Reliable determination of osmium isotopes in Greenland and Antarctic snow at the sub-femtogram per gram levels

AHHYUNG LEE$^{1,2}$, CHANGHEE HAN$^1$, KHAMHUN LEE$^2$, YEONGCHEOL HAN$^2$, SEOKHYUN RO$^1$ AND SUNGMIN HONG$^1$

1Inha University, Department of Ocean Sciences
2Korea Polar Research Institute

Presenting Author: leeahyung@inha.edu

Determination of osmium (Os) isotopes has proved to provide a valuable tool for exploring the potential impacts of human activities on biogeochemical cycles of Os in diverse environments due to a significant difference between the isotopic composition ($^{187}\text{Os}/^{188}\text{Os}$) of continental crust and seawater (~1.4 and ~1.06, respectively) and anthropogenic sources (~0.20). However, the accurate measurement of Os isotopic composition in polar snow remains an analytical challenge, because its concentrations are at the sub-femtogram per gram concentrations (1 fg g$^{-1} = 10^{-15}$ g g$^{-1}$) and therefore sophisticated ultrasensitive and ultraclean analytical techniques are required for reliable measurements of Os isotopes. Here, we present an analytical protocol for determining the Os isotopic compositions in snow pits from the NEEM (North Greenland Eemian Ice Drilling Project) site in northwest Greenland and Tourmaline Plateau (TP) in Antarctica. Our method involved adding a $^{190}\text{Os}$ spike and oxidation solution (Jones reagent) to frozen samples, followed by oxidation of all Os species to OsO$_4$ in a high-pressure asher (HPA-S) at 300°C and 128 bar for 16 h. The resulting OsO$_4$ was purified and trapped in HBr by distillation for the Os separation. The separated Os was measured using negative thermal ionization mass spectrometry (N-TIMS). The total procedural blank was determined to be 3.98 fg g$^{-1}$. Our method was validated using six MPI-1 Os standards at the concentration level of 25 fg with the confirmation that 13% of the Re interference effect exists and mean $^{190}\text{Os}/^{188}\text{Os}$ ratio of 1.985 ± 0.018, comparable to the reference value (1.983 ± 0.010). The measured $^{187}\text{Os}/^{188}\text{Os}$ ratios of the NEEM samples, covering the early 2000s, were 1.220–1.230 ± 0.074–0.108, suggesting that Os derived from natural sources can account for Os deposition in recent Greenland snow. In contrast, the relatively low $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.570–0.940 ± 0.046) were observed in the TP samples, covering the late 2010s, indicating significant present-day fluxes of anthropogenic Os in Antarctica. Our method allowed us to determine Os isotopes in polar snow at the sub-femtogram per gram levels, which would help us understand the anthropogenic perturbation of the global Os cycle using polar snow and ice archives.