

Geochemical investigation of Pt, Pd, Rh, Ru and Au in cobalt-rich deposits from the Tuamotu plateau (French Polynesia)

PGE
Nodules
Ferromanganese crusts
Tuamotu

Planitoïdes
Nodules
Encroûtements polymétalliques
Tuamotu

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ABSTRACT

Pt, Pd, Rh, Ru and Au contents were determined in 35 samples of hydrogenous ferromanganese crusts and nodules from the Tuamotu Plateau (French Polynesia), collected during the Nodco II cruise undertaken by IFREMER during March 1987. These samples are characterized by high Pt and Rh contents. A statistical analysis including PGE and data on Mn, Fe, Ni, Co and Cu contents does not reveal significant correlations between the elements. Although meteoritical origin of PGE remains possible, the process of fractionation and deposition is probably hydrogenetic as confirmed by normalization diagrams to chondrite C1. This point of view is supported by the determination of some partition coefficients of PGE between the oxidized phase and the aqueous medium. The deposition mechanism is discussed.

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RÉSUMÉ

Étude géochimique, Pt, Pd, Rh et Au dans les encroûtements cobaltifères du plateau des Tuamotou (Polynésie française).

La présente étude rapporte la détermination systématique de Pt, Pd, Rh, Ru et Au ainsi que des éléments mineurs et majeurs dans 35 échantillons d'encroûtements et de nodules enrichis en cobalt prélevés lors de la campagne Nodco II de l'IFREMER sur le plateau des Tuamotu en Polynésie Française. Des teneurs élevées en Pt et Rh caractérisent ces encroûtements. Une étude statistique des données ne permet pas de mettre en évidence de corrélations significatives des PGE (Platinum Group Elements) avec les autres éléments de la paragenèse. Toutefois si l'origine météoritique des PGE reste plausible, l'étude montre que le dépôt est probablement d'origine hydrogénétiq ue, comme en témoignent des diagrammes de teneurs normalisés aux chondrites. Ceci est confirmé par une étude des coefficients de partage de quelques PGE entre la phase oxydée que constituent les encroûtements et la phase aqueuse. Le mécanisme de dépôt est discuté.

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INTRODUCTION

The platinum group elements (PGE) are characteristic of basic and ultra-basic cumulate rocks where processes of differentiation are controlled by the fugacities of oxygen and sulphur (Amossé *et al.*, 1987, 1990) – as well as other elements such as chlorine – which are associated with the magmatic fluid phase (Balhaus and Stumpfl, 1986). These elements can be concentrated as a result of a remobilization in complex environments where unusual differentiation processes may occur. For example, the presence of significant amounts of Pd and Rh – in the absence of Pt – that we have recently found within hydrothermal quartz veins (unpublished) is a consequence of differentiation of PGE between a particular type of fluid and the solid phase. Similarly, the anomalous Pt enrichment in polymetallic nodules and crusts with high Co contents would also appear to result from a particular type of differentiation process.

Although the Pt anomaly in polymetallic encrustation has been known for about ten years, it has been the subject of few studies (Agiorgitis and Gundlach, 1978; Halbach *et al.*, 1984; Hodge *et al.*, 1985; Hein *et al.*, 1988; Terashima *et al.*, 1988; Halbach *et al.*, 1989). Other than these investigations, further data concerning Pd and Ir were published in Goldberg *et al.* (1986).

Recent developments in analytical techniques have permitted analysis of a wide range of geological materials for the PGE. Despite the current economic importance placed on these precious metals, the small amount of available information is due not only to analytical difficulties but, more importantly, to the problems of recovering samples from great water depth.

The Nodco I and Nodco II cruises undertaken by Ifremer in the Tuamotu Archipelago (French Polynesia) have led to the collection of a considerable number of samples from various depths. Furthermore, extensive experience in the ultra-trace measurement of PGE in a wide range of geological materials has enabled the Chemistry Laboratory of the Institut Dolomieu to attempt a systematic investigation of the distribution of these elements in the samples collected by the Ifremer within the studied area. Correlations between the elemental concentrations were investigated to help to elucidate the processes of accumulation of precious metals in this deep-sea environment.

GEOLOGICAL ENVIRONMENT OF COBALT-RICH DEPOSITS

Cobalt-rich polymetallic deposits have been systematically studied since the early 1980's, and have been identified in various geological environments: chains of midplate seamounts, fossil ridges and associated plateaus as well as island arcs. In the Pacific Ocean, their distribution is

related to three NW-SE trending main volcanic structures: the Emperor Seamounts-Hawaiian Ridge, (Glasby and Andrews, 1977; Clark *et al.*, 1984; Hein *et al.*, 1985a, 1985b, 1986, 1987a; De Carlo *et al.* 1987; Keating *et al.*, 1986) the Mod-Pacific Mountains-Line Islands Ridge, (Halbach *et al.*, 1982, 1984; Cronan, 1984; Commeau *et al.*, 1984; Aplin and Cronan 1985) the Marshall and Ellice Islands (Cronan, 1984; Commeau *et al.*, 1984; Schwab *et al.*, 1985; Hein *et al.*, 1986, 1987a; Keating *et al.*, 1986) and Tuamotu Archipelago (Mero, 1965; Ranchin, 1972; Pichocki, 1984; Pichocki and Hoffert, 1987; Le Suavé *et al.*, 1986, 1989).

As a general rule, cobalt-rich deposits (> 0.5 % wt Co) are located on topographic highs (800-2 000 m water depth) devoid of or with limited sedimentation over the last tens of millions of years; their formation is considered by different authors as being related to the oxygen minimum layer in the water column (Halbach *et al.*, 1982).

The occurrence of cobalt-rich deposits in French Polynesia, and more specifically in the Tuamotu archipelago, has been known since 1970 (Ranchin, 1972; Pichocki, 1984; Pichocki and Hoffert, 1987). The two sites which first sampled by dredges (R/V *La Coquille*), were re-investigated during the Nodco I cruise of the R/V *Jean Charcot* (1986), and the use of "Seabeam", high resolution side-scan sonar, unmanned submersible "Epaulard" and dredges has made it possible to identify a fossil reef structure (Le Suavé *et al.*, 1986). Detailed petrological and geochemical studies have led to a model which takes into account the subsidence of the archipelago (starting during the Middle to Upper Eocene), variations of the palaeo-environment and, more particularly, the effects of Antarctic Bottom Water. This model is supported by the interpretation of seismic data collected at the same site during the Nodco II cruise (Pichocki, 1987; Le Suavé *et al.*, 1989).

The Nodco II cruise, carried out in March 1987, was aimed at the exploration of a large area, extending from the western to the southern part of the archipelago, over a distance of 1 000 km. Three new sites have been identified and surveyed in detail; two of these are located to the north west of Matahiva Island (Fig. 1); the third is situated at the southwestern boundary of the surveyed area.

Depending on their location, the volcanic structures on which cobalt-rich deposits have developed are more or less controlled by the tectonic activity which took place during the different periods of construction of the archipelago. Thus, in the western part, considered to be the region where magmatism first occurred (Pautot, 1975), two main structural directions (N10°W and N80°E) have been identified. The first trends is interpreted as the initial grain of the oceanic crust; the second is believed to represent the direction of the Marquesas fracture zone (Le Suavé and Pautot, 1988). At the intersection of these two trends, more intense volcanic activity has taken place, leading to the construction of smooth-shaped structures as represented on Figure 2 (Matahiva North site).

Different types of substrates are identified from site to site: more or less altered or brecciated volcanic rocks,

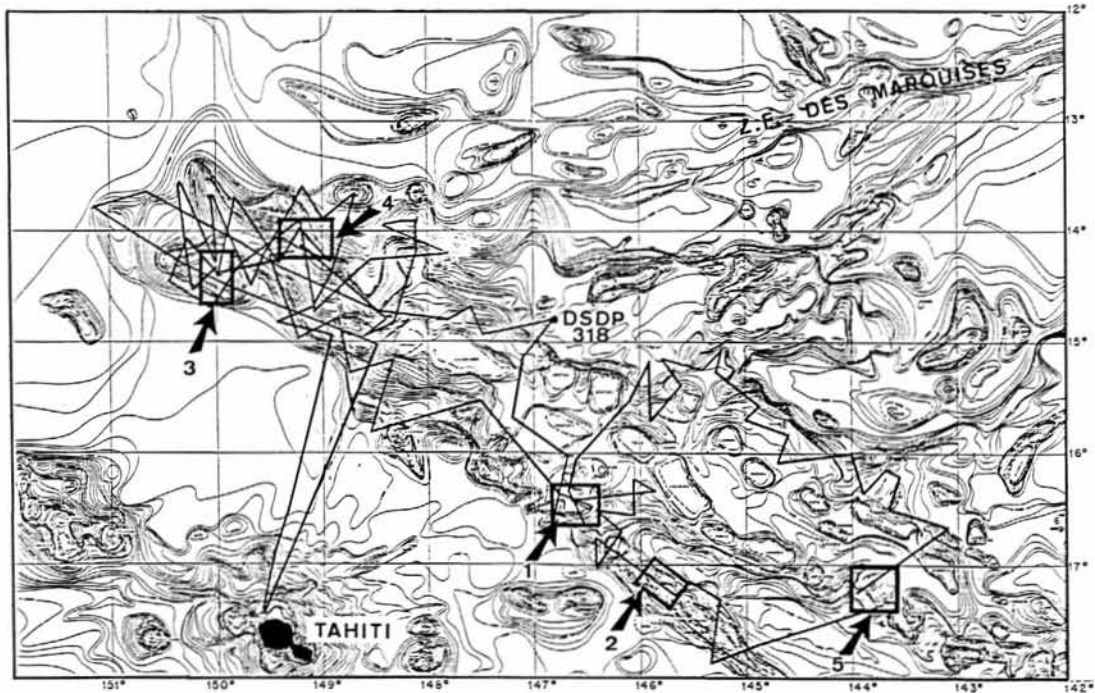


Figure 1

Location of cobalt-rich deposit sites in the Tuamotu archipelago. (Tracks are relative to the Nodco II geophysical and bathymetric cruise).

Situation des sites des dépôts cobaltifères dans l'Archipel des Tuamotus. (Les traits représentent l'itinéraire de la campagne Nodco II de relevés géophysiques et bathymétriques).

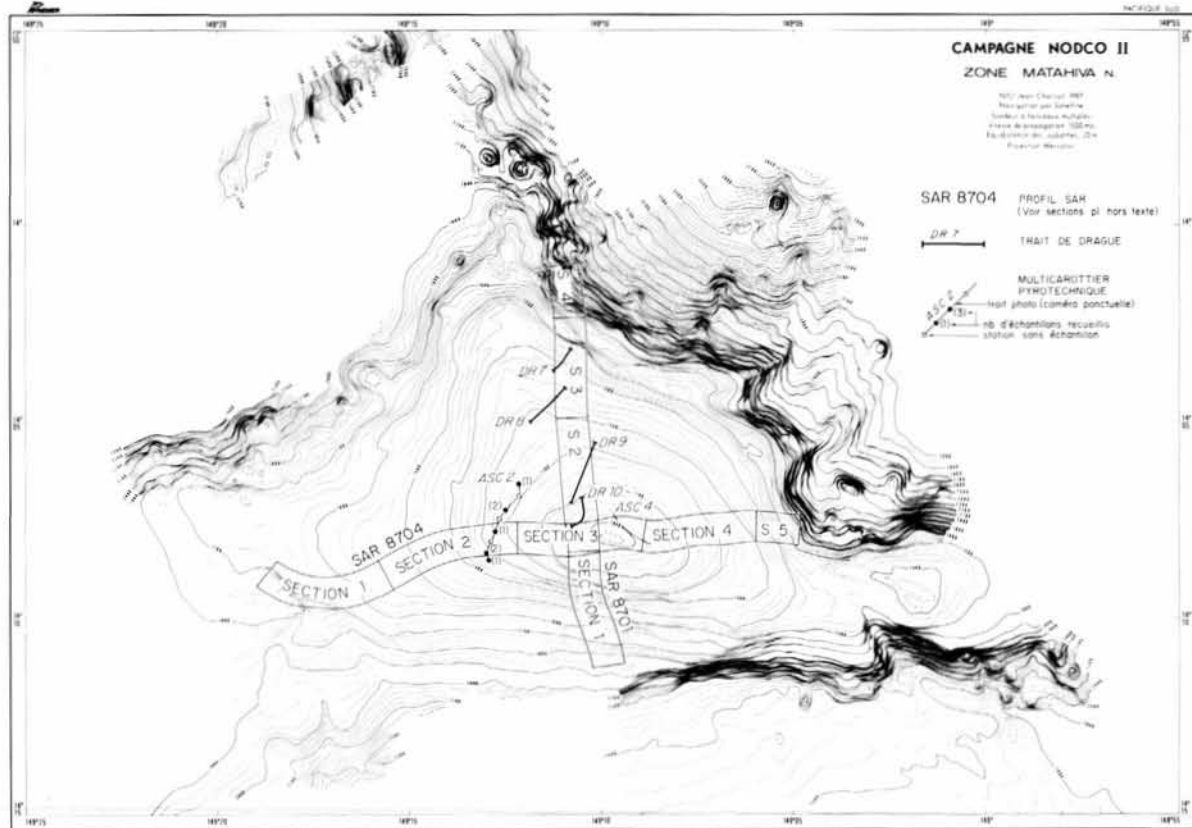


Figure 2

Bathymetry and detailed map of the North Matahiva site.

Relevés bathymétriques et carte détaillée du site de Matahiva Nord.

Table 2
Metal contents of oxidized crusts and nodules from the Tuamotu archipelago.
 Teneurs en éléments des nodules et des encroûtements oxydés de l'archipel des Tuamotu.

N° Sample	Description, emplacement	Pt ppb	Pd ppb	Rh ppb	Au ppb	Ru ppb	Co ppm	Ni ppm	Cu ppm	Mn %	Fe %
DR 2-1	Outer crust, Matahiva W (920-1027 m)	572	1,5	71	21	16	13 100	5 800	588	27,57	16,62
DR 4-1	Middle crust, Matahiva W (050-990 m)	440	2,8	44	5,5	0,5	13 200	5 600	667	26,84	15,27
DR 4-2	Polished crust, (Idem)	464	5	36	19	3	7 600	4 300	571	21,57	15,75
DR 5	Vitreous outer crust, Matahiva W (770-900 m)	608	5,5	41	7	18	12 200	7 600	824	30,67	14,80
DR 6-1	Porous crust Matahiva NW 2900 m	283	5	34	15	20	6 000	4 000	848	20,09	19,61
DR 7-2	Inner crust, Matahiva N (1370-1440 m)	716	10	43	24	10	15 000	7 100	1 000	27,82	16,50
DR 7-4	Outer and middle crust, (Idem)	645	9	76	31	29	10 900	6 500	1 394	25,51	16,75
DR 9-1	Outer crust (2 cm), Matahiva N (1100-1300 m)	1 284	20	48	30	21	12 600	10 800	1 371	32,47	12,50
DR 9-2	Vitreous outer crust, (Idem)	1 225	73	59	14	37	13 000	8 500	1 176	31,90	15,73
DR 9-2-1b	Outer crust, (Idem)	1 233	10	33	10	7	8 700	7 600	1 410	26,50	13,60
DR 9-3-1	Outer crust, (Idem)	482	2	55	14	1,5	10 200	5 600	686	25,33	15,75
DR 9-6-1b	Botryoidal outer crust, (Idem)	672	17	60	10	25	12 200	7 800	1 230	30,10	13,10
DR 9-6-2b	Core, (Idem)	1 811	12	86	7	14	4 300	4 500	1 160	19,30	20,20
DR 9-7-1b	Outer crust on a 10 mm nodule, (Idem)	526	19	54	4	14	13 700	7 800	1 100	27,20	13,20
DR 9-8-1	Outer crust on a 10 mm nodule (Idem)	596	62	49	30	18	14 100	7 700	1 030	28,64	16,00
DR 9-8-2	Inner crust, (Idem)	1 240	7,2	96	38	20	12 100	6 200	941	28,95	15,59
DR 10-1-1	Outer crust, Matahiva N (1080 m)	588	1,4	70	45	18	15 200	7 900	765	31,02	14,71
DR 10-1-2	Inner crust, (Idem)	610	4,6	64	17	10	9 300	5 300	647	24,40	15,80
DR 10-4-1	Compact outer crust, (Idem)	715	3	55	10	1	18 900	8 500	857	32,45	13,16
DR 10-4-2	Compact inner crust, (Idem)	496	8	34	6	0,1	1 100	2 000	233	14,35	10,67
DR 10-3	Outer crust, (Idem)	583	17	48	38	36	15 800	9 400	882	30,26	14,10
DR 10-N	2 cm nodule, (Idem)	459	42	58	9	22	10 100	6 100	857	27,02	17,21
DR 11-1	Outer and inner crust, Haraiki W (1450 m)	770	3	62	10	12	10 800	5 400	1 375	27,11	17,56
DR 11-2-1	Botryoidal outer crust, Haraiki W (1450 m)	248	17	20	25	14	10 000	5 200	765	26,81	18,31
DR 11-2-2	Compact inner crust, (Idem)	544	25	46	17	10	5 400	3 700	1 455	19,37	17,00
DR 11-3	Outer crust (2 cm), (Idem)	305	29	38	24	23	13 900	6 000	647	28,86	15,58
DR 12-1	Botryoidal crust, Haraiki W (1300-1600 m)	224	45	22	7	3,7	10 200	5 700	848	25,37	16,60
DR 12-1b	Botryoidal crust, (Idem)	240	13	40	6	12	9 600	5 900	900	23,40	16,40
DR 12-2b	Calcitized inner crust, (Idem)	334	17	133	4,5	26	6 200	3 800	1 730	19,60	21,30
DR 12-N	Small nodules, Haraiki W (1300-1600 m)	773	35	66	34	8	4 200	6 800	6 182	19,68	16,80
DR 17-1	Botryoidal outer crust Matahiva N (2150-2330 m)	242	14	21	25	240	5 700	3 800	1 758	22,16	20,97
DR 18-2	Botryoidal outer crust, Matahiva NW (1450 m)	531	3	48	54	11	9 700	6 900	970	28,78	16,00
DR 19-1	Compact outer crust, Matahiva NW (1400-1920 m)	3 880	5	140	15	0,2	3 600	3 000	2 061	18,46	28,63
DR 19-1b	Outer crust (10 mn), (Idem)	742	10	45	9	31	15 000	4 700	640	24,10	17,84
DR 19-2	Porous inner crust, (Idem)	1 300	7	73	32	0,5	13 800	4 600	1 212	25,95	17,90

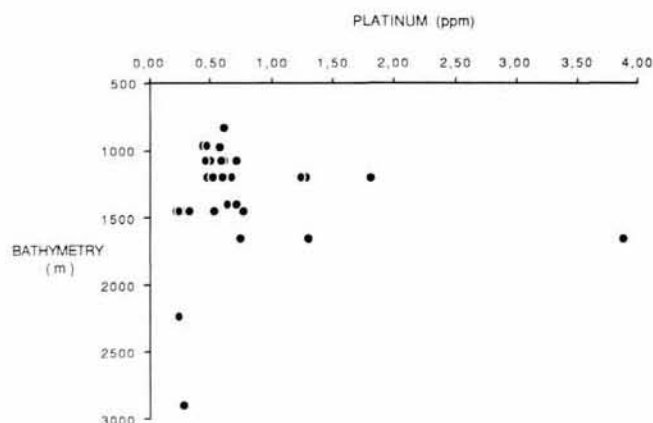


Figure 3

Relationship between Pt contents in oxides and water depth.
 Relation entre les teneurs en platine des oxides et la profondeur d'eau de prélèvement.

hyaloclastites, and carbonates (dated, in part, as of Lutetian) with a variable extent of phosphatization. The maximum thickness of the recovered polymetallic deposits is 6 to 8 cm.

EXPERIMENTAL PROCEDURE

Samples, containing about one-third water by weight, were ground in an agate ball mill and then overdried at 110°C for two hours. This procedure is controlled by a second heating to a temperature of 150°C. In this case the weight variation is only 1% of the former. All powdered samples prepared in this manner were stored in sealed tubes in order to prevent the uptake of moisture typical of Fe-Mn oxide material.

The analysis of major (Mn and Fe) as well as minor elements (Co, Ni and Cu) was performed by flame atomic absorption, using appropriately diluted aliquots and internal standards. The platinum group elements (Pt, Pd, Rh and Ru) and also Au, were analysed by electrothermal atomic absorption following a method based on the procedure for PGE assay in silicate rocks (Amossé *et al.*, 1986).

- 1g of the powdered sample is fused with 4g Na₂O₂ and 1g KNa CO₃ in a zirconium crucible.
- After cooling, the fused sample is dissolved in water and acidified with HCl. The solution is evaporated to dryness in a sand-bath, in order to precipitate out the silica in an insoluble form.
- The dry residue is re-dissolved in water, filtered and then made up with 4M HCl to yield a solution which is split into two aliquots. One aliquot is spiked with Pd chloride and used for the determination of Pt, Rh and Au. In fact, the addition of Pd favours the precipitation of Pt during the analytical steps described below. The second aliquot is retained for the analysis of Pd.
- Both solution aliquots are spiked with 10 mg Se and 1 mg Te in the form of dissolved oxides. The solutions are reduced by boiling with stannous chloride for 10 minutes, then cooled, the precipitate of Se and Te which contains the PGE co-precipitated as selenides and tellurides is filtered through Millipore 0.22 μ membranes to separate the filtrate. The recovered precipitate is taken up in a few drops of *aqua regia* and used to make 2 ml sample solutions.

Instrumental analysis was performed on a Varian AA 875 atomic absorption spectrometer equipped with a GTA 95 electrothermal atomizer furnace and an automatic sampler. This arrangement permits the programming of the various steps of drying, ashing and atomization within the furnace. The detection limits obtained with this method are as follows – Pt: 0.5 ppb; Ru: 0.3 ppb; Rh: 0.1 ppb; Pd: 0.1 ppb; Au: 0.1 ppb. In a previous paper (Amossé *et al.*, 1986), we have shown that the recovery rate of PGE is about 95 to 100% according to the element. These values were calculated by extraction of PGE added in known quantities to artificial rock solutions. The analytical

method was tested by analysis of the USGS International Standard PCC1. Our results as well as values proposed by some authors are given in Table 1.

Table 1

Study of the International Standard PCC1-USGS. The values of Gladney, Flanagan and Abbey are "Proposed values".
Etude du standard International PCC1-USGS. Les valeurs de Gladney, Flanagan et Abbey sont des valeurs recommandées.

Element	This work	Aruscavage (1984)	Bornhorst (1984)	Gladney (1983)	Flanagan (1976)	Abbey (1983)
Pt	11.6	5.7	–	10.2	8	10
Pd	5.2	4.36	–	6.3	13	5
Rh	1.3	1.1	–	1	1	1
Au	0.9	–	0.5	0.86	0.7	1.6

RESULTS AND DISCUSSION

The analytical results obtained from 35 samples collected during the Nodco II expedition are presented in Table 2. A large degree of scatter in the precious metal contents is immediately apparent. Pt displays concentrations ranging from 224 ppb to 3880 ppb. The exceptionally high later value was confirmed on a duplicate of the same sample (DR 19-1), but was not found in another sample from the same dredge-haul (DR 19-1b). The heterogeneity of PGE contents in Tuamotu Fe-Mn crusts appears to be characteristic of this type of mineralization.

The analytical results reveal relatively high Rh concentrations which are correlated with Pt, as discussed below. The negative Pd anomaly observed here appears to be another geochemical characteristic of this type of deposit.

The variation of Pt contents as function of water depth is given in Figure 3. There is a tendency for Pt enrichment in the depth interval 1 200-1 700 m, and contents are in good agreement with the results obtained by Hodge *et al.*, (1985), Terashima *et al.*, (1988) and Halbach *et al.*, (1989), for various sites in the North Pacific. However, the small number of samples in the present study do not enable us to draw any statistically valid conclusions.

Because the encrustations formed over a time-span of about 20-30 My (Halbach *et al.*, 1984; Halbach, 1986), to 40-45 Ma (Pichocki, 1987) a study of the previous metal concentrations across the different oxidized layers may reveal periods during which PGE's were preferentially concentrated. A comparison between inner and outer layers was undertaken for selected samples (DR9-6-1b/2b, DR9-8-1/2, DR10-1-1/2, DR10-4-1/2, DR12-1b/2b and DR19-1/2). Because of the possible late overgrowth of calcite within the cores of these samples, a valid comparison can only be made if the inner and outer zones of the crusts have similar Mn + Fe contents. The Pt content of the internal crust is normalized to the same Mn + Fe contents as that of the external crusts. The Pt ratios between external and internal crusts are, respectively, for the samples cited above: 2,95-2,08-1,18-1,26-1,3-0,36. It can be seen

that the inner parts of the crusts and nodules have significantly higher Pt contents than the outer layers. However, the sample pair DR 19-1/2 appears anomalous in this respect. If the processes governing the enrichment of PGE are linked to the depth of deposition, the variation in PGE contents may be explained by subsidence of the Tuamotu plateau with time or possibly with a diminution of metal supply from an external source.

The origin of the PGE in these samples is still a matter of controversy. The discovery of some Fe-Ni micrometeorites with PGE-rich cores in one crust sample from the Tuamotu (Kosakevitch, 1987) does not necessarily imply that the observed PGE concentrations are derived from an extra-terrestrial source. In fact, when the PGE sample concentrations are normalized to chondrite values – a classic procedure for the study of geochemical fractionation in terrestrial ultrabasic complexes – the abundance pattern is not flat. We have drawn (Fig. 4) the normalized diagram for the mean values of samples collected in different ranges: < 1 200 m; 1 200-1 700 m and > 1 700 m. Spectra 1 and 2 reveal a strong negative anomaly for Pd and Ru, while Pt and Rh remain close to chondrite values. The anomalies observed here appear to be a geochemical characteristic of this type of deposit and are typical of a strong hydrogenetic differentiation process. All the observations made on PGE distribution in magmatic or hydrothermal environments show another behaviour depending on fO_2 , fS_2 and fCl_2 . (Amossé *et al.*, 1987; Fischer *et al.*, 1988; Amossé *et al.*, 1990). Diagram 3 is obtained with two samples and has a low statistical

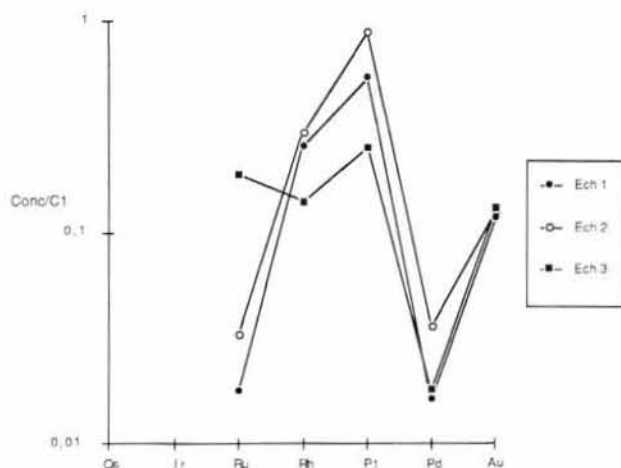


Figure 4

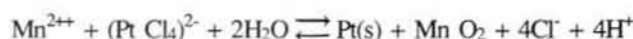
Normalized patterns with respect to chondrite C1 for the mean of samples: Pattern 1: < 1200 m; pattern 2: for 1200-1700 m; pattern 3: > 1700 m.

Diagrammes normalisés à la chondrite C1 pour les teneurs moyennes des échantillons: Diagramme 1: < 1200 m; diagramme 2: pour 1200-1700 m diagramme 3: > 1700 m.

weight. Nevertheless an evolution of the PGE precipitation process with depth can be seen which is characterized by an increasing Ru content. This increase is corroborated by the results that we have recently obtained for a nodule collected at water depth of 4 500 m near Marquisas Islands (cruise Tahino 03). In this sample we observe the same Pt and Ru concentration (68 ppb). Other authors (*e.g.* Hein *et al.*, 1988) have also proposed a hydrogenous origin for the PGE in nodules. However, even if the process of concentration is hydrogenous in nature, the ultimate origin of the PGE may be in meteorites. Prior to their incorporation into nodules, the PGE may have been dissolved in sea-water in the form of complex chlorides. The high chlorinity of sea-water favours the formation of chloride complexes typical of PGE. An investigation of $^{187}Os/^{186}Os$ ratios in manganese nodules (Palmer *et al.*, 1988) has led to the conclusion that 10-20% of the Os metal comes from meteorites, the rest being derived from a terrestrial source, mainly peridotites.

Despite the consensus that most of the PGE in deep-sea deposits have a terrestrial origin, the exact physico-chemical process that controls their precipitation and incorporation remains unclear. It has been proposed by several authors (Goldberg *et al.*, 1986; Brookins, 1987) that Pt can be precipitated as a tetravalent oxide species. The Pt hydroxide so formed could be adsorbed onto manganese oxides; this hypothesis is supported by the negative Pd anomaly mentioned above, since Pd does not form a stable oxide species under such conditions.

The onset of platiniferous mineralization coincides with the oxygen minimum zone, (although Rougerie and Wauthy (1986) do not agree on this hypothesis) thus leading Halbach *et al.*, (1989) to suggest a mechanism for the precipitation of Pt(s) involving the following redox reaction:



It would appear that a calculation of the free enthalpy of this reaction should include a term for the adsorption energy of Pt(s) on MnO_2 . This is because adsorption has a significant effect on the reaction mechanism. Using the analytical results of the present study we have attempted to find relationships between elements by calculating a correlation matrix (see Table 3). Only Pt shows a significant correlation with Rh and Cu. A correlation with Fe is essentially due to sample DR 19-1. By contrast, no correlation is seen between Pt and Mn.

Previous studies (*e.g.* Hodge *et al.*, 1985, Terashima *et al.*, 1988) have pointed to a strong correlation ($r > 0.7$) between Mn, Ni and Co. The weak correlation observed for our samples can be explained as follows. The Mn/Ni and Mn/Co ratios being high, the process which controls the precipitation of Ni and Co is more dependent on the physicochemical conditions, or Mn oxide stoichiometry, than on Mn concentration of the crusts. Such a feature is probably even more important for PGE, for which concentrations in water and crusts are respectively 10^5 and 10^4 lower.

Table 3
Correlation coefficient for analysed elements.
Coefficients de corrélation pour les éléments analysés.

Pt	Pd	Rh	Au	Ru	Co	Cu	Ni	Mn	Fe	
1.000	-0.024	0.805	0.011	-0.173	-0.229	0.466	-0.083	-0.067	0.417	Pt
	1.000	-0.079	0.022	0.108	0.051	0.212	0.288	0.234	0.042	Pd
		1.000	0.173	-0.248	-0.064	0.331	-0.033	-0.129	0.229	Rh
			1.000	0.121	0.197	0.103	0.308	0.076	-0.245	Au
				1.000	-0.123	0.286	-0.098	-0.017	0.176	Ru
					1.000	-0.366	0.691	0.456	-0.424	Co
						1.000	0.005	-0.057	0.457	Cu
							1.000	0.478	-0.510	Ni
								1.000	0.229	Mn

The positive correlation coefficient between Pt and Rh displays a similar fractionation process. This is supported by the respective positions of the elements on the normalization diagram.

Ru has no significant correlation with the other elements. As noted above, its behaviour seems opposed to that of Pt. It must be noted that dissolution of Ru in sea water is very difficult owing to the chemical stability of the mineralogical phases, rutheniridosmine and laurite, existing in ultrabasic rocks and meteorites.

The average gold content of the studied oxides is low and behaviour appears to be controlled by absorption phenomena on Mn oxides.

Any genetic hypothesis must take into account the observed differentiation of the different PGE in the studied samples. In this context, it is important to establish partition coefficients for the PGE between the solid paragenesis and the solute phase containing complexes in sea-water. Thus, we present some preliminary data concerning the measurement of ultratrace dissolved matter in water samples from the Tuamotu site. The results of these analyses are given in Table 4.

Table 4
Analysis of a sea-water sample from Tuamotu archipelago.
Depth : 1000 m; Location : 16°27'30"S; 146°33'48"W.
Analyse d'un échantillon d'eau de mer provenant de l'Archipel des Tuamotu. Profondeur du prélèvement : 1000 m; Situation : 16°27'30"S; 146°33'48".

Element	Pt	Pd	Au
Contents ng/l (ppT)	< 1	37	2.2

The analytical difficulties associated with this type of determination are considerable because of the risk of sample contamination. Taking into account the large volumes of water sampled, the detection limit for Pt in the present study is of order of ppT. Goldberg *et al.* (1986) obtained values ranging from 0.1 to 0.2 ppT increasing slightly with water depth. It must be noted that the Pd content values are much higher than that published by Hodge *et al.*, (1985) (0.05 ppT). From Goldberg *et al.* Pt values, and our Pd and Au values, we calculate partition coefficients C_{ox}/C_{sol} , which are respectively 10^7 , 10^2 and 10^3 . It must be noted that activities of PGE ions in solution are much

lower, due to the formation of complex chlorides. The partition coefficient for Pt is higher than those observed in magmatic or hydrothermal processes (10^4). A partition coefficient of 10^7 is a typical value for an electrochemical process, which can be summarized by an Eh-pH diagram. In such a process, the exchange is favoured by fast diffusion of ions in the aqueous medium. Thus, the low Pd (and Au) content, can be explained by the formation of a slightly soluble species in the conditions prevailing during Mn and Fe oxide formation. Even through our results need to be confirmed by further studies, we nevertheless show levels of Pd that indicate a partition coefficient between solid and liquid which is far less favourable for precipitation than for Pt.

Whatever the precise nature of solid/liquid partitioning, it remains necessary to determine the physico-chemical mechanisms that may operate during the hydrogenous concentration of PGE. This approach should include quantitative analysis of the phases present as well as laboratory studies aimed at simulating the ambient conditions during the deposition of PGE. Such work is in progress at the Grenoble laboratory in order to elucidate these problems.

CONCLUSION

An investigation of the distribution of PGE in polymetallic Co-rich nodules and encrustations from the Tuamotu Plateau (French Polynesia) confirms the anomalously high Pt contents already measured elsewhere in the North Pacific where Fe-Mn crusts occur. Furthermore, the present study reveals in one sample, the presence of the highest Pt contents so far recorded from this type of material. The observed concentrations of Pt constitute a potential economic reserve for this metal, which could be extracted as a by-product of the deep-sea mining of Co.

For the first time, a systematic set of data has been collected for Rh, Ru, and Au as well as other major and minor elements. The hydrogenous nature of the deposit, and the ultimate source of the PGE are discussed. Nevertheless, confirmation of the hydrogenous origin of the deposit will only be obtained on the basis of experimental thermochemical study.

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