

## Nondestructive Search for Micrometer-Scale Platinum-Group Minerals in Mantle Peridotite with Microbeam X-Ray Fluorescence Analysis

Because of their strong siderophile (iron-loving) character, platinum-group elements (PGEs: Ru, Rh, Pd, Os, Ir, and Pt) are highly concentrated in metallic phases in the Earth's interior and meteorites, but are scarcely distributed in silicate phases. For example, the Earth's silicate mantle contains PGE only on the order of 1 ppb [1]. Thanks to such sparseness, the PGE abundances in the Earth's mantle are sensitive to chemical processes that involve metallic phases, such as core-mantle segregation in the early Earth, late-stage meteorite bombardment (so-called late veneer), and core-mantle chemical interactions during the Earth's history. In other words, PGEs in the mantle are useful tracers for understanding the chemical evolution of the Earth's interior.

A critical point in discussing the chemical evolution of the Earth's interior using PGEs is that their distributions in the mantle are not well identified, and therefore, the behavior of PGE during differentiation processes (e.g., partial melting) in the mantle is unclear. Recent PGE analyses using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) revealed that PGEs in mantle peridotite are highly concentrated in base-metal sulfides (i.e., Fe-Ni-Cu sulfides). On the other hand, discrete

platinum-group minerals (PGMs), such as Pt-Ir-Os alloys and Ru-Os sulfides, have been detected in peridotite by scanning electron microprobe (SEM) and LA-ICP-MS analyses. These observations suggest that base-metal sulfides and/or PGMs dominate and control the PGE budget in the mantle. However, PGE concentrations in base-metal sulfides are strongly variable (<1 ppm to several tens ppm) even within single hand specimens [2], while the modal abundances of PGMs are difficult to determine because PGMs in mantle peridotite are generally extremely small (<<10  $\mu\text{m}$ ). Thus, it is still unclear to what extent PGEs in the mantle are hosted by base-metal sulfides and PGMs in the mantle.

In this study, we tried to reveal how abundantly and pervasively PGMs exist in mantle peridotite using X-ray fluorescence analysis combined with the microbeam technique (micro-XRF) at SPRING-8. The extremely high brilliance of synchrotron radiation X-ray enables the X-ray beam to penetrate a rock sample up to several thousands  $\mu\text{m}$  depths, which is much greater than penetration depths of other nondestructive analytical methods (cf., SEM, a few  $\mu\text{m}$ ; proton microprobe, a few tens  $\mu\text{m}$ ). In addition, the high directionality of the synchrotron radiation

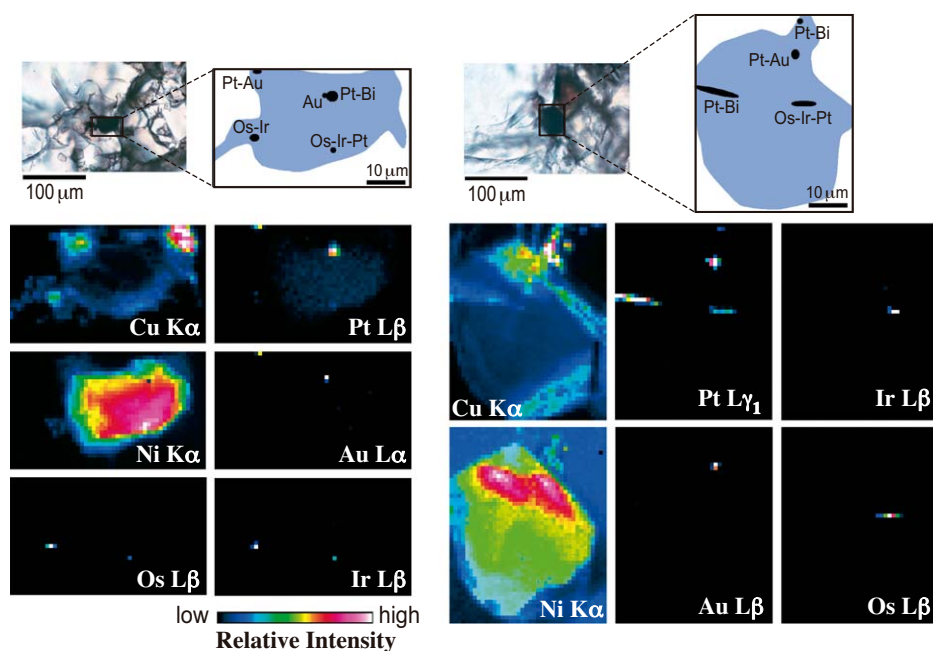


Fig. 1. Distribution maps of Ni, Cu, Au, and PGE in the Fe-Ni-Cu sulfides that include PGE microphases. Colors indicate relative intensities of the fluorescent X-ray lines of each element, which reflect the concentration and thickness distribution of the element. The pixel size of the element maps is 1.0  $\mu\text{m} \times 1.0 \mu\text{m}$  (= step size of scan). The locations and element combinations of the PGE microphases are shown as filled ovals in the schematic illustrations. Modified after Ref. [3].

X-ray is suitable for making a sub-micrometer spot size, which is comparable to that of SEM and much smaller than that of LA-ICP-MS analysis. These features enable us to conduct highly efficient "see-through" searches for minerals throughout thick rock samples on a sub-micrometer scale. Using this technique, we were able to find micrometer-scale PGM from the interior of a peridotite sample much more efficiently than with conventional analytical techniques [3].

We analyzed a spinel lherzolite from the Horoman peridotite complex, Japan, at beamlines **BL20XU** and **BL47XU**. The sample consists of a typical depleted lherzolite mineral assemblage with accessory Fe-Ni-Cu sulfides and other opaque minerals. A 150- $\mu\text{m}$ -thick thin section was used for the analysis. For spot analyses, we used an incident beam of 15 keV or 113 keV cut with a slit into 20  $\mu\text{m}$   $\times$  20  $\mu\text{m}$  to 40  $\mu\text{m}$   $\times$  40  $\mu\text{m}$  spot size. For microbeam scanning, we used a 15-keV beam focused with a Fresnel zone plate to 1.0  $\mu\text{m}$  width and 0.65  $\mu\text{m}$  length. The photon fluxes (photons/s) are  $\sim 2 \times 10^{10}$  for the 15-keV broad beam,  $\sim 1 \times 10^7$  for the 113-keV broad beam, and  $1\text{--}2 \times 10^{10}$  for the 15-keV microbeam.

We first conducted spot analyses of the Fe-Ni-Cu sulfide and spinel grains in the sample with a broad

beam. Among the 16 Fe-Ni-Cu sulfides and 8 spinel grains analyzed, we detected emission lines of PGE from two Fe-Ni-Cu sulfides. We then conducted a two-dimensional scan of these two sulfide grains with a 15-keV microbeam, and revealed that PGEs were concentrated in several grains of micrometer-scale phases in each sulfide (Fig. 1). The size of the PGE microphases ranges from  $\sim 1$  to 10  $\mu\text{m}$  in maximum dimension. Combinations of elements detected in the microphases are Os-Ir, Os-Ir-Pt, Pt-Au, Pt-Bi, and Au (Fig. 2). Some of the element combinations (Pt-Au, Ir-Os, and Ru-Os-Ir) are rare in PGM found in peridotite samples, although all the combinations were reported from ore deposit samples.

The total amounts of PGE in the microphases that we found are estimated to be roughly on the order of 100 pg, assuming that the thicknesses of the microphases are comparable to their minimum dimensions in the two-dimensional map (Fig. 1). This corresponds to  $\sim 10\%$  of the PGE budget in the thin section, but this value cannot be applicable to other portions of the sample because of the strong heterogeneity of the PGE microphase distribution. A further increase in the efficiency of this method is necessary for a more accurate estimation of the PGE budget in peridotite samples.

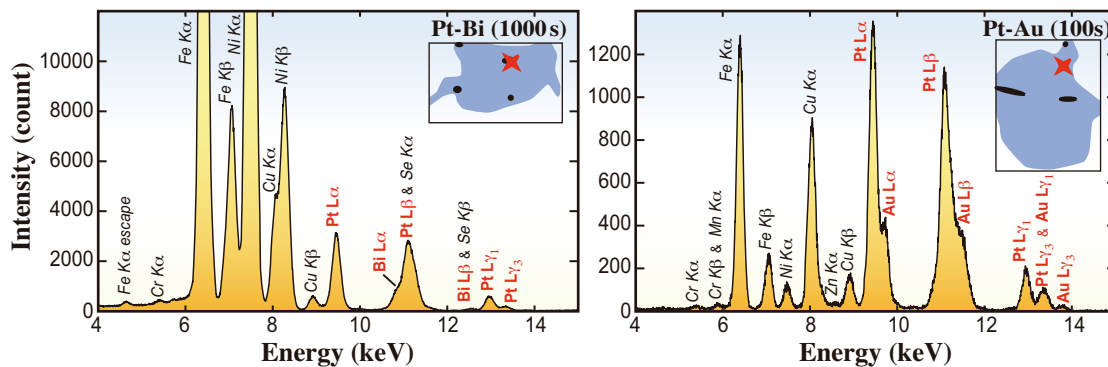


Fig. 2. Examples of fluorescent X-ray spectra of the PGE microphases. Fluorescent X-ray lines from the PGE microphases are labeled with red letters, and those from the host Fe-Ni-Cu sulfides and surrounding silicate minerals are with black letters. The locations of the microphases are shown as red stars in the insets. The acquisition times are shown in each panel. Modified after Ref. [3].

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## References

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