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Precise measurements of radiogenic ^{40}Ca using two double spikes (^{42}Ca-^{43}Ca and ^{43}Ca-^{46}Ca) techniques in Thermal Ionization Mass Spectrometer

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Calcium (Ca) is the fifth most abundant element, with six naturally occurring isotopes: ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca. Their diverse isotopic compositions drive various fractionation processes in nature, fueling interest across scientific fields like Solar System evolution, crust-mantle processes, seawater evolution, weathering, and paleotemperature reconstruction. Apart from investigating mass-dependent Ca stable isotopic fractionation ($\delta^{44/40}Ca$), researchers delve into radiogenic ^{40}Ca, originating from the decay of ^{40}K (with a half-life of 1.277 Ga), which forms the foundation of K-Ca geochronology. thermal-ionization mass spectrometers (TIMS) have been utilized for ^{40}Ca measurements ($\varepsilon^{40}Ca$), adjusting for instrumental mass-dependent fractionation to $^{42}Ca/^{44}Ca$ = 0.31221, with an external precision of ± 1ε-unit (2SD) [1]. In this study introduces a novel technique utilizing double spikes of ^{42}Ca-^{43}Ca and ^{43}Ca-^{46}Ca to measure $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$, respectively. Epsilon notation ($\varepsilon^{40}Ca$) denotes excess radiogenic ^{40}Ca, computed from measured $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$ values. By employing this method, we've attained precision in $\varepsilon^{40}Ca$ measurements comparable to that of traditional techniques. In conventional measurement methods, a ^{40}Ca signal was obtained at 20-30V, and measurements were conducted over several hours to enhance internal precision. Faraday cup liners, responsible for measuring the substantial ^{40}Ca signal, needed replacement every six months due to cup degradation.

With our proposed technique, maximum signal intensity (^{40}Ca) is achieved at 10-15V, and the analysis time is reduced to 2-3 hours. This improvement has bolstered our counting statistics, enabling us to achieve internal and external precision levels comparable to those of the traditional technique. Throughout the analysis, we've measured several carbonate standards: NIST standards SRM 915a and SRM 915b, Seawater, silicate standards USGS BCR-2 and BHVO-2. Additionally, we've measured in-house standards SIL_STD1 and SIL_STD2, prepared with doped single elements ICPMS Ca solution and ^{40}Ca spike. External precision of $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$ measurements surpasses ±0.06 and ± 0.08‰, respectively. Using this new technique for $\varepsilon^{40}Ca$ measurements improves K-Ca dating and offers a potential tracer for weathering and Ca flux into seawater.

[1] Antonelli, M.A., DePaolo, D.J., Christensen, J.N.,Wotzlaw, J.F., Pester, N.J. and Bachmann, O. ACS Earth and Space Chemistry 5.9 (2021), 2481-2492.