

A 50-Year Record of Platinum, Iridium, and Rhodium in Antarctic Snow: Volcanic and Anthropogenic Sources

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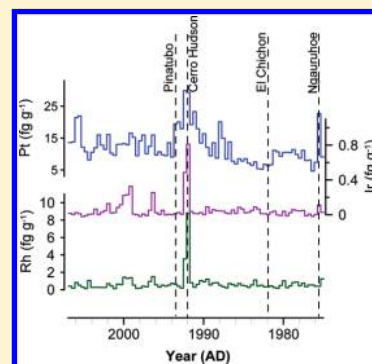
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S Supporting Information

ABSTRACT: Antarctic snow preserves an atmospheric archive that enables the study of global atmospheric changes and anthropogenic disturbances from the past. We report atmospheric deposition rates of platinum group elements (PGEs) in Antarctica during the last ~50 years based on determinations of Pt, Ir, and Rh in snow samples collected from Queen Maud Land, East Antarctica to evaluate changes in the global atmospheric budget of these noble metals. The 50-year average PGE concentrations in Antarctic snow were 17 fg g⁻¹ (4.7–76 fg g⁻¹) for Pt, 0.12 fg g⁻¹ (<0.05–0.34 fg g⁻¹) for Ir, and 0.71 fg g⁻¹ (0.12–8.8 fg g⁻¹) for Rh. The concentration peaks for Pt, Ir, and Rh were observed at depths corresponding to volcanic eruption periods, indicating that PGEs can be used as a good tracer of volcanic activity in the past. A significant increase in concentrations and crustal enrichment factors for Pt and a slight enhancement in enrichment factors for Rh were observed after the 1980s. This suggests that there has been large-scale atmospheric pollution for Pt and probably for Rh since the 1980s, which may be attributed to the increasing emissions of these metals from anthropogenic sources such as automobile catalysts and metal production processes.



INTRODUCTION

Platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir, and Pt) are noble metals that are extremely rare in the Earth's crust (0.05–0.4 ppb).¹ They are useful tracers for processes in the Earth's interior² and accretion of extraterrestrial dust.^{3–5} World-wide production of PGEs has been rising steadily over the past few decades because of the increased use of these metals, such as in catalysts, jewelry, and electronics.^{6,7} In particular, Pt, Rh, and Pd have been used in automobile catalytic converters, and their production has dramatically increased worldwide since the 1970s.^{6–8} Recently, Ir has also joined their ranks in new generation catalytic converters.⁹ The introduction of catalytic converters has resulted in air quality improvements but has also led to high occurrences of PGEs in the environment,^{10–12} specifically in urban air^{13–15} and soil.^{16–18} Currently, an assessment of the potential impact of this new contamination on humans and the ecosystem is of great interest.^{6,9} Compared to the available data on PGE pollution levels close to source regions, however, relatively few time records of change in PGEs have been determined at remote polar locations because of the extremely low concentrations and associated analytical challenges. Therefore, the impact of increasing PGE levels on the global environment over time is difficult to evaluate. Currently, data on Pt and Ir are available from snow layers from Greenland¹⁹ and ancient ice from Greenland and Antarctica,^{4,20,21} but reliable data for Rh in snow and ice from polar regions have not been reported. Here, we

present the first time series for PGE (Pt, Ir, and Rh) deposition in Antarctica and determined the changes in the global background atmospheric level over a recent 50-year period.

EXPERIMENTAL SECTION

Sample Description. Snow pit samples were collected from two sites in Queen Maud Land, East Antarctica in December 2007 (Supporting Information (SI) Figure S1) during the Japanese-Swedish IPY Antarctic expedition. Pit-A (77°18'S, 39°47'E) was at Dome Fuji, the second highest summit in East Antarctica, at an altitude of 3785 m and approximately 1000 km from the nearest coast. Pit-B (75°53'S, 25°50'E) was located at an altitude of 3656 m and was approximately 600 km from the nearest coast. Sampling at a 5 cm interval allowed a continuous sequence to be obtained from the surface to a depth of 4 m at both sites. The snow samples collected were immediately transferred to ultraclean 500 mL wide-mouth low-density polyethylene (LDPE) bottles and kept frozen until analysis. Extreme precaution was taken during collection, handling and storage to prevent the possibility of snow contamination.²² Age dating of

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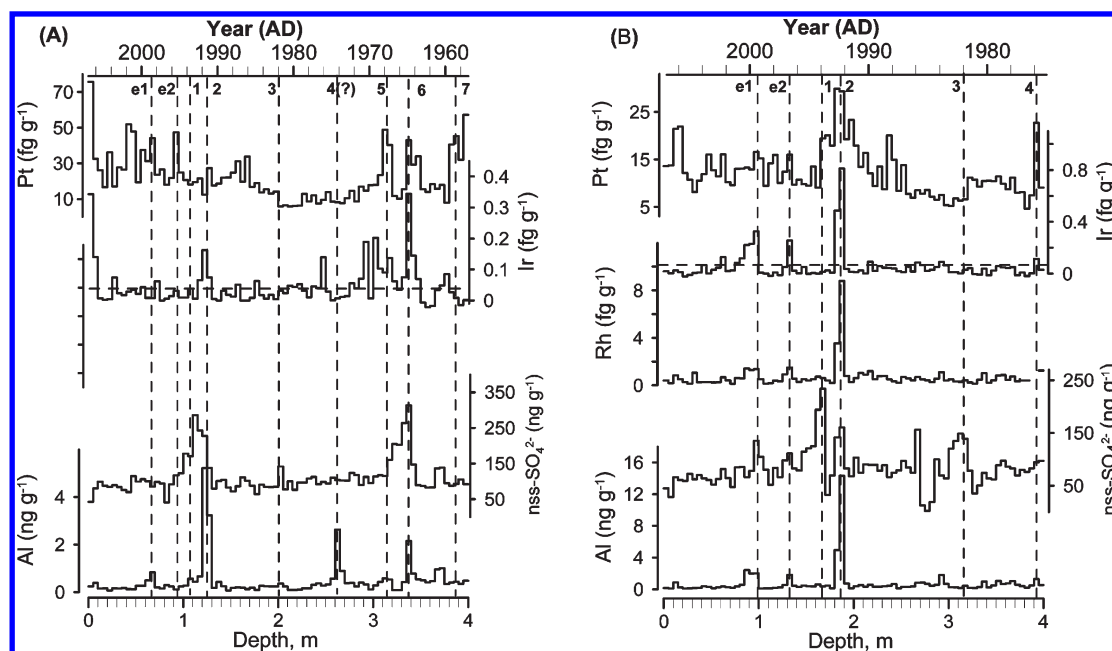


Figure 1. Concentrations of Pt, Ir, Rh, nss-SO_4^{2-} , and Al in (a) Pit-A and (b) Pit-B as a function of depth. Vertical dashed lines indicate layers corresponding to volcanic eruptions: (1) Pinatubo, (2) Cerro Hudson, (3) El Chichon, (4) Ngauruhoe, (5) Deception Island, (6) Agung, (7) Carrán-Los Venados, and (e1) and (e2) Erebus. Horizontal dashed lines indicate procedural detection limits.

the samples was established based on nss-SO_4^{2-} concentration peaks (Figure 1), which indicate layers of large volcanic deposition from Mt. Pinatubo (1993–1994), Mt. Cerro Hudson (1991–1992), and Mt. Agung (1964–1965). These volcanic nss-SO_4^{2-} signals are well documented in Antarctic snow.^{23,24} The estimated snow accumulation rate for the interval between Mt. Pinatubo/Mt. Cerro Hudson (1993–1994) and Mt. Agung reference peaks was $\sim 8 \text{ cm y}^{-1}$ (25 mm water equivalent per year, w.e.y^{-1}) at Site-A, which agrees with the findings of previous studies.^{23,25} The snow accumulation rate at Site-B for the interval between Mt. Pinatubo and Mt. Cerro Hudson reference peaks was $\sim 12.5 \text{ cm y}^{-1}$ (40 mm w.e.y^{-1}). These mean snow accumulation rates (8 and 12.5 cm y^{-1} for Site-A and Site B, respectively) were assumed to apply to the full depths of the pits. Pit-A was estimated to cover approximately 50 years (1957–2007) and Pit-B, 32 years (1975–2007).

Analytical Procedure. Because of the ultralow concentration levels ($\text{fg g}^{-1} = 10^{-15} \text{ g g}^{-1} = \text{ppq}$) of PGEs in Antarctic snow, it was necessary to preconcentrate the samples before the instrumental analyses. Preconcentration was performed by nonboiling evaporation to increase the concentrations by a factor of ~ 60 . The recovery and precision of the preconcentration step was confirmed with standard solutions ($0.1\text{--}20 \text{ fg g}^{-1}$). The recoveries were $93 \pm 1\%$, $101 \pm 1\%$ and $111 \pm 2\%$, and experimental blanks were 0.11 , 0.10 , and 0.26 fg g^{-1} for Pt, Ir, and Rh, respectively. An inductively coupled plasma sector field mass spectrometer (ICP-SFMS) (Element2, Thermo Finnigan MAT, Germany) coupled with an APEX microflow nebulization desolvation system (APEX HF, ESA, USA) was used for analyses. The desolvation system rendered the oxide production negligible ($\text{BaO/Ba} < 0.02\%$). The procedural detection limits for Pt, Ir, and Rh were 0.43 , 0.05 , and 0.15 fg g^{-1} when the instrumental detection limits (three times the standard deviation (1σ) of 10 measurements of the blank ($1\% \text{ UP HNO}_3$ solutions); 26 , 3.0 , and 9.0 fg g^{-1} , respectively) were corrected for the preconcentration factor of 60. The accuracy of the instrumental analyses was confirmed by SLRS4 and SLRS5

river water certified reference materials (National Research Council, Canada) and artificial monitoring solutions prepared by diluting the river water reference materials and spiking them with a PGE standard solution. The analytical method and the ultraclean working conditions are described in detail elsewhere.²⁶

RESULTS

Platinum and Ir concentrations were determined in Pit-A samples ($n = 80$), and Pt, Ir, and Rh concentrations were determined in Pit-B samples ($n = 80$) (Figure 1). Rhodium was not measured in Pit-A samples and in two samples from Pit-B because of insufficient sample volume. For Ir in Pit-B, most samples fell near or below the procedural detection limit (0.1 fg g^{-1} for Pit-B analyses); thus, only Pit-A data are considered for Ir in the discussion.

The average concentrations were 17 fg g^{-1} for Pt (average of the two pits, Pit-A: 22 fg g^{-1} and Pit-B: 12 fg g^{-1}), 0.12 fg g^{-1} for Ir (Pit-A) and 0.71 fg g^{-1} for Rh (Pit-B). In both pits, the concentrations varied widely with depth. The maximum concentrations of Pt, Ir, and Rh were 76 , 0.34 , and 8.8 fg g^{-1} , respectively, and the minimum concentrations were 4.7 , <0.05 , and 0.12 fg g^{-1} , respectively.

The contribution from sea salt spray was negligible, as evaluated from the PGE/Na ratios in the snow samples and in the surface seawater.²⁷ To assess the crustal contribution to the PGE concentrations, crustal enrichment factors (EF_c) were calculated using the PGE/Al ratios in the snow samples and the average continental crust.¹

$$\text{EF}_c = [\text{X/Al}]_{\text{snow}} / [\text{X/Al}]_{\text{crust}}$$

The average EF_c values were 14×10^3 , 650 , and 2.0×10^3 for Pt, Ir, and Rh, respectively. This indicates that the crustal contribution is very low, particularly for Pt and Rh. The time series of EF_c are illustrated in Figure 2 and summarized in SI Table S1.

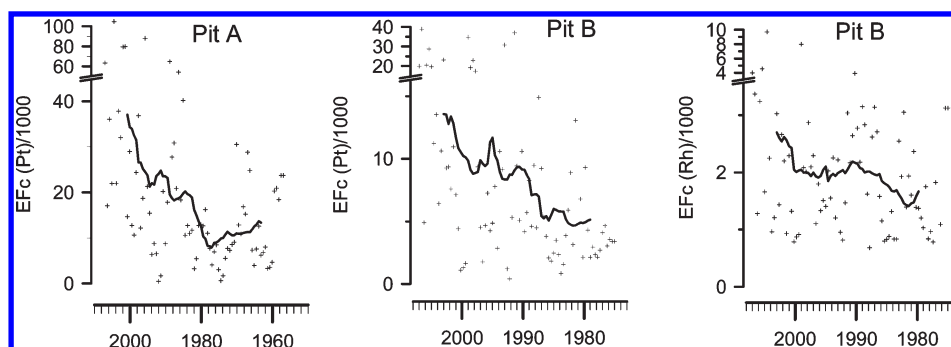


Figure 2. The time series of crustal enrichment factors (EF_c) of Pt and Rh in Antarctic snow. Solid lines represent the 21-point running mean.

DISCUSSION

Three distinct features could be observed from our PGE data set (Figure 1). First, there were highly elevated concentration peaks in many volcanic layers (dashed lines 2, 4, 5, 6, and 7 in Figure 1). Second, notable increasing trends in Pt concentration and its enrichment factor (Figures 1 and 2) were observed, starting in the 1980s, along with a moderately increasing trend in the EF_c of Rh (Figure 2). Before the 1980s, the Pt levels were low, with the exception of three peaks related to volcanic eruptions (dashed lines 5, 6, and 7 in Figure 1a). Third, a relatively constant background concentration was noted for Ir and Rh throughout the entire pit.

Volcanic Deposition. Volcanic gas and ash emissions are expected to contain high concentrations of PGEs.^{28–30} The contribution of volcanic eruptions to the aerosol loading of the Antarctic atmosphere can depend on various factors, such as the location of the volcano, the eruption strength and the composition and aerosol size distribution of the ejected material.^{31–33} We used the $nss\text{-SO}_4^{2-}$ and Al concentrations in the samples (Figure 1) as volcanic gas and ash indicators, respectively^{19,24,34,35} (Figure 1, SI Table S2 and Figure S2). In Figure 1, dashed lines 1, 2, and 3 correspond to the volcanic layers of the Pinatubo (15°N, 1991), Cerro Hudson (45.5°S, 1991), and El Chichon (17°N, 1982) eruptions, respectively.²⁴ The Pinatubo and El Chichon eruptions did not affect the PGE concentrations in the two pits. In contrast, the Pt, Ir, and Rh profiles exhibited pronounced peaks in the Cerro Hudson layer in both snow pits. Despite the higher snow accumulation rate at Site-B, the Pt and Ir concentration peaks in the Pit-B profiles corresponding to Cerro Hudson (Figure 1b) were more extreme than in Pit-A (Figure 1a). This was also revealed in the Al profiles (Figure 1a, b). The concentrations in Pit-A may have been affected by possible postdepositional processes, such as dilution due to condensation-sublimation in the summit area²³ and/or surface snow mass transport under strong wind conditions.²⁵

A significant Pt spike (dashed line 4) with a slight increase in Ir was observed at a depth of 390 cm (~ 1974) in Pit-B. The corresponding rise in the Al concentration was observed in Pit-A. Temporally, the Pt and Al spikes coincided with a peak in the acidity profile (1974–1975) in the firn core collected from James Ross Island,³¹ which is attributed to the Mt. Ngauruhoe eruption (37°S, 1974). Therefore, our data suggest that this volcanic eruption also probably contributed to the PGE concentration in the remote Antarctic atmosphere. No corresponding peaks of Pt and Ir in Pit-A were detected, whereas a pronounced Ir peak was observed in the layer slightly above the volcanic ash signal (Al)

corresponding to line 4, which may reflect the complexity of transport pathways of volcanic aerosols from midlatitudes to remote Antarctica and lead to differences in the efficiency of the transport of volcanic PGEs to different localities within inland Antarctica.²¹

The Pt concentration profile of Pit-A has three remarkable peaks (dashed lines 5, 6, and 7 in Figure 1a), with moderate increases in the Ir concentration in the following layers: 300–320, 335–350, and 375–400 cm. This period was not included in Pit-B because of the difference in snow accumulation rates. The two upper peaks (dashed lines 5 and 6) coincided with elevated concentrations of Al and $nss\text{-SO}_4^{2-}$. These peaks can be linked to the multiple eruptions on Deception Island (62.5°S, 1967–1970)^{31,36} and the Agung eruption (8°S, 1963) that was recorded in the 1964–1965 layer in the snow.^{23,24} The lowermost peak (dashed line 7) corresponds to the 1957–1960 period; we surmise that the contribution comes from the eruptions of Carrán-Los Venados (known as Nilahue in some studies) (40°S, 1955) and/or Cordon Caulle (40.5°S, 1960). The temporally coinciding volcanic signals were recorded in an electrical conductivity profile obtained from the H15 ice core from East Antarctica³⁷ and in a profile of H_2SO_4 obtained from the Dome C ice core from East Antarctica.³⁸

There were also other small peaks in the Pt, Ir, and Rh concentrations, such as the dashed lines e1 and e2 in Figure 1, which coincided with weak peaks in $nss\text{-SO}_4^{2-}$ and Al. It is more difficult to assign these peaks to specific historical volcanic eruptions, but Mt. Erebus is a possible candidate. Mt. Erebus is the southernmost active volcano on Earth, located on Ross Island, Antarctica and has been continuously active since 1972 (SI Figure S1). The volcanic gas plume quiescently emitted from Mt. Erebus was proposed to be a possible source of PGEs and trace elements in East Antarctica.³⁹

The deposition fluxes of Pt, Ir, and Rh from the identified volcanic eruptions were evaluated (SI Table S2) using the average concentrations in the corresponding depth intervals and the snow accumulation rates at the sites. The factors that affect the volcanic deposition of PGEs in Antarctic snow are also summarized—the distance of the volcano from the site (SI Figure S2) and the volume of the ejected material (which can depend on the VEI: volcanic explosivity index)⁴⁰ (SI Table S2). Large eruptions ($VEI > 4$) in the Southern Hemisphere, such as the Cerro Hudson (1991), Agung (1963), and Carrán-Los Venados (1955), and nearby small eruptions ($VEI < 3$), such as those of Ngauruhoe (1974) and Deception Island (1967–1970), were found to have significantly affected the atmospheric PGE budget of Antarctica. In contrast, the PGE

concentrations were not notably affected by Northern Hemisphere eruptions (Pinatubo (1991) and El Chichon (1982)). Aerosol transport to Antarctica from relatively small eruptions ($VEI < 3$) in the Northern Hemisphere is likely to be hindered by atmospheric general circulation and removal of the aerosols from the atmosphere.³¹ However, materials emitted from large explosive eruptions (if the emitted materials reach the stratosphere) in the low latitudes of the Northern Hemisphere can reach the Antarctic atmosphere through stratospheric transport,^{34,41} as can be seen in $nss\text{-SO}_4^{2-}$. Nonetheless, the Pinatubo and El Chichon events (SI Table S2 and Figure 1) were not identified in the PGE record, perhaps because of the different enrichment of PGE in volcanic emissions from individual volcanoes.²¹

Post-1980 Temporal Trend. Our data showed that the atmospheric Pt concentrations in Antarctica were significantly enhanced over the past ~30 years in both snow pits (Figure 1). The recent increase was more clearly identified in Pit-A, which covers a longer time period (1957–2007) than Pit-B (1975–2007). Pit-A had a lower and more constant background level of Pt concentration, below ~2 m (before the 1980s), compared with the upper layers. To analyze the temporal trend in background concentrations, two time periods were considered: pre-1980 and post-1980. The corresponding depth intervals are 225–400 cm (pre-1980; 44 samples) and 0–225 cm (post-1980; 36 samples) for Pit-A and 335–400 cm (pre-1980; 13 samples) and 0–335 cm (post-1980; 67 samples) for Pit-B. Comparisons of the mean concentrations and mean EF_c values for the two specific time periods (excluding known volcanic events shown in SI Table S2) are given in SI Table S1. An increase in the Pt concentrations occurred in the remote Antarctic atmosphere during the last three decades, suggesting an increase in the global background atmospheric concentration of Pt. The EF_c of Pt shows a more significant increase, with a moderate increase in the EF_c of Rh since ~1980 (Figure 2), indicating that the Rh increase is less intense than that of Pt. Although there are very limited reliable data for Ir in the post-1980 period, a significant increase was not observed for the EF_c of Ir post-1980. Based on SI Table S1 and Figure 2, the enhancement of atmospheric PGEs during the past three decades was observed to occur in the following order: Pt > Rh \gg Ir.

The most likely source of the atmospheric PGE increase since ~1980 is anthropogenic emission resulting from the wide application of PGEs in industrial processes, particularly automobile exhaust catalytic converters. In our data set, there was no increase in the Ir concentration (Figure 1, SI Table S1), showing that global atmospheric Ir was not disturbed by recent anthropogenic activities. This is consistent with previous studies that found the natural background level of Ir to be dominantly geogenic.^{17,19}

Dust reaching Antarctica is mainly from South America, with substantial contributions from Australia and South Africa, but some dust from the Northern Hemisphere carrying anthropogenic contamination also reaches Antarctica (ref 42 and references therein). Air mass backward trajectories for Dome Fuji indicated that air parcels could be transported from any directions over the course of a year.⁴³ Catalytic converters were introduced in South America in the 1990s (1996 in Brazil and Argentina).^{13,44} Although their use has been relatively low (12% in 2001 in Argentina), significant pollution for Pt, Pd, and Rh has been detected in the air and soils and linked to automobile catalysts.^{13,44} This technology has been used since 1987 in Australian cars, and approximately 52% (in 2000) of cars have been fitted with catalytic converters, resulting in environmental

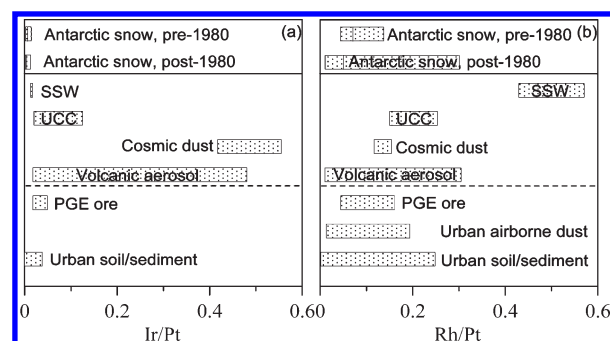


Figure 3. A comparison of the (a) Ir/Pt and (b) Rh/Pt ratios of potential atmospheric sources with values measured in Antarctic snow pits. The dashed line separates natural (upper panel) and anthropogenic (lower panel) sources. The ranges for cosmic dust and surface seawater were calculated assuming a relative standard deviation of 10%. The vertical lines in Antarctic snow indicate average values. The data references are as follows: Antarctic snow (this study), surface seawater,²⁷ continental crust,^{1,49,50} cosmic dust,⁴⁸ volcanic aerosol,²⁸ PGE ore,⁵⁷ urban airborne dust,^{13–15} and urban soil/sediment.^{16–18}

contamination of PGEs in Australian urban environments.¹⁸ After World War II, the Republic of South Africa became the main producer of Pt, and in the past three decades, Pt production increased by a factor of nearly two in this region.^{7,45} The identified area with mine tailings is above 35 million m²,⁴⁶ and ore processing has been identified as an important regional pollution source based on determinations of PGEs in environmental (snow, aerosol) samples in Russia and Finland (ref 6 and references therein), even though the emission rates of PGEs from the metal production processes have not been estimated.⁶

We do not consider the volcanic input from Mt. Erebus to be responsible for the post-1980 increase in background Pt because there was no change in the concentrations of the trace elements found in the eruptive material of Mt. Erebus during the corresponding period.⁴⁷

Ir/Pt and Rh/Pt Ratios as Source Indicators. Figure 3 shows a comparison of the Ir/Pt and Rh/Pt ratios of potential atmospheric sources with the values measured in Antarctic snow. Significant natural sources of atmospheric PGEs include cosmic, volcanic and crustal dust, whereas anthropogenic sources include mining and metal production (in particular, PGE ore processing) and exhaust from automobiles.

The Ir/Pt ratio of snow samples, which was 0.006 on average (0.002–0.015 for Pit-A), is relatively low compared with major natural sources—cosmic dust (0.49)⁴⁸ and crustal dust (0.02–0.1)^{1,49,50} (Figure 3a). The average value for the pre-1980 (1957–1980) samples was 0.008, which is three times as high as the post-1980 samples (1980–2007; average 0.003). The considerably lower Ir/Pt ratios observed in the pre-1980 samples (0.008) (SI Table S1), before the worldwide use of automobile catalytic converters, indicate that there was already enhancement of the atmospheric Pt level before the use of catalytic converters. Possible sources at that time include (i) PGE mining and smelting, especially in South Africa⁴⁵ and (ii) chemical industries in which PGEs were used as catalysts.⁴⁵ The petroleum industry was a large consumer of Pt starting at the time of World War II, and the production of ammonia consumed the Pt–Rh catalyst.⁴⁵ Because of these applications, worldwide Pt output increased by ~8 fold from the 1930s to the 1970s.⁴⁵ For Ir, there is no published inventory before the 1980s, but Ir was probably much

less important than Pt in industrial applications in the past because the recent Ir production rate is still very low (~ 3 tons y^{-1}) compared to Pt (205 tons in 2007).⁷

The Rh/Pt ratios of our snow pit samples varied over a relatively wide range (Figure 3b), which indicates that multiple sources contribute to the atmospheric Pt and Rh budget. However, most samples had low values, except for a few with Rh/Pt ratio >0.1 including the 1991 volcanic layer (Rh/Pt ratio = 0.3). The average Rh/Pt ratio (0.06) of the snow pit samples was low compared to both the crustal (0.15–0.25)^{1,50} and cosmic dust (0.14)⁴⁸ ratios. The wide range of combinations and concentrations of Pt, Rh, and Pd in catalytic converters required in various vehicle models⁹ likely caused the diversity of the content and ratio of PGEs in vehicle exhaust.¹⁰

Average Deposition Fluxes during the Last 50 Years. The average fluxes of Pt, Ir, and Rh were calculated by multiplying the average concentrations by the mean annual snow accumulation rates for the time periods covered by the snow pits samples (25 mm $w.e.y^{-1}$ for Site-A and 40 mm $w.e.y^{-1}$ for Site-B) (SI Table S3). The estimated fluxes were as follows: Pt: 0.6 ± 0.3 (Pit-A) and 0.49 ± 0.21 (Pit-B) $ng\ m^{-2}\ y^{-1}$, Ir: 0.003 ± 0.002 $ng\ m^{-2}\ y^{-1}$, and Rh: 0.03 ± 0.04 $ng\ m^{-2}\ y^{-1}$ (0.02 ± 0.01 $ng\ m^{-2}\ y^{-1}$ when excluding the high volcanic peak at a depth of 180–190 cm). There are a few published deposition fluxes obtained from polar ice, rainwater from Seoul and Tokyo (only for Pt), and snow from the Alps and Greenland to which we can compare our results (SI Table S3 and Figure S3).

Both the average concentration (0.12 ± 0.08 $fg\ g^{-1}$) and calculated deposition flux (0.003 ± 0.002 $ng\ m^{-2}\ y^{-1}$) for Ir were comparable to those observed in the Antarctic Dome C ice sample,²⁰ which had an average concentration of 0.31 ± 0.12 $fg\ g^{-1}$ and a flux of 0.010 ± 0.004 $ng\ m^{-2}\ y^{-1}$ (recalculated from the concentration and snow accumulation rate). However, the results were approximately 1 or 2 orders of magnitude lower than those of another study²¹ of Antarctic ice core samples corresponding to the Holocene period (average fluxes: 0.18 $ng\ m^{-2}\ y^{-1}$ for Dome C, 0.04 $ng\ m^{-2}\ y^{-1}$ for Vostok, reaveraged from the original data sets). We note that the latter study²¹ obtained a relatively high Ir concentration (the averages were 6 $fg\ g^{-1}$ for Dome C and 2 $fg\ g^{-1}$ for Vostok) with high Ir/Pt ratios (close to or greater than 1). The high Ir/Pt ratio is difficult to explain solely in terms of natural contributions such as volcanic (≤ 0.5 , compiled from several literature values of volcanic gases and lavas),^{28,51–53} crustal (0.02–0.1),^{1,49,50} and cosmic dust (0.49).⁴⁸

The Pt flux calculated for our snow pit samples (SI Table S3) is up to 1 order of magnitude higher than that recorded in ice cores in Greenland (0.15 $ng\ m^{-2}\ y^{-1}$) and Antarctica (Dome C: 0.11 $ng\ m^{-2}\ y^{-1}$, Vostok: 0.04 $ng\ m^{-2}\ y^{-1}$)^{4,21} because of the elevated Pt concentration in the atmosphere caused by anthropogenic pollution in recent years. The rainwater estimates of the Pt flux in Seoul (26.8 $ng\ m^{-2}\ y^{-1}$)⁵⁴ and Tokyo (284 $ng\ m^{-2}\ y^{-1}$)⁵⁵ and estimates using ombrotrophic peat bog from Massachusetts (550 – 770 $ng\ m^{-2}\ y^{-1}$)¹⁶ and atmospheric aerosol from Germany (730 $ng\ m^{-2}\ y^{-1}$)¹⁴ are 2–3 orders of magnitude higher than in Antarctica. Recent snow estimates from Greenland¹⁹ (for Pt and Ir) and the Alps⁵⁶ (for Pt and Rh) are also 2–3 orders of magnitude higher than our Antarctic snow estimates. For Rh, only two estimates from Alps (27 $ng\ m^{-2}\ y^{-1}$) snow/ice⁵⁶ and Massachusetts (210 $ng\ m^{-2}\ y^{-1}$) peat bog¹⁶ are available for comparison and these values are also 3 orders of magnitude higher than our estimates. Such a difference in the flux is evidently linked to differences in the precipitation amounts (~ 1400 mm

for Seoul and Tokyo, ~ 300 mm for Alps, ~ 250 mm for Greenland vs 25 mm (Site-A) for Antarctica), and their concentrations in the atmosphere.

■ ASSOCIATED CONTENT

S Supporting Information. Figures showing locations of sampling sites and volcanoes mentioned in the text and tables and figure summarizing the EF_c s and atmospheric deposition fluxes of PGEs are reported along with the data tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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