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Evaluation of matrix effects on MC-ICPMS isotope ratio measurements

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MC-ICPMS is now commonly used to detect sub-permil isotopic variations for several metallic chemical elements. High precision isotope ratio measurements are therefore required, necessitating precaution for method validation in order to obtain accurate results. Although mass discrimination is known to be the main analytical bias of this technique, its modelisation for implementing corrections is still debated. Furthermore, matrix effects induced by incomplete analyte isolation may add unpredictable mass discrimination and lead to misleading corrections.
Matrix effects were investigated on Pb isotope ratios measurements. Experiments were conducted on a Neptune MC-ICPMS (ThermoFisher Scientific) operated at IFREMER (Pôle Spectrométrie Océan, Brest France). The isotopic standard NIST981 was doped systematically with Na, Ca, a mixture of Na and Ca, In and U at different concentrations, with [matrix element]/[Pb] ratios ranging from 0 to 50. 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb were corrected for mass discrimination by doping Pb solutions with NIST997 Tl isotopic standard.
Our results show that the internal Tl correction reduces considerably the bias induced by the matrix (factor 7, 5, 5 and 2 for Na, Ca, In and U respectively), although remaining discrepancies on Pb isotope ratios of up to 160ppm are still apparent. Surprisingly, heavier matrix elements (In, U) generates less bias than lighter matrix elements (Na, Ca). Biases appear already at low matrix concentration ([X]/[Pb]=0.1) and tend to stabilise at [Na]/[Pb]=1, [Ca]/[Pb]=1, [In]/[Pb]=5 and [U]/[Pb]=10. Pb and Tl isotopes signals are enhanced to different extent with increasing matrix, making the ratios 208Pb/205Tl and Eps(Pb)/Eps(Tl) not constant.
Evidence of matrix effects for other elements under study (e.g. Fe, Ni, S) will also be demonstrated. This work shows that investigations on remaining matrix in post-chemistry samples are required when looking at relatively small isotopic variations. In case complete analyte separation is not achievable, one may consider enlarging uncertainties on isotope ratio results to cover for matrix effect biases.