

Determination of PGE concentrations and Osmium isotopes in sea ice using isotope dilution ICP-SFMS and N-TIMS

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The platinum group element (PGE) concentrations of polar ice are extremely low (10^{-15} g/g), requiring their preconcentration by drying large volumes of sample prior to analysis using an ICP-MS. The extant procedures [1-3], however, do not permit determination of Os and Os isotopes that in combination with other PGEs are powerful tracers of various terrestrial and extra-terrestrial sources [4]. Moreover, they cannot be used to determine PGE contents of sea ice, which may contain up to 1.5% of seasalt: presence of Na⁺ in plasma leads to significant suppression of the ion beams and in worse cases would clog-up the nebulizer. Here, an improved analytical method is presented that allows us to measure Os isotope ratios and Os, Ir, Pt, and Pd concentrations in the same sample aliquot of sea ice.

Samples collected from the Ross Sea (CORSAKS II cruise) were spiked with ¹⁹¹Ir, ¹⁰⁶Pd, ¹⁹⁰Os, and ¹⁹⁸Pt spikes and frozen at -20 °C in quartz-glass ampoules. They were then oxidized at 300 °C using a mixture of HNO₃ and H₂O₂ in a high pressure asher [4,5]. The resulting OsO₄ was separated and purified using distillation and Os isotopes measured with Dartmouth Triton using N-TIMS following the procedure given in [6]. The water remaining after distillation was dried and PGEs separated from seasalt using cation exchange column chromatography. The PGE concentrations were then determined by isotope dilution using Thermo Finnigan Element 2 coupled to a highly sensitive APEX nebulizer. Indium was used as an internal standard to assess any remaining signal suppression. Oxide formation was < 0.5% for HfO. Potential interference masses were monitored and corrections applied when necessary. This method can be extended to obtain PGEs and Os isotopes in sample of polar ice cores, where sample volumes are limited.

[1] Gabrielli *et al* (2004) *JAAS*. **19**, 831-837. [2] Soyol-Erdene *et al* (2011) *ES&T* **45**, 5929-5935. [3] Petaev *et al* (2013) *PNAS* **110**, 12917-12920. [4] Chen & Sharma (2009) *Anal. Chem.* **81**, 5400-5406. [5] Chen *et al* (2009) *PNAS* **106**, 7724-7728. [6] Paul *et al* (2009) *Chem. Geol.* **258**, 136-144