氏　名	周笑羽
授与した学位	博　士
専攻分野の名称	理　学
学位授与番号	博甲第　　５９８０　　号
学位授与の日付	平成３１年　３月２５日
学位授与の要件	自然科学研究科　　地球惑星物質科学　専攻 （学位規則第４条第１項該当）
学位論文の題目	Analytical development for precise and accurate determination of highly siderophile elements in geological samples and its application to the study of Horoman peridotite massif, Japan （地質試料中の強親鉄性元素の高精度・高確度分析方法の開発と幌満かんらん岩への応用）
論文審査委員	教授　田中　亮吏　　教授　中村　栄三　　教授　神崎　正美 教授　小林　桂　　准教授　国広　卓也　　教授　Hao Cheng (Tongji University)

学位論文内容の要旨

We presented a newly developed purification procedure for highly siderophile elements (HSEs) from geological samples using a cation exchange resin (AG 50W-X12) and three additional purification steps (i.e., Eichrom-Ln resin, Chelex100 resin and cation exchange resin AG 50W-X8). Two new methodologies for the purification of HSEs contains: (1) a 50W-X12 cation exchange resin can more effectively separate HSEs, in particular Ru, from matrix elements than the 50W-X8 resin generally used in previous studies, (2) When the HF-desilicification was performed during sample decomposition, Chelex 100 can effectively separate Pd from the Zr fluoro-complex, which however, cannot be removed solely by Ln resin. With careful purification and utilisation of the desolvating nebulizer system, the ratios of interferences relative to the measured intensities of HSE isotope masses were reduced by less than a few hundred parts per million. Thus, no interference correction is required for HSE measurement for both desilicified and non-desilicfied geological samples. Using this method, the HSE mass fractions and $^{187}Os/^{188}Os$ ratios of geological reference materials in ultramafic to mafic compositions were evaluated.

Horoman peridotite complex is one of the least altered peridotite massifs in the world and preserve the unique chemical and isotopic compositions, which may record the multiple mantle processes. In this study, we determined HSE abundances and $^{187}Os/^{188}Os$ ratios of a suite of samples, ranging from fertile plagioclase lherzolites through refractory spinel lherzolites to highly depleted spinel hazrburgites, and subordinated dunite. The positive correlations between fertility indicator (i.e., Al_2O_3 contents) and $^{187}Os/^{188}Os$ ratios in Horoman samples may reflect variable degrees of melt extraction. Also, the stronger depletion of Pd, Pt and Re concentrations in harzburgites indicate that these samples may have experienced higher degrees of melt extraction than plagioclase lherzolites and spinel lherzolites. Furthermore, it is observed that the fertile plagioclase lherzolite samples had very suprachondritic $^{187}Re/^{188}Os$ ratios, in particular, these samples also had the least radiogenic Pb isotopic compositions, which indicate that these samples may undergo the variable addition of Re from a basaltic component, containing unradiogenic Pb isotope ratios, at least ~ 1-1.5 Ga. Dunite however presented different behavior of HSEs and Os isotopic compositions compared to lherzolites and harzburgites. The enrichment of Pd, Pt and Re concentrations and much higher $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios compared to primitive upper mantle may be the result of fluid/melt alteration.

論文審査結果の要旨

Highly siderophile element (HSE; Ru, Pd, Re, Os, Ir, and Pt) geochemistry is one of the most important and sensitive tracer to unravel the origin and evolution of the Earth's mantle. However, analytical difficulty has been pointed out to measure the HSE in natural samples with high accuracy. Ms. Zhou Xiaoyu developed a new purification procedure for separating HSE from the geological samples. To evaluate the accuracy of HSE determination, recoveries of HSE after desilicification treatment using hydrofluoric acid combined with the inverse aqua regia decomposition was evaluated. It has been known that desilicification treatment make it difficult to remove the interference molecules which forming fluoro-complexes. She solved this problem by developing a new separation method using three sets of additional ion chromatography by achieving very low HSE blank. Using this procedure, she measured five international reference materials and evaluated the reliability of reference values for their HSE mass fractions and $^{187}Os/^{188}Os$ values. She also developed an advanced method for the measurement of $^{187}Os/^{188}Os$ using a newly installed thermal ionization mass spectrometer equipped with $10^{13}\Omega$ amplifier.

Using the developed analytical method, she measured HSE and $^{187}Os/^{188}Os$ in Horoman peridotite samples. Horoman peridotite massif is representative and unique orogenic peridotite complex in the world which preserved unradiogenic Pb isotopic compositions. By combing with previously reported dataset, this study first presented the comprehensive geochemical dataset including H-Li-O-Sr-Nd-Hf-Pb-Os isotopic compositions from the peridotite massif. She unraveled the multiple mantle process in Horoman peridotite massif which has not been deciphered clearly in the previous studies, such as melt-rock and fluid-rock interaction processes. These results include new findings which has not been found even in other peridotite massif in the world. Thus, this study will provide a new insight to explain the HSE geochemistry in the Erath's mantle.

By these evaluation, the dissertation committee recommended that Ms. Zhou Xiaoyu be awarded the degree of Doctor of Philosophy in Science.