High-precision collision-cell MC-ICPMS analysis of Ca isotopic ratios (including ^{40}Ca)

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Ca isotopic ratios have traditionally been measured by TIMS due to its high sensitivity and a precision of ~0.1 ‰ (2sd) in $\delta^{44/40}$Ca has been achieved using double spike techniques [1,2,3]. Compared with TIMS, Ca isotope analysis by MC-ICPMS faces three big challenges: 1) interference of $^{40}Ar^+$ from the plasma on $^{40}Ca^+$; 2) high background noise due to scattered ^{40}Ar which can severely affect the low-abundance Ca isotopes; and 3) the presence of hydrocarbon interferences especially for the minor isotopes. Earlier MC-ICPMS work avoided some of these issues by presenting data as $\delta^{44/42}$Ca, instead of $\delta^{44/40}$Ca, with 0.1-0.2‰ (2sd) precision using sample-standard bracketing [e.g. 4].

We report Ca isotopic measurements using an IsoProbe MC-ICPMS operated in collision/reaction cell mode using a $10^{10}\Omega$ resistor for ^{40}Ca. A flow of H_2 (0.8 ml/min) through the collision cell eliminates ^{40}Ar interference on ^{40}Ca via charge transfer and enables precise measurements of ^{40}Ca. Blanks (2% HNO_3, $2x10^{-13}$ A ^{40}Ca) and Ca samples (1 ppm, $4x10^{-9}$ A ^{40}Ca) show a residual ^{40}Ar intensity of ca. $4x10^{-14}$ A, implying negligible Ar interferences on measured ratios.

Internally ^{44}Ca/^{40}Ca-normalized ^{42}Ca/^{40}Ca and ^{43}Ca/^{40}Ca ratios of Ca-isotope standard SRM915b within a day yield 2sd of 72 ppm and 260 ppm respectively after correction for Sr^{2+} interference. Identical normalized ^{42}Ca/^{40}Ca and ^{43}Ca/^{40}Ca ratios are obtained for natural apatite and aragonite without chemical separation, and form the basis of an accurate double spike correction. We are currently investigating the use of a ^{43}Ca-^{46}Ca double spike (DS) for mass bias correction of solution mode analyses, and are comparing results of this with data obtained in both solution and laser-ablation (LA) modes [5] using sample-standard bracketing. Alternating with unknown samples, six sets of measured Ca isotope ratios obtained by laser abation of a SRM915b pellet agree within the internal error (2se = 0.2‰) over a 6-hour period.

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Seasonal variations of chemical weathering rates and CO_2 consumption in Yangtze River basin

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Continental erosion controls atmospheric CO_2 levels on geological timescales through silicate weathering. Rivers play an important role in long-term carbon cycle by transporting rock weathering products to oceans. The Yangtze River (Changjiang) is the largest river in Asian and drains the tectonic uplifted Himalaya and Qinghai–Tibet Plateau which are of especial importance because of the possible connections with late Cenozoic climate change.

In this study, water samples of the Yangtze River were collected at Nanjing twice a month from May, 2010 to April, 2011. Major ions (Cl, SO_4, NO_3, Ca, Mg, K, Na, Sr) in the dissolved load were determined. There were linear correlations between Ca/Na ,1000*Sr/Na, HCO_3/Na and Mg/Na. Na-normalized ratios of major ions were used in an inverse model to calculate the contribution of the six end-members(i.e. atmosphere, industry pollution, agriculture pollution, carbonates weathering, silicates weathering and evaporates dissolution). Results show that in the monsoon season (May-August) carbonate weathering contributed more to the dissolved load than in the dry seasons. Almost 60% of major ions were derived from carbonates weathering while carbonates contribution reduced to near 40% in dry seasons. The variation of contributions from silicate weathering shows an opposite trend, that means it is low (about 1%) during the monsoon season but can increase astonishingly to 32% in dry seasons. In the whole year, carbonates weathering and silicate weathering consumed $8.32*10^{11}$mol and $1.61*10^{11}$mol CO_2, respectively in the Changjiang basin.

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