

## **D<sub>2</sub> as the reaction gas to improve robustness of K isotope analysis by collision cell MC-ICP-MS**

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Stable K isotope is a newly emerging research tool for various research areas. K isotope investigations have mushroomed since five to ten years ago due to high-precision K isotope ratio analytical methods developed intensively. K isotope ratio measurements using collision cell multi-collector ICP mass spectrometers (CC-MC-ICP-MS), emerging in the last 2-3 years, have boosted the K isotope investigation due to its high signal sensitivity and convenience during analysis. However, previous studies have reported that trace-level Ca contaminants can induce severe K isotope offset, which shows a significant influence of Ca contamination on the robustness of K isotope analysis by CC-MC-ICP-MS. In this study, we demonstrate that the cause why Ca contamination lays the influence on K isotope analysis by CC-MC-ICP-MS is the formation of positively charged calcium-hydride molecules in the collision cell. Usage of D<sub>2</sub> other than H<sub>2</sub> generates <sup>40</sup>CaD<sup>+</sup> that does not interfere with <sup>41</sup>K<sup>+</sup> as <sup>40</sup>CaH<sup>+</sup> does, so the influence can be dramatically reduced using D<sub>2</sub> instead of H<sub>2</sub> (the default gas) as the reaction gas that goes into the collision cell, which makes the robustness of K isotope analysis by CC-MC-ICP-MS significantly enhanced. K isotopic results of seven geo-standards by this method agree well with the literature data, which confirms the validity of the method. With the improved method, we have performed K isotope studies on a 17 mg lunar basalt fragment from China's Chang'e-5 lunar returned samples at sub-microgram K consumption. Six mineral separates (plagioclase and pyroxene, three each) picked up from the lunar basalt fragment, weighted low down to 0.5 mg and 400 ng K mass, have shown varied K isotopic compositions with δ<sup>41</sup>K of plagioclase from -0.60‰ to +0.03‰, and pyroxene from -0.37‰ to -0.18‰, which firstly reveals significant millimeter-scale K isotope variability in lunar samples worldwide.