High precision analysis of stable potassium (K) isotopes by the collision cell MC-ICP-MS "Sapphire" and a correction method for concentration mismatch

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Stable potassium (K) isotopes $({}^{41}K/{}^{39}K)$ have shown great promise as novel isotope tracers for a wide range of bio-, geo-, and cosmo-chemical processes. However, high-precision stable K isotope analysis remains a challenge for plasma source mass spectrometry due to intense argon-related interferences produced directly from argon plasma.

Here, we provide an assessment on the analytical figures of merit of a new generation collision/reaction cell equipped multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS), *Sapphire* from Nu Instruments, for K isotope analysis based on our extensive tests over a duration of ~8 months. The unique design of a dual ion beam path provides a rare opportunity to make direct a comparison of the performance by collision/reaction cell to that of the conventional "cold plasma" method using the same instrument.

Our results showed that the use of helium and hydrogen as collision/reaction gases can mitigate argon-related interferences to negligible levels at optimal flow rates. Compared to the "cold plasma" mode which requires extremely high mass resolution to partially resolve ⁴¹K⁺ from ⁴⁰AgH⁺ interference, the collision cell mode operates at low mass resolution, yet yielding >2 orders of magnitude higher K sensitivity (>1000 V/ppm) and ensuring the capability for simultaneous ⁴⁰K analysis. One challenge of the collision/reaction cell measurements is its higher susceptibility to matrix effects, requiring effective sample purification prior to analysis. More significantly, the collision/reaction cell mode shows a more pronounced effect associated with concentration (or ion intensity) mismatch between the sample and standard, and such an effect may not be fully eliminated through conventional concentration matching practice. Instead, we developed a convenient correction method that significantly reduces the burden to the operator and increases sample throughput. Using this correction method, we demonstrate that accurate K isotope analysis with a long-term precision of 0.05‰ (2SD) can be routinely achieved using the collision/reaction cell on Sapphire, representing a major advance to stable K isotope analysis.