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メタデータ	言語: en 出版者: The Geochemical Society of Japan 公開日: 2016-05-10 キーワード (Ja): キーワード (En): 作成者: Morishita, Yuichi, Usui, Akira メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10297/9395">http://hdl.handle.net/10297/9395</a>

# EXPRESS LETTER

## Microanalysis of platinum in hydrogenetic ferromanganese crust using SIMS

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(Received August 11, 2015; Accepted September 19, 2015; Online published October 23, 2015)

Heretofore the presence of platinum in the hydrogenetic ferromanganese crust has been known yet, the host to platinum has remained poorly understood. Here we first report on the microanalysis of platinum in ferromanganese crust using secondary ion mass spectrometry (SIMS). SIMS microanalysis revealed that Pt concentration of vernadite was between 0.21 and 1.22 ppm, and that of brown matrix was very low (around the detection limit of 0.036 ppm or less) in a ferromanganese crust. The SIMS spatial resolution was 3  $\mu\text{m}$  by 3  $\mu\text{m}$  on the sample surface, and several tens of nanometers along the depth. A novel Pt detection method using SIMS was performed, in which most SIMS depth profiles show homogeneous Pt concentrations (0.21 to 0.55 ppm), however, some profiles detected local enrichment of Pt on the nm level.

Keywords: hydrogenetic ferromanganese crust, platinum, microanalysis, SIMS

### INTRODUCTION

The ferromanganese crust is a type of marine sedimentary rock that often covers the surface of rock outcrops on seamounts at various depths. Among bulk chemical compositions of ferromanganese crusts, several metal elements have been watched with interest; as they may be suitable candidates for a future submarine ore deposit. As for precious metals, the presence of platinum was confirmed in ferromanganese crusts (Halbach *et al.*, 1984). Platinum is one of the most important rare metals, and it is used as a vital part of the three-way catalyst used in exhaust gas purification in cars. The resources of platinum group metals including platinum are unevenly distributed on earth, and 95% of the world reserve exists in the Bushveld Complex of the Republic of South Africa. Therefore the platinum in ferromanganese crusts that are much more widely distributed should attract considerable attention. Although the development of ferromanganese crust resources is not economically feasible at present, the increasing cost of production for on-land mining may make the use of marine deposits compatible in the future.

Hydrogenetic ferromanganese crusts and nodules are believed to be the aggregates of fine-grained iron-man-

ganese oxide minerals and various detritus. Each mineral is usually smaller than 1  $\mu\text{m}$  across and thinner than 0.01  $\mu\text{m}$  in thickness. The minerals are characterized by diffracted X-ray diffraction patterns, and of poorly crystalline nature (e.g., Burns and Burns, 1979; Giovanoli, 1980; Usui *et al.*, 1989). Thus independent crystals are not usually observed under optical microscopes, but forms variable growth patterns, lamination, columns, dendrites, and stromatolite-like structures.

Here we present the first preliminary report on platinum microanalysis of ferromanganese crust using secondary ion mass spectrometry (SIMS). Since SIMS has a very high spatial resolution in depth profiling analysis, it is suitable for analyzing ferromanganese crust, though several analytical challenges remain.

### SAMPLES FOR ANALYSIS

The ferromanganese crust used in this study is HPD#956-R15 that was collected by a ROV Hyper Dolphin 3K from the Takuyo Daigo Seamount located about 150 km southwest of the Minamitorishima Island in the northwestern Pacific Ocean. The sampling location (22°45' N, 153°16' E) was 1,440 m in water depth. The ferromanganese crust consists of vernadite, rock fragments, fossils and clay minerals. The thickness of the crust is about 10 cm (Fig. 1), and the <sup>10</sup>Be-dated growth rate is about 4 mm/m.y. (Usui, unpublished).

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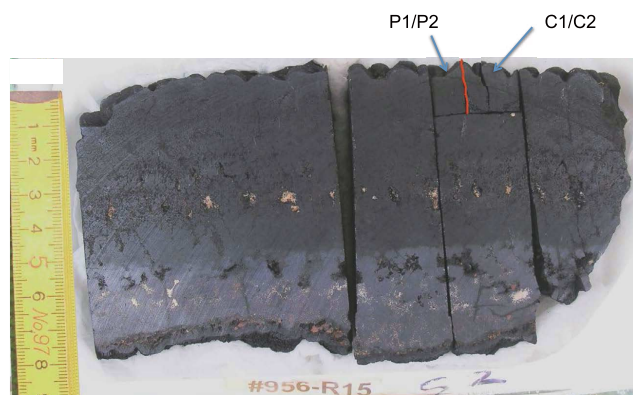


Fig. 1. Ferromanganese crust HPD#956-R15 used in this study. Small slabs P1, P2 (the reverse side of the P1 slab), C1 and C2 (the reverse side of the C2 slab) were cut from the crust. The samples correspond to the uppermost (youngest) part of the crust.

Small thin slabs P1, P2 (the reverse side of the P1 slab), C1 and C2 (the reverse side of the C1 slab) were cut from the crust (Fig. 1). P1 and P2 slabs were each stuck onto a 25 mm diameter disc of silica glass, and were polished. During the producing polished thin sections from the P1 and P2 slabs, cut off chips (P1 and P2 chips, respectively) were kept for bulk chemical analysis. The polished thin section of P1 was used as the SIMS standard (mentioned later). The polished surface of P2, which was coated with carbon (*ca.* 25 nm thick), was analyzed to ascertain its platinum concentration using SIMS. C1 and C2 slabs are samples for bulk chemical analysis, where C1 and C2 are adjacent to P1 and P2, respectively.

## ANALYTICAL METHODS

### SIMS analysis

We determined Pt concentrations of pieces of ferromanganese crust using a Cameca ims-1270 SIMS at the Geological Survey of Japan, AIST. A defocused  $\text{Cs}^+$  primary beam was restricted to 15  $\mu\text{m}$  in diameter by a circular aperture to obtain a homogeneous primary beam of about 0.15–0.30 nA. Negative secondary ions were detected using a total impact energy of 20 kV (a primary accelerating voltage of +10 kV and a secondary extraction voltage of –10 kV). The centering of the primary beam was ascertained each time by looking at the beam position in the 1.5 mm by 1.5 mm field aperture which corresponded to 15  $\mu\text{m}$  in diameter of the primary beam. A square field aperture of 300  $\mu\text{m}$  by 300  $\mu\text{m}$  was introduced into the secondary ion optics, limiting the analyzed area of the sample surface to a central square measuring 3  $\mu\text{m}$  by 3  $\mu\text{m}$  to avoid the crater-edge effect. A normal-incidence electron gun was used for charge compensa-

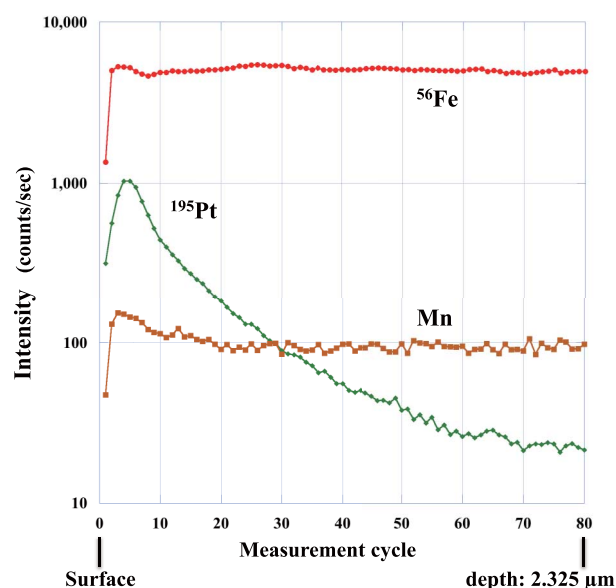


Fig. 2. SIMS depth profiles of  $^{195}\text{Pt}$  and matrix Mn and  $^{56}\text{Fe}$  in the standard P1. The depth of the sputtered crater is 2.325  $\mu\text{m}$  that is measured by a surface profiler.

tion on the sample surface to achieve better stability in secondary ions.

$^{195}\text{Pt}^-$  secondary ions, as well as  $^{55}\text{Mn}^-$  and  $^{56}\text{Fe}^-$  as reference ions, were detected at a mass resolving power of 3,000 without energy filtering using an electron multiplier (EM). An energy window of 50 eV was adjusted to the energy distribution curve in order to ensure that the same energy band of secondary ions was always targeted for measurements. 4, 4 and 10 seconds were allocated for  $^{55}\text{Mn}^-$ ,  $^{56}\text{Fe}^-$ , and  $^{195}\text{Pt}^-$  measurement, respectively, in each measurement cycle. We conducted depth profiling in cycles until sufficient data was obtained for each measurement. EM counting noise is 4.4 cpm (0.073 cps) obtained by a 520 sec long blank test without Cs ion bombardment but with electron gun on. The detection limit was 0.036 ppm ( $3\sigma$ ) if the background noise indicates a Poisson distribution.

### Standardization

Quantitative SIMS analyses require a standard sample. Although calibration curves constructed from doped glasses with known concentrations are normally used for geochemical research in silicate systems, it is difficult to obtain homogeneous distributions of trace elements in standard samples since precious metals like Pt commonly form discrete phases. Therefore ion implantation (an ion beam of the desired element is accelerated in order to implant itself into the sample surface of the standard) was conducted rather than preparing a glass standard. The sample should have a similar chemical composition and

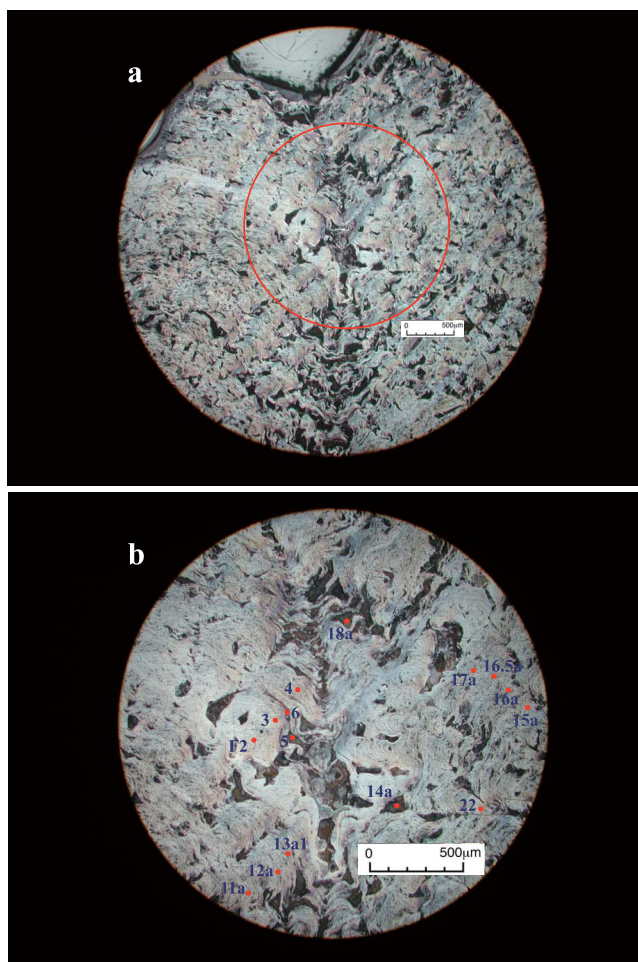


Fig. 3. Photomicrographs of the ferromanganese crust surface (P2 disc). (a) shows a low magnification photo of the uppermost part of the crust (Fig. 1) facing the seawater. The top plain hemisphere-shaped area was filled with seawater before collection. The red circle represents the area of (b). (b) expands (a) by two times. SIMS analysis points are shown in (b). The upper part of the photo corresponds to the upper (younger) part of the crust; therefore the crust has grown upward in the photo.

crystallographic structure to the target minerals. But the main constituent mineral of ferromanganese crust is vernadite that is a kind of clay mineral with low crystallinity. Due to this, we could not prepare a uniform or similar single crystal for a SIMS standard sample. Instead we tried to find the next best candidate to serve as a SIMS standard sample. Eventually, the idea of using ferromanganese crust itself as a standard sample explained in next paragraph was decided on.

A similar ferromanganese crust was thus prepared for analysis. The P1 slab for the standard sample was originally adjacent to the P2 slab that was for analysis, so there should be a strong similarity between the two slabs. The

P1 slab was made into a polished disc, which was then implanted with Pt ions at 1.0 MeV and a density of  $3 \times 10^{14}$  atoms/cm<sup>2</sup> by the Mining and Mineral Sciences Laboratories, CANMET to produce a Pt standard disc. Implanted Pt ions should be placed at a certain depth according to the implant energy. Ion implantation can be simulated for the Pt distribution in a mineral using the TRIM (Transport of ions in matter) program by the Monte Carlo method. Since we do not have enough data to calculate for vernadite, Pt distribution in pyrite is calculated at the implanted energy of 1 MeV using the TRIM. The depth of the maximum intensity of Pt is calculated to be 0.145  $\mu\text{m}$ , and all the Pt ions exist within 0.3  $\mu\text{m}$  from the surface.

## RESULTS AND DISCUSSION

### *Standardization by the RSF and conversion factor*

The concentration of the Pt implanted in the standard P1 disc was measured by SIMS (Fig. 2). The maximum intensity of Pt appears at the depth of 0.13  $\mu\text{m}$ , which is similar depth of 0.145  $\mu\text{m}$  for pyrite TRIM calculation. The shape of the Pt distribution should be symmetrical along depth (a Gaussian distribution); however, Fig. 2 shows a long-tail shape toward the depth. It usually occurs that Pt ions are repelled deeper by high-energy primary ions (knock-on effect), but the tail in Fig. 2 is unusually too long compared with similar standard measurements (e.g., Au implanted in pyrrhotite, Morishita and Hammond, 2007). The reason for the long-tail distribution of Pt is not known but it may depend on the nature of the standard mineral (vernadite). Further analysis by continuous sputtering makes a deeper crater, which introduces vague uncertainties to the obtained data. Therefore the measurement was stopped at 80 cycles.

Quantitative analysis by SIMS requires a relative sensitivity factor (RSF) defined in Appendix 1. The RSF for a specific matrix element was used to calculate the concentration in the unknown sample. Mn and Fe were selected to be matrix elements because the major constituent elements of vernadite are Mn and Fe. Mn and Fe bulk analysis was conducted by a combination of the ICP/AES and ICP/MS methods using the external standard of JMn-1 at the Geological Survey of Canada, Ontario. Mn and Fe content were 18.7% and 15.3%, respectively.

Now we should consider the existing natural Pt abundance in the P1 standard. We averaged all Pt intensities from vernadite measurements of the P2 disc, and deducted the average value (count/sec) from the P1 measurement as background Pt. The background deduction was reflected in the following RSF calculations, but its influence is less than 1% because the amount of implanted Pt was overwhelmingly large compared to the natural Pt in vernadite.

Table 1. SIMS microanalysis of the concentration of Pt in ferromanganese crust (sample P2)

Loc.	Target	File No.	Cycles	<sup>195</sup> Pt (av)	Mn (av)	<sup>56</sup> Fe (av)	Pt (ppm)_Mn	Pt (ppm)_ <sup>56</sup> Fe	Note
F2	vernadite	Pt9@53.adp	49	0.26	32.70	2010	0.32	0.28	average
3	vernadite	Pt9@54.adp	22	0.36	29.70	1710	0.55	0.52	average
4	vernadite	Pt9@55.adp	35	0.23	38.70	2220	0.23	0.22	average
5	brown matrix	Pt9@56.adp	10	0.04	10.60	282	-0.05	-0.05	average
6	matrix + vernadite	Pt9@57.adp	33	0.13	46.40	1950	0.09	0.08	average
11a	vernadite	Pt11a.adp	24	1.03	73.50	4010	0.73	0.73	average
	vernadite (max)	Pt11a.adp		5.00	73.50	4010	3.78	3.77	Pt peak
12a	vernadite	Pt12a.adp	24	0.45	63.40	3450	0.33	0.33	average
13a1	vernadite	Pt13a1.adp	25	1.40	61.60	3080	1.22	1.32	average
	vernadite (max)	Pt13a1.adp		3.60	61.60	3080	3.23	3.51	Pt peak
14a	brown matrix	Pt14a.adp	44	0.11	8.10	341	0.03	0.03	average
15a	vernadite	Pt15a.adp	28	0.47	96.70	4970	0.23	0.25	average
16a	vernadite	Pt16a.adp	46	0.40	89.60	5710	0.21	0.18	average
16.5a	vernadite	Pt16.5a.adp	24	0.50	80.50	4460	0.30	0.29	average
17a	vernadite	Pt17a.adp	37	0.40	81.80	5180	0.23	0.19	average
18a	brown matrix	Pt18a.adp	39	0.13	7.98	666	0.04	0.03	average
22	vernadite	Pt22.adp	22	0.58	84.90	5480	0.34	0.28	average

Loc. (locality) is shown in Fig. 2.

(max) and the Pt peak in Note represents the maximum peak of Pt.

(av) denotes the average intensity in counts per second.

Cycles is the number of measured cycles.

Pt (ppm)\_Mn and Pt (ppm)\_<sup>56</sup>Fe are background revised concentrations in ppm for Mn and <sup>56</sup>Fe matrix, respectively.

Near-zero negative values appear because the EM counting noise of 0.073 cps is deducted from each raw data in order to calculate Pt concentrations.

The Pt RSF value for Mn matrix ( $RSF_{Mn}$ ) was calculated to be  $3.48 \times 10^{17}$  (atoms/cm<sup>3</sup>), and that for <sup>56</sup>Fe matrix ( $RSF_{56Fe}$ ) was  $1.89 \times 10^{19}$  (atoms/cm<sup>3</sup>). The Pt concentration (atoms/cm<sup>3</sup>) can be calculated using the following equation:

$$Pt \text{ (atoms/cm}^3\text{)} = RSF_M \times {}^{195}Pt_i/M_i \quad (1)$$

where  $RSF_M$  is the Pt RSF value for the Mn or <sup>56</sup>Fe matrix as a reference mass  $M$ ;  ${}^{195}Pt_i$  or  $M_i$  is the intensity of <sup>195</sup>Pt or the reference mass (Mn or <sup>56</sup>Fe), respectively. The Pt concentration (ppm) can then be calculated using the following equation with the conversion factor (Appendix 2),

$$Pt \text{ (ppm)} = RSF_M/6.17 \times 10^{15} \times {}^{195}Pt_i/M_i. \quad (2)$$

The long-tail distribution of Pt for the standard measurement might introduce a ~10% reduction of the RSF, which corresponds to ~10% reduction of the calculated Pt concentrations.

#### Bulk chemical analyses

The bulk platinum concentrations of both the P1 and P2 chips and the C1 and C2 slabs were analyzed. The sample sizes of P1, P2, C1 and C2 were 1.25 g, 1.03 g, 2.43 g or 2.64 g, respectively. They were determined by

the combination of the fire-assay and ICP-MS methods at Actlabs, Ontario, Canada. The detection limit of platinum was 0.0001 ppm. The platinum concentrations of P1 and P2 chips were 0.224 ppm and 0.224 ppm, respectively. The platinum concentrations of C1 and C2 slabs were 0.216 ppm and 0.217 ppm, respectively. It is considered that 0.224 ppm of Pt represents the Pt content of the P1 and P2 samples, but there is a possibility of the existence of a slightly lower platinum concentration nearby.

Halbach *et al.* (1984) reported on the Pt concentrations in younger (younger than 10 Ma) seamount crusts, and the average value of six bulk analyses was found to be 0.267 ppm. The Pt concentrations tended to be high in older crusts (Halbach *et al.*, 1984). Our sample is taken from the youngest (<1 Ma) top layer of the crust (Figs. 1 and 3a), and 0.224 ppm of Pt is consistent within the range of the bulk analysis value in younger crusts from Halbach *et al.* (1984). Northwestern Pacific ferromanganese crusts are generally composed of two distinct layers, younger and older generations. Koschinsky and Halbach (1995) indicated that major composition of the younger generation is hydrogenetic vernadite (similar amount of Mn and Fe) prevailing over the northwestern Pacific with variable amount of associated metallic elements. Thus our sample taken from the top of younger generation is comparable to a typical hydrogenetic ferromanganese precipitates in the crusts.



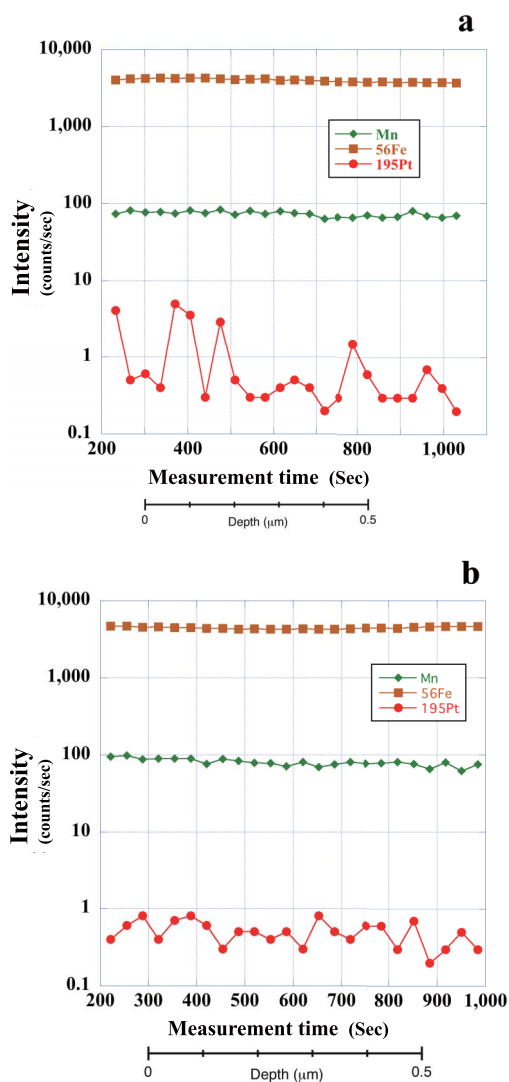


Fig. 4. Depth profiles of Pt intensity in vernadite (P2 disc). The horizontal axis indicates measurement time at 0 sec equal to the sample surface. Depth of the crater is also shown along the horizontal axis. The vertical axis represents the intensity on a logarithmic scale in counts per second. The first ca. 25 nm is in the carbon coating and the ion intensities become stable after the 200 sec, thus the profiles are shown after stabilization. (a) (Pt11a.adp in Table 1; Loc. 11a in Fig. 3b) shows a fluctuating Pt profile with matrix Mn and  $^{56}\text{Fe}$  profiles. The mean and maximum Pt concentrations are 0.73 and 3.78 ppm, respectively. (b) (Pt16.5a.adp in Table 1; Loc. 16.5a in Fig. 3b) shows representative Pt profiles, with matrix Mn and  $^{56}\text{Fe}$  profiles of most SIMS measurements.

#### SIMS microanalyses

SIMS microanalysis was conducted for the P2 disc sample. The analysis area is within the red circle in Fig. 3a and analysis points are shown in Fig. 3b, which is magnifying Fig. 3a by two times. Pt concentrations were

calculated using Eq. (2) with the  $\text{RSF}_M$ . Table 1 shows the average counts per sec of  $^{195}\text{Pt}$ , Mn and  $^{56}\text{Fe}$  ion intensities for the displayed measurement cycles. The EM counting noise of 0.073 cps is deducted from each set of raw data to calculate the Pt concentrations. Pt concentrations based on the Mn or  $^{56}\text{Fe}$  matrix were finally obtained using the RSF for Mn or  $^{56}\text{Fe}$ , respectively.

The Pt concentration of vernadite was found to range from 0.21 to 1.22 ppm based on the Mn matrix, and from 0.18 to 1.32 ppm based on the  $^{56}\text{Fe}$  matrix. The Mn matrix based calculations are quite consistent with the  $^{56}\text{Fe}$  matrix based calculations (Table 1), suggesting that Mn and Fe are uniformly distributed in vernadite. The amount of Mn in vernadite is higher than Fe, however Mn sensitivity is lower than Fe (e.g., Storms *et al.*, 1977), resulting in a lower Mn intensity compared to Fe (Table 1). A high  $^{56}\text{Fe}$  count is preferable to a low Mn count in terms of statistical processing, however, the Fe content might be fluctuated in the crusts because Fe also exists as other Fe containing minerals. Mn, on the other hand, exists only in vernadite and it is expected that relatively abundant Mn is more reliable as a reference matrix. Therefore, Mn is used as the reference matrix, despite  $^{56}\text{Fe}$  also being suitable for such use (Table 1). On the contrary, the difference in Pt concentrations between Mn and Fe matrix based calculations might partly reflect Mn or Fe fluctuation in the vernadite.

The interstice among vernadite clusters is filled with brown colored fine-grained sediment, which is called brown matrix in Table 1. The Pt concentration of a brown matrix at Loc. 5 in Fig. 3b (Pt9@56.adp) is less than the detection limit of 0.036 ppm. On the other hand, Pt concentrations of brown matrices at Loc. 14a and Loc. 18a in Fig. 3b (Pt14a.adp and Pt18a.adp, respectively) are equal to the detection limit. Thus, a small amount of Pt might exist in the brown matrix but the concentration is apparently lower than that in the vernadite if it is the case.

The measurements Pt11a.adp (Loc. 11a) and Pt13a1.adp (Loc. 13a1) give additional lines for data deduction in Table 1. Since both depth profiles present somewhat fluctuating amounts of  $^{195}\text{Pt}$  (counts/sec), the maximum concentration was calculated for the highest Pt peak of each profile. Figure 4 compares a depth profile of fluctuating Pt intensity (Fig. 4a, Pt11a.adp) with a depth profile of common Pt intensity (Fig. 4b, Pt16.5a.adp, Loc. 16.5a). Most depth profiles show that Pt is distributed uniformly along the depth (e.g., Fig. 4b); however, Pt occasionally shows local enrichment (e.g., Fig. 4a). The spatial resolution along the depth is several tens of nanometers (Fig. 4). Au local enrichment was found using SIMS measurements from the Kalahari Goldridge deposit (South Africa), and it was revealed that Au existed as Au nano particles in pyrrhotite (Morishita and Hammond, 2007). The profile in Fig. 3a does not show

clear evidence of Pt nano particles, but it suggests occasional inhomogeneous existence of Pt on the nm level.

## CONCLUSIONS

SIMS microanalysis revealed that Pt existed in the vernadite of hydrogenetic ferromanganese crust (The spatial resolution was 3  $\mu\text{m}$  by 3  $\mu\text{m}$  on the sample). The Pt concentration of vernadite in a very young (<1 Ma) crust was between 0.21 to 1.22 ppm in the vernadite clusters, and that in brown matrix was negligible (around the detection limit of 0.036 ppm or less). The SIMS depth profiles show that Pt is usually distributed uniformly in vernadite, but occasionally exhibits inhomogeneity on the nm level.

**Acknowledgments**—This work was partly supported by funding from the Takahashi Industrial and Economic Research Foundation, and from JSPS. We thank two anonymous reviewers and Dr. Y. Sano, the associate editor, for their critical reviews.

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## APPENDIX 1: CALCULATION OF RSF

RSF (relative sensitivity factor) is defined by the following equation (e.g., Wilson *et al.*, 1989);

$$\text{RSF (atoms/cm}^3\text{)} = (F C I_M t) / (d \sum I_E - d I_{\text{bkg}} C)$$

where F is the ion implantation density (atoms/cm<sup>2</sup>), C is the number of measurement cycles, I<sub>M</sub> is the matrix ion intensity (counts/s), t is the analysis time in a cycle (s/cycle), d is the crater depth (cm),  $\sum I_E$  is the sum of the targeted ion counts (counts), I<sub>bkg</sub> is the background ion intensity (counts/cycle).

After the SIMS depth profiling analysis of the P1 standard for its Pt concentration, the depth of the sputtered borehole was measured using a surface profiler to determine the relative sensitivity factor (RSF).

## APPENDIX 2: CALCULATION OF CONVERSION FACTOR

The density of in-situ vernadite is 2.0 g/cm<sup>3</sup> (Hein *et al.*, 2000), so vernadite containing 1 ppm Pt by weight has 2.0  $\times$  10<sup>-6</sup> gPt/cm<sup>3</sup> and the number of atoms in 1 g of Pt is 3.087  $\times$  10<sup>21</sup> atoms/gPt.

Thus 1 ppm of Pt is 2.0  $\times$  10<sup>-6</sup> gPt/cm<sup>3</sup>  $\times$  3.087  $\times$  10<sup>21</sup> atoms/g Pt = 6.17  $\times$  10<sup>15</sup> (atoms/cm<sup>3</sup>). This value is used as a conversion factor (Larocque and Cabri, 1998) for RSF normalization of the SIMS data.