

Precise determination of dissolved platinum in seawater of the Japan Sea, Sea of Okhotsk and western North Pacific Ocean



Asami Suzuki ^{a,*}, Hajime Obata ^a, Ayako Okubo ^{b,1}, Toshitaka Gamo ^a

^a Atmosphere and Ocean Research Institute, The University of Tokyo, Japan

^b Japan Atomic Energy Agency, Japan

ARTICLE INFO

Article history:

Received 30 December 2013

Received in revised form 8 October 2014

Accepted 9 October 2014

Available online 17 October 2014

Keywords:

Pt

Anthropogenic

Western North Pacific Ocean

ABSTRACT

Platinum is among the least abundant elements in the earth's crust and is now widely used in various products such as catalytic converters in automobiles and anticancer drugs. Consequently, the concentration of Pt in urban aquatic environments is increasing. However, little is known about the distributions and geochemical cycles of Pt in the ocean owing to its low concentrations in seawater (<0.2 pmol/L). In this study, we report an improved analytical method for determining sub-picomolar levels of Pt in seawater, and reveal the distributions of Pt in the Japan Sea, Sea of Okhotsk, and western North Pacific Ocean.

For determining sub-picomolar levels of Pt in seawater, we used isotope-dilution ICP-MS (Inductively Coupled Plasma Mass Spectrometry) after column preconcentration with an anion exchange resin. This method facilitated highly accurate analysis of Pt in seawater using small sample volumes (~1 L). The detection limit and procedural blank value for this method were 0.015 and approximately 0.01 pmol/L, respectively. We obtained conservative vertical distributions, with nearly constant Pt concentrations between 0.19 and 0.25 pmol/L in the Japan Sea, Sea of Okhotsk, and western North Pacific Ocean. Judging from the constant dissolved Pt profiles, little anthropogenic influence of Pt is apparent in the open oceans at the present time.

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1. Introduction

Platinum (Pt) is a transition metal and because of its low reactivity is also considered a noble metal. It is present in very low concentration in the earth's crust (0.01 mg/kg; Wedepohl, 1995). Platinum has a high melting point (1769 °C) and boiling point (4170 °C). Industrial demand for Pt is increasing because of its use as an automobile catalyst. Catalytic converters are installed in the exhaust system of cars in order to decompose nitrogen oxides and carbon monoxide released from the engine as well as hydrocarbons released by incomplete combustion of gasoline. Installation of catalytic converters in automobiles began in Japan in 1973, in the USA in 1975, and in Europe in 1986. A reported increase in the accumulation of Pt in ice cores implies that anthropogenically released Pt has spread over the entire northern hemisphere (Barbante et al., 2001). Moreover, Pt is also used in anticancer drugs, which could be related to the elevated Pt concentrations detected in aquatic environments (Kümmerer and Helmers, 1997). Consequently, the effect of anthropogenic Pt in marine environments should be investigated from the start of the Pt contamination process.

The distribution and geochemical cycle of Pt in ocean water have been studied for a long time; however little is known because precise

determination of extremely low concentrations of Pt in seawater (10^{-15} – 10^{-12} mol/kg) is difficult. In addition, studies on Pt in seawater have shown that different oceanic regions show different types of vertical profiles. For example, published work has demonstrated the recycled type profile in the eastern North Pacific Ocean (0.46–1.17 pmol/L; Hodge et al., 1986); the scavenged type in the Indian Ocean (0.17–1.6 pmol/L; Van den Berg and Jacinto, 1988); and the conservative type in the Atlantic and the western North Pacific Oceans (0.11–0.28 pmol/L; Colodner et al., 1993). These studies employed different analytical methods; therefore it is uncertain which data is the most reliable (Ravizza, 2001). Analytical artifacts should also be considered. Specifically, Pt spikes might not be fully equilibrated with naturally occurring Pt in the sample utilized for isotope dilution analyses (Colodner et al., 1993), or the UV irradiation time for the samples might affect the detected Pt concentrations for voltammetric analyses (Obata et al., 2006). Moreover, the presence of an intensive matrix background or reagent-derived peaks might also interfere with voltammetric analyses (Cobelo-Garcia et al., 2014).

In this study, we improved the analytical method for detection of sub-picomolar levels of Pt in seawater using a column preconcentration method with an anion exchange resin and isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). Herein, we report the distributions of Pt in the western North Pacific Ocean and its marginal seas.

* Corresponding author.

¹ Present affiliation.

2. Methods

2.1. Samples

The sampling locations for this study are shown in Fig. 1. The sampling stations covered areas of open ocean and marginal basins, CR-19 (North Pacific; 40°N, 144°E), CR-27 (western North Pacific; 46°N, 159°E), CR-30 (Sea of Okhotsk; 45°N, 145°E), and CR-47 (Japan Sea; 42°N, 138°E). The Japan Sea is a semi-closed marginal sea and is more isolated than the Sea of Okhotsk. The water in the Japan Sea can communicate with the neighboring open ocean through four narrow straits (Tsushima, Tsugaru, Soya, and Tatar) with sill depths of less than 130 m.

Seawater samples were collected in 12 L acid-precleaned X-Niskin bottles mounted on a SeaBird CTD-36 carousel array hung by a titanium-armored cable during a KH-10-2 R.V. Hakuho-maru cruise (June 21–July 14, 2010). The distance between the array and the sea-floor was monitored using a pinger (model 2216, Benthos). Immediately after the recovery of the Niskin-X bottles, water samples were filtered through a capsule filter (0.2 μm pore-size; Acropak; PALL Co.) in a closed space filled with clean-air, which was passed through a HEPA filter. Platinum contamination from the capsule filter was evaluated by passing 1 L of Milli-Q water (MQW) through the filter, and the amount of Pt in the MQW was determined. The concentration of Pt in the MQW was below the detection limit (0.015 pmol/L). The filtered seawater samples were acidified to 0.024 M with HCl, and stored until completion of the cruise for analysis at the Atmosphere Ocean Research Institute, University of Tokyo. Auxiliary data (temperature and salinity) were obtained using CTD sensors (Seabird, Model SBE-9-plus). In this study, we report data of practical salinity, not absolute salinity. Dissolved oxygen data were obtained with a DO sensor (SBE-43, Seabird).

2.2. Analytical methods

The Pt concentration in seawater was determined by the isotope dilution method according to previous studies (Colodner et al., 1993; Obata et al., 2006). The rationale for this method is based on Eq. (1) in which two isotopes (A and B) are present and the spike solution is enriched in isotope A. X is the number of moles of the sample, and Sp is the number of moles of the added spike. A_{sp} and A_n are the atomic

abundance (%) of isotope A in the spike and natural sample, respectively, and B_{sp} and B_n are the atomic abundance (%) of isotope B in the spike and natural sample, respectively. R is the ratio of A/B measured via ICP-MS. Assuming that Pt in the added spike solution and in natural samples is completely equilibrated, R is obtained by using the following equation:

$$R = \frac{A}{B} = \frac{A_n X + A_{sp} Sp}{B_n X + B_{sp} Sp} \quad (1)$$

In this study, hydrochloric acid was added to seawater samples to be 0.5 M HCl, and then the enriched spike solution was added to each seawater sample. In seawater, spiked Pt is believed to form PtCl_4^{2-} or PtCl_6^{2-} and is equilibrated with the Pt originally present in the seawater.

The number of moles of sample present in a solution spiked with an isotope-enriched tracer (X) in Eq. (1) is calculated using the following equation:

$$X = \frac{A_{sp} Sp - RB_{sp} Sp}{RB_n - A_n} \quad (2)$$

We evaluated the suitability of the amount of spike added to the seawater sample by introducing an error multiplication factor (F), as done in previous studies (Heumann, 1988; Ohata et al., 1998). The precision of the determinations ($|\frac{dX}{X}|$) is never better than that of the isotope ratio ($|\frac{dR}{R}|$) as shown in Eq. (3).

$$\left| \frac{dX}{X} \right| = F \left| \frac{dR}{R} \right| \quad (3)$$

The error multiplication factor (F) can be calculated using Eq. (4) and Eq. (5).

$$\frac{dX}{dR} = \frac{A_n B_{sp} - A_{sp} B_n}{(RB_n - A_n)^2} \times Sp = X \times \frac{A_n B_{sp} - A_{sp} B_n}{(RB_n - A_n)(A_{sp} - RB_{sp})} \quad (4)$$

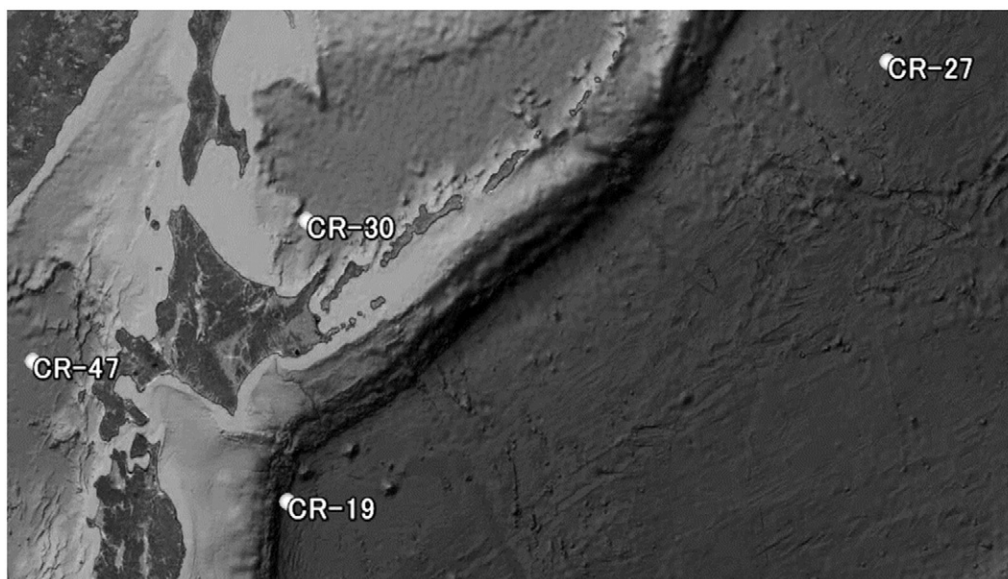


Fig. 1. Sampling locations during R.V. Hakuho-maru KH-10-2 cruise. Stations CR-19 and CR-27 are located in the western North Pacific, CR-30 is in the southern Sea of Okhotsk, and CR-47 is in the Japan Sea.

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