23.5	1.00	1.82	-	-

Note: Data for CI chondrite and primitive mantle are from [McDonough et al. \(1995\)](#). – represents the primitive mantle and chondrite are used as reference for PGEs composition, as they are not nodules, and the values of Fe and Mn are not marked.

Table 2. REY (10⁻⁶) and some trace elements (10⁻⁶) data for samples in study area

Sample No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREY	δCe	Y _{SN} /Ho _{SN}	Ni	Co	Cu
S01	202	1 348	44.8	190	39.0	9.81	40.5	8.72	41.9	149	7.83	22.8	3.67	24.5	3.80	1 987	3.27	0.70	4 037	3 923	1 939
S02	186	1 015	43.9	151	37.1	8.75	40.4	7.95	38.8	147	7.85	22.0	3.80	25.6	3.76	1 592	2.59	0.69	3 375	3 366	1 928
S03	182	1 293	40.7	177	32.8	9.10	38.2	7.00	37.9	138	7.45	21.4	4.07	26.7	4.27	1 882	3.47	0.68	3 898	4 131	1 756
S04	224	1 291	53.2	208	47.2	11.0	50.2	8.83	44.1	178	9.00	23.2	4.33	24.5	3.92	2 002	2.73	0.73	3 968	4 097	1 888
S05	192	1 519	43.3	213	43.6	9.97	45.0	7.73	41.9	179	7.75	21.5	4.11	22.7	3.91	2 175	3.84	0.85	4 494	3 665	1 953
S06	201	1 125	42.0	178	38.4	9.11	39.6	7.67	39.9	150	8.41	21.0	3.97	23.2	3.72	1 741	2.82	0.65	4 580	3 688	2 056
S07	143	1 046	30.7	122	27.0	6.84	28.4	5.36	24.4	124	5.31	14.9	2.64	15.4	2.95	1 475	3.64	0.86	4 175	3 772	1 955
S08	222	1 609	48.3	211	41.6	10.7	43.3	7.73	40.8	155	8.43	22.9	4.17	23.7	3.91	2 298	3.58	0.67	3 817	4 110	1 404
S09	221	1 476	48.1	194	39.9	9.72	42.0	8.26	38.1	151	8.66	23.5	4.19	22.6	4.01	2 140	3.30	0.64	4 124	3 767	1 808
S10	243	1 437	52.0	217	41.6	10.3	41.8	8.03	40.0	151	8.25	20.8	3.88	23.7	4.19	2 152	2.95	0.67	3 840	3 988	1 495
S11	244	1 555	49.7	208	47.1	11.1	45.9	8.02	42.3	163	8.58	23.2	4.19	23.8	4.18	2 275	3.25	0.70	3 455	4 598	1 177
S12	218	1 509	50.8	216	44.7	12.1	45.9	8.77	41.5	160	8.86	24.4	4.22	22.6	4.24	2 211	3.31	0.66	3 890	4 518	1 785
S13	225	1 545	46.3	208	39.3	10.4	43.6	8.04	40.3	157	7.98	22.5	4.01	24.5	4.32	2 229	3.49	0.72	3 871	3 946	1 597
S14	217	1 329	43.5	182	40.4	9.17	39.6	7.09	35.3	138	7.54	18.9	3.46	19.7	3.58	1 956	3.15	0.67	3 180	3 474	1 529
S15	250	1 622	52.0	226	45.1	11.5	47.1	8.43	41.8	160	8.93	24.1	4.52	24.8	4.51	2 371	3.28	0.66	4 152	4 353	1 677
S16	217	1 586	47.2	204	43.3	10.9	45.0	8.01	38.5	166	8.51	22.5	4.07	23.4	4.26	2 263	3.61	0.72	4 560	3 720	2 096
S17	215	1 595	44.4	187	41.6	9.43	42.9	7.44	35.7	141	7.61	20.3	3.58	21.5	4.11	2 236	3.76	0.68	3 732	4 324	1 599
S18	199	1 424	42.1	187	41.7	9.85	40.9	7.53	37.1	145	7.94	20.0	3.81	20.9	3.94	2 046	3.59	0.67	3 942	3 843	1 467
S19	215	1 435	45.3	201	41.2	10.3	42.8	7.81	38.2	154	7.89	21.2	4.08	21.6	4.06	2 095	3.35	0.72	4 324	4 164	2 063
S20	217	1 363	45.8	197	42.7	10.5	42.8	7.96	38.7	156	8.21	21.2	4.08	23.6	4.22	2 027	3.15	0.70	3 951	3 824	1 853
S21	200	1 341	42.6	189	37.8	9.70	40.4	7.49	37.9	158	7.91	21.0	3.98	21.5	4.24	1 965	3.35	0.73	3 983	3 573	1 947
S22	216	1 574	47.3	199	42.5	10.0	47.4	7.80	41.4	161	8.36	21.7	4.21	22.9	4.14	2 247	3.59	0.71	4 567	4 186	1 965
S23	205	1 485	42.7	194	38.6	9.38	42.5	7.18	38.0	145	7.78	19.7	3.91	21.5	3.80	2 119	3.66	0.68	4 641	4 582	1 858

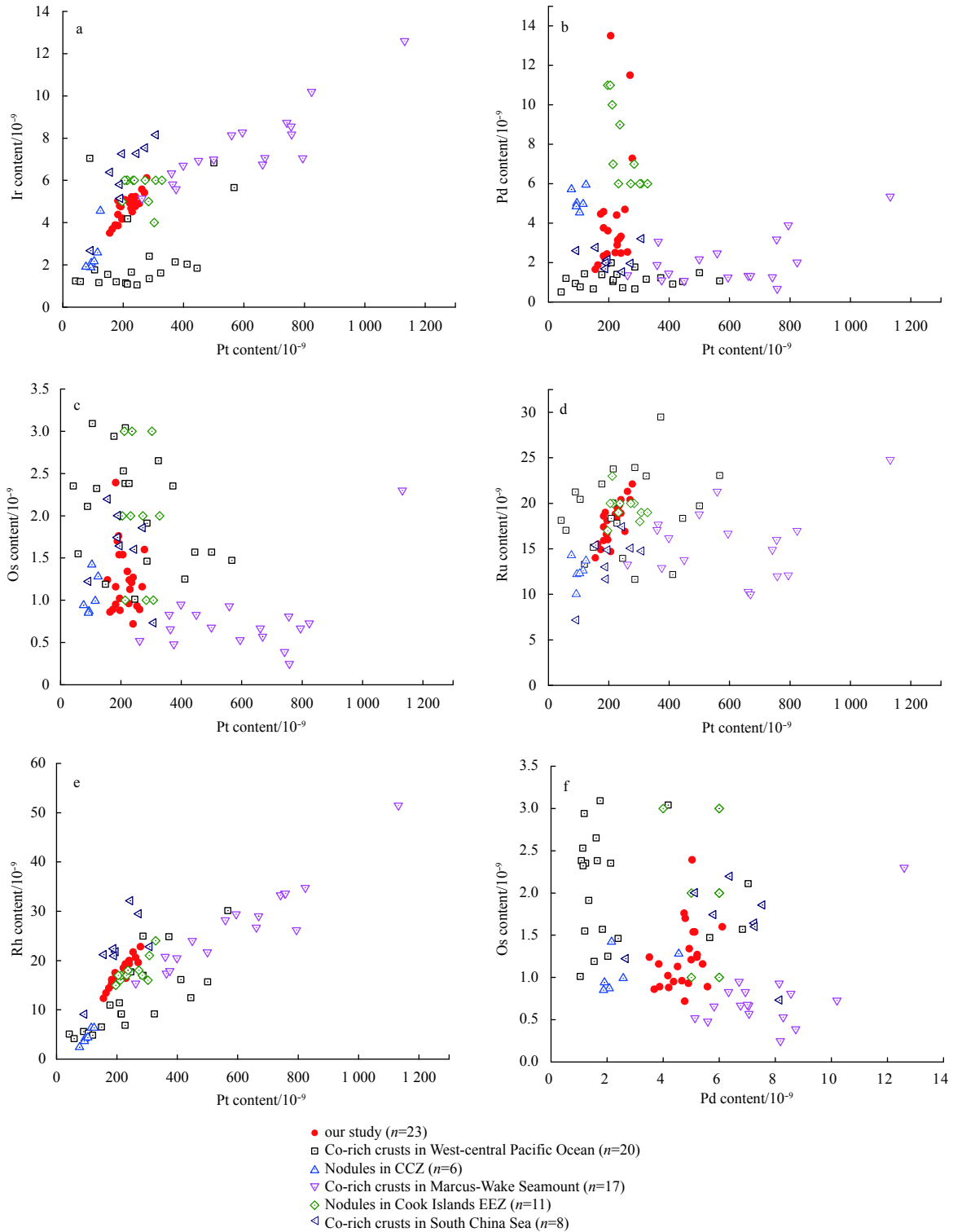


Fig. 2. Relationships among PGEs elements in nodule and crusts. Co-rich crusts in West-central Pacific after Sun et al. (2006), nodules in Clarion–Clipperton Zone (CCZ) after He et al. (2006), Co-rich crusts in Marcus-Wake Seamount after Ren et al. (2016), nodules in Cook Islands, Exclusive Economic Zone (EEZ) after Hein et al. (2015), and Co-rich crusts in South China Sea after Guan et al. (2017).

and Co-rich crusts display no obvious correlations, and Pd is significantly enriched in polymetallic nodules compared to Co-rich crusts (Fig. 2b).

Figure 3 shows CI chondrite-normalized PGEs patterns of the samples in study area. The PGEs distribution curves of the

samples are highly consistent, and obviously left leaning with gradual enrichment from Os to Pt and strong depletion of Pd.

All samples exhibit obvious positive Pt anomalies. Pt/Pd ratios range from 23.6 to 104 with an average of 68.0. The Pt anomaly (Pt/Pt^* ; Table 1) was calculated as follows:

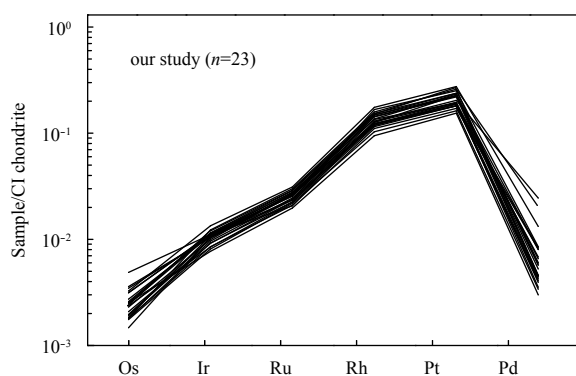


Fig. 3. CI chondrite-normalized PGEs patterns of the samples.

$$Pt/Pt^* = \frac{Pt_N}{\sqrt{Rh_N \times Pd_N}},$$

where the Pt_N , Rh_N , and Pd_N are CI chondrite-normalized values, and Pt/Pt^* range from 3.61 to 9.61 with an average of 7.49.

5 Discussion

5.1 Comparison of PGEs between nodules and crusts

Deep-sea polymetallic nodules and Co-rich crusts comprise mainly poorly crystallized and amorphous Fe-Mn (oxyhydr) oxides (Hein and Koschinsky, 2014; Hein et al., 2013). Bonatti et al. (1972) classified such nodules according to their Mn/Fe ratios, with ratios <2.5 indicating a hydrogenetic type, ratios >5 a diagenetic type, and ratios of 2.5–5.0 a mixed type. Hydrogenetic nodules are generally formed by precipitation of Fe and Mn (oxyhydr) oxides from seawater, and comprise predominately δ - MnO_2 containing $FeOOH \cdot xH_2O$ (Dymond et al., 1984; Halbach et al., 1981), with their mineralizing substances being derived directly from seawater. Here, the Mn/Fe ratios of polymetallic nodules range from 1.01 to 1.28 with an average of 1.11, which, together with the Mn-Fe-(Cu+Co+Ni)×10 differentiation diagram and REY discrimination diagrams (Figs 4, 5), confirm that they are of the hydrogenetic type.

The major characteristics of PGEs in polymetallic nodules and Co-rich crusts (Table 3) can be summarized as follows:

(1) The Pt content of PGEs in polymetallic nodules and Co-rich crusts is obviously the highest, followed by Rh and Ru. The Pd content in polymetallic nodules is higher than that of crusts, indicating that Pd is more enriched in nodules than crusts. The contents of other PGEs in nodules are not absolutely higher or lower than those of crusts, noting that the Pt content of polymetallic nodules in our study is significantly lower than that of Marcus-Wake Seamount crusts.

(2) The average Σ PGE content of polymetallic nodules in the study area is equivalent to that of crusts in the South China Sea,

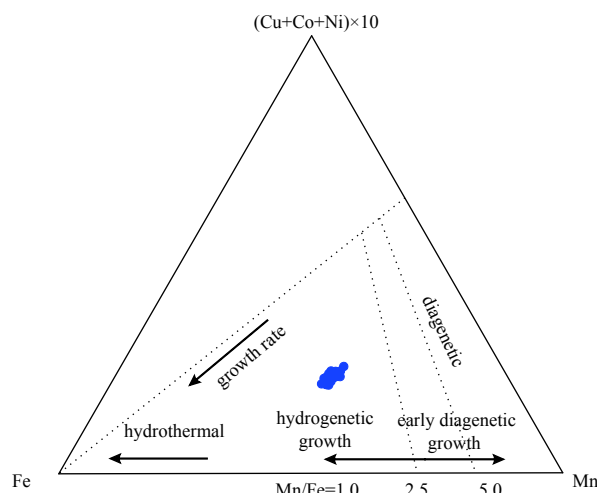


Fig. 4. Ternary major element geochemical discrimination diagram of the Fe-Mn nodules genetic types (modified after Bonatti et al. (1972)).

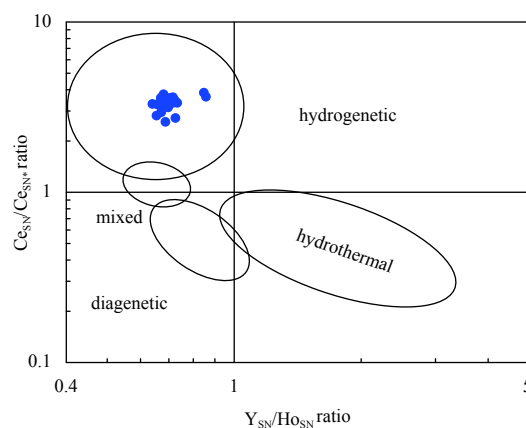


Fig. 5. Data for nodules of our study plot in the hydrogenetic fields in discrimination graphs (Bau et al., 2014) of Ce_{SN}/Ce_{SN}^* ratio vs. Y_{SN}/Ho_{SN} ratio. Subscript SN stands for Post Archean Australian Shale (PAAS) normalized.

and significantly higher than that of nodules in the CCZ, East Pacific, but significantly lower than that of Co-rich crusts in Marcus-Wake Seamount. In general, without considering the Σ PGE content of the hydrogenetic crusts in the South China Sea, the Σ PGE content of hydrogenetic Co-rich crusts in the open ocean is higher than that of hydrogenetic polymetallic nodules, whereas the Σ PGE content of polymetallic nodules is obviously higher than that of mixed-type nodules from the CCZ. Σ PGE content of Co-rich crusts is relatively low in the South China Sea, possibly

Table 3. PGEs content (10^{-9}) and major parameters of PGEs in Co-rich crusts and polymetallic nodules

	Sample type	Pt	Pd	Rh	Ru	Ir	Os	Σ PGE	PPGEs/IPGEs	Pt/Pt*	Pt/Pd
Our study	hydrogenetic	213	4.02	17.4	18.0	4.73	1.23	258	9.79	7.49	68.0
Marcus-Wake Seamount crusts	hydrogenetic	600	2.05	27.3	15.6	7.59	0.75	653	26.70	22.70	366.0
CCZ nodules	mixed-type	101	5.17	4.55	12.5	2.53	1.06	127	7.08	5.61	19.7
Cook Islands nodules	hydrogenetic	254	7.73	17.8	19.5	5.64	2.00	306	10.40	5.92	35.9
West-central Pacific crusts	hydrogenetic	252	1.12	12.3	19.1	2.40	2.06	289	11.60	18.00	238.0
South China Sea crusts	hydrogenetic	206	2.24	22.5	13.7	6.28	1.62	252	10.60	7.78	98.3

Note: All values are averaged. The quantity and source of samples are consistent with Fig. 2.

due to the dilution of the terrigenous materials and the high deposition rate (the mean growth rate of South China Sea crusts is 19.20 mm/Ma, higher than most hydrogenetic crusts worldwide (Hein et al., 2000)).

(3) Polymetallic nodules in our study area as well as polymetallic nodules and Co-rich crusts from other areas are enriched in Pd-group PGEs (PPGEs: Rh+Pt+Pd), but depleted in Ir-group PGEs (IPGEs: Os+Ir+Ru). In general, the PPGEs/IPGEs ratios of nodules are lower than those of crusts, i.e., a greater degree of differentiation of PGEs occurs in crusts than in nodules.

(4) Consistent with the PPGEs/IPGEs, the average Pt/Pt* of Co-rich crusts is higher than that of polymetallic nodules, indicating that Co-rich crusts are more enriched in Pt than polymetallic nodules.

(5) The Pt/Pd ratios vary significantly both in polymetallic nodules and Co-rich crusts (19.7–366), but the average Pt/Pd ratios of polymetallic nodules are lower than that of Co-rich crusts.

In addition, the CI chondrite-normalized PGEs patterns of polymetallic nodules in the study area and those of nodules and Co-rich crusts from other regions are highly consistent (Fig. 6), with all being characterized by positive Pt anomalies, gradual enrichments from Os to Pt, and gradual depletions from Pt to Pd, suggesting a consistent source of PGEs for the polymetallic nodules and Co-rich crusts.

5.2 Possible sources of PGEs in polymetallic nodules and Co-rich crusts

Sources of PGEs in polymetallic nodules and Co-rich crusts remain under debate (Brownlee et al., 1984; Wiltshire et al., 1999; Koide et al., 1991). Previous studies have suggested that extraterrestrial materials may be partial providers of PGEs in polymetallic nodules and Co-rich crusts, with their PGEs patterns being similar to those of iron meteorites (Sun et al., 2006; He et al., 2006). Halbach et al. (1989) discovered Ni-rich meteorites in the Central Pacific Ocean Seamount area, and suggested that seawater and cosmic particles could be a source of PGEs in Co-rich crusts. However, the Σ PGE content of meteorites is much higher than those of nodules and Co-rich crusts (Fig. 6). Furthermore, iron meteorites have low Pt/Pd ratios (mean 7.87; Wilson et al., 1997) compared with nodules and crusts (Sun et al., 2006; He et al., 2006). Iron meteorites are therefore not the main source of PGEs in crusts and nodules.

The chondrite-normalized PGEs patterns of seawater display negative Pt anomalies, with gradual depletion from Os to Ir and Rh to Pt and enrichment from Pt to Pd, the converse of trends in nodules and crusts (Fig. 6). This implies that seawater and nodules/crusts have a relationship of source and sink with PGEs in nodules and crusts being derived directly from seawater. Ren et al. (2016) compared the geochemical characteristics of REY and PGEs of Co-rich crusts from West Pacific Seamount and concluded that REY distribution patterns with positive Ce anomalies, and unique PGEs patterns with positive Pt and negative Pd anomalies in Co-rich crusts, are due to the selective adsorption of REY and PGEs from seawater by oxides in the crusts. The preferential absorption of Ce from seawater by oxides in crusts resulted in significant positive Ce anomalies in the NASC-normalized REY patterns of Co-rich crusts (Ren et al., 2016). Besides, Hodge et al. (1985) also suggested that the mechanism of Pt anomaly formation in polymetallic nodules is similar to that of Ce anomalies in rare-earth-element series. Thus, the preference of the oxides for Pt over Pd leads to the unique PGEs patterns, which further indicates that PGEs in polymetallic nodules and crusts are derived directly from seawater.

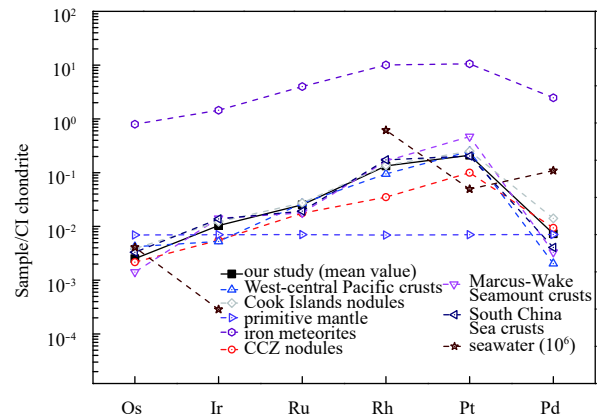


Fig. 6. CI chondrite-normalized PGEs patterns of the samples and comparison with other geological bodies. The quantity and source of samples are consistent with Fig. 2. The iron meteorites values are from Wilson et al. (1997), the seawater values are from Nozaki (1997), and data for CI chondrite and primitive mantle are from McDonough and Sun (1995). Data sources are consistent with Fig. 2.

5.3 Main factors affecting Pt enrichment

Although the PGEs patterns in polymetallic nodules and Co-rich crusts are very consistent (Fig. 6), the comparison of Pt/Pt* values of hydrogenetic nodules with these of hydrogenetic crusts and mixed-type diagenetic nodules in Section 5.2 indicates that Pt/Pt* values of hydrogenetic crusts > hydrogenetic nodules > mixed-type nodules (Table 3). Based on this and the correlation characteristics of Pt and Pd in nodules (Fig. 2b), we suggest that there is a difference in enrichment of Pt from seawater between nodules and crusts during their growth.

Previous studies have suggested that PGEs in the ocean are mostly in the form of complexes. Halbach et al. (1989) suggested that Pt in seawater exists mainly in divalent and tetravalent states, and that Pt enrichment in Co-rich crusts may be due to the co-precipitation of Pt²⁺ with MnO₂ in seawater. Sun et al. (2006) proposed that sedimentary water depth and seawater oxygen fugacity are the dominant factors leading to differences in Pt enrichment between crusts and nodules. The negative correlation between Pt and Fe₂O₃ of nodules and Co-rich crusts, and a lack of correlation with MnO (Fig. 7), indicates that iron mineral phases and manganese mineral phases in polymetallic nodules and crusts do not promote the concentration of Pt from seawater. This is inconsistent with the results of previous studies that Pt enrichment in the crusts is related to manganese mineral phases, whereas Pt enrichment in nodules is related to the iron mineral phases (Sun et al., 2006; He et al., 2006).

Halbach et al. (1989) found that the Pt content in Co-rich crusts is closely related to water depth, the shallower the depth at which crusts grow, the higher their Pt content, and thus the higher their PGEs content. In this study, the Pt in polymetallic nodules of this study shown negative correlation with water depth (Fig. 8), implying that the sedimentary water depth also affects Pt enrichment in polymetallic nodules.

In addition, Pt/ Σ PGE ratios in the polymetallic nodules in study area vary between 0.80–0.84 and with an average of 0.82, whereas values in Co-rich crusts of the Marcus-Wake Seamount are 0.88–0.94 and with an average of 0.91 (Ren et al., 2016). This indicates that there is a difference during Pt adsorption in seawater by the nodules and crusts, and that crusts may preferentially

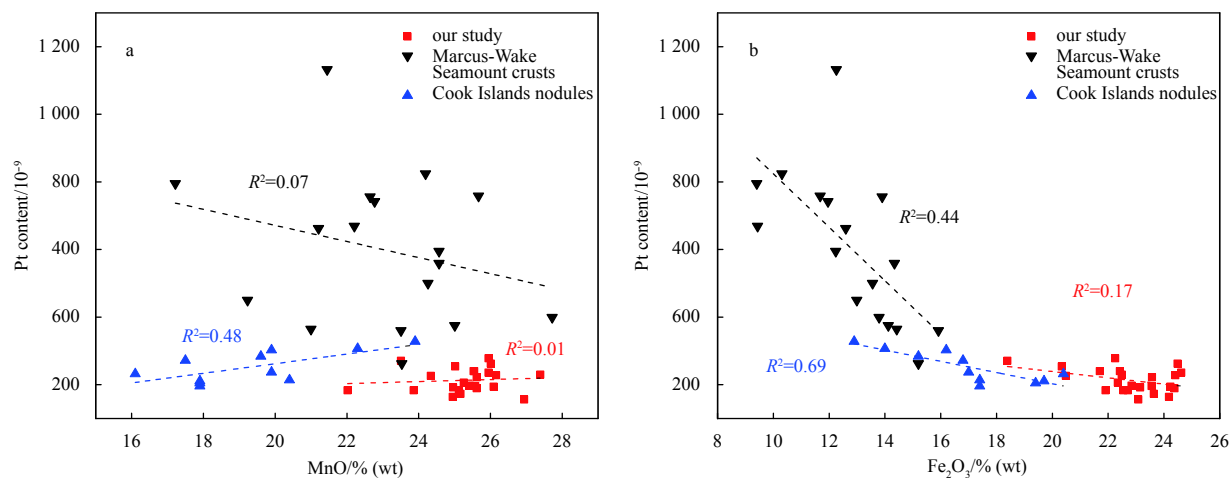


Fig. 7. Correlation between MnO, Fe₂O₃ and Pt in nodules and crusts. The data of nodules and crusts are the same with Fig. 2.

absorb Pt. If Pt enrichment in nodules and crusts were affected only by sedimentary water depth, then Pt should be preferentially enriched in shallower crusts as depth increases, with Pt contents being lower in deeper seawater where polymetallic nodules grow, and with Pt/ Σ PGE ratios of nodules and crusts being similar.

To improve our understanding of the Pt enrichment mechanism of hydrogenetic nodules and crusts in seawater, we hypothesized the following model (Fig. 9).

The shallower Co-rich crusts are closer to the OMZ, where a reduction reaction of [PtCl₄]²⁻ occurs in seawater, with Pt²⁺ being reduced to Pt⁰. As the sedimentary water depth increases, the oxygen fugacity in the seawater gradually increases, and colloidal particles of hydrous δ -MnO₂ adsorb Pt⁰ that formed near the OMZ and co-precipitate into the crusts (Halbach et al., 1989). Furthermore, few Pt²⁺ ions in seawater are directly adsorbed and enriched by negatively charged δ -MnO₂ with very large specific

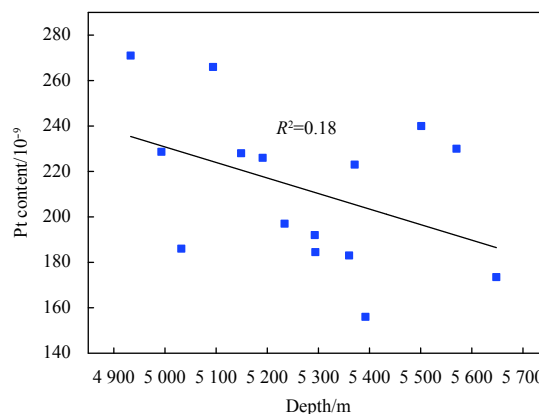


Fig. 8. Plot of depth vs. Pt content. Pt contents of samples in the same station are averaged.

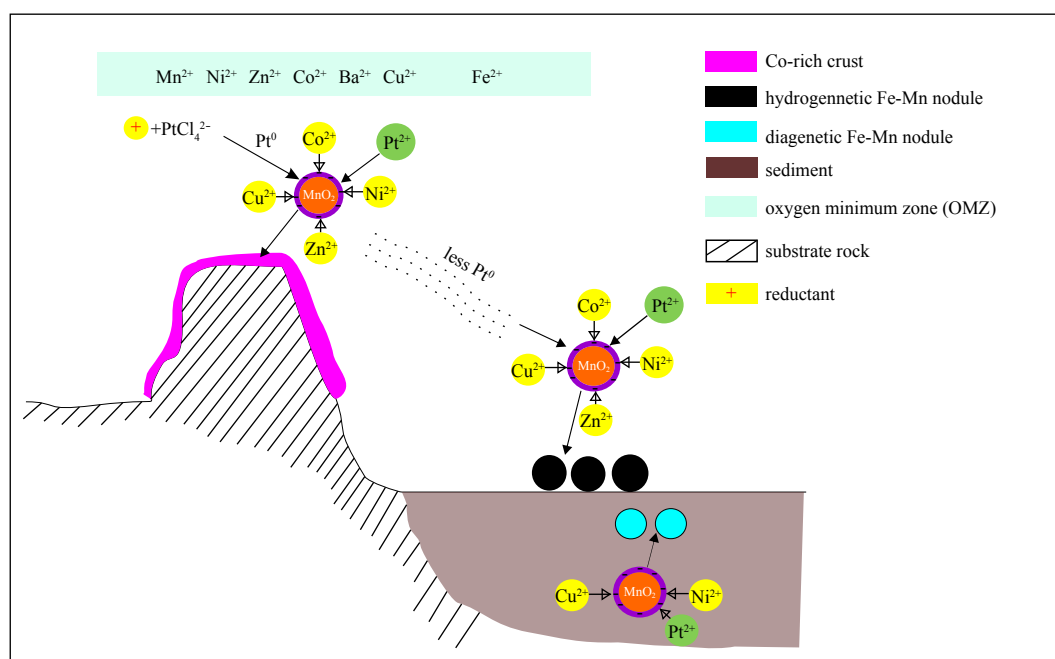


Fig. 9. Enrichment of Pt in polymetallic nodules and Co-rich crusts.

surface area (Fig. 9). The positively charged amorphous iron hydroxide repels the Pt^{2+} , with Fe_2O_3 and Pt thus exhibiting a negative correlation (Fig. 7). With the increasing of water depth, the manganese oxides in the shallower Co-rich crusts adsorb large amounts of Pt from the seawater, reducing the Pt content of deeper seawater. Consequently, the total Pt content of hydrogenetic nodules is lower than that those of shallower hydrogenetic crusts, and the percentage of Pt in ΣPGE of the hydrogenetic nodules is also lower than that in the hydrogenetic crusts.

Diagenetic nodules generally grow inside sediments or are completely buried by them (Fig. 9). The main sources of ore-forming materials in these nodules are provided by cold pore-water, and they are more enriched in Ni and Cu than the hydrogenetic nodules (Dymond et al., 1984; Halbach et al., 1981). Previous studies have shown that Pt in mixed-type nodules is positively correlated with Cu and Ni in the CCZ (He et al., 2006), and the Pt content is significantly lower than that of hydrogenetic nodules both in study area and the EEZ of Cook Islands (Table 3). This may indicate that the Pt content of pore-water is lower than that of seawater, but further research is needed to confirm this.

6 Conclusions

(1) Polymetallic nodules in the study area are of the hydrogenetic type with an average ΣPGE content of 258×10^{-9} , significantly lower than that of Co-rich crusts in Marcus-Wake Seamount, higher than that of mixed-type nodules in the CCZ of the East Pacific Ocean, and similar to that of crusts in the South China Sea.

(2) The CI chondrite-normalized PGEs patterns of polymetallic nodules and Co-rich crusts are highly consistent, with all being characterized by gradual enrichment from Os to Pt and positive Pt anomalies. These characteristics are the converse of those of PGEs in seawater, which implies that PGEs in the nodules and crusts should be mainly derived directly from seawater.

(3) The Pt content and Pt/ ΣPGE ratios of hydrogenetic nodules are significantly lower than those of hydrogenetic crusts in the same area, likely due to differences in sedimentary water depth and oxygen fugacity of ambient seawater.

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