



Significant calcium stable isotopic ($^{44}\text{Ca}/^{40}\text{Ca}$) variability in a hand-specimen size diabase due to selective weathering of plagioclase and clinopyroxene

Anupam Banerjee and Ramananda Chakrabarti

Indian Institute of Science, Centre for Earth Sciences, Bangalore, India (anupam.gg.2006@gmail.com)

Calcium stable isotopic compositions ($^{44}\text{Ca}/^{40}\text{Ca}$) of different silicate rock standards show limited variability [1, 2]; however, significant fractionation between co-existing minerals (e.g., clinopyroxene, orthopyroxene, olivine) have been reported for igneous and metamorphic rocks [3, 4]. In the low temperature regime, larger variability has been observed in $^{44}\text{Ca}/^{40}\text{Ca}$. For example, $^{44}\text{Ca}/^{40}\text{Ca}$ values of river water samples show significant variability ($\sim 1.5\%$) which is explained by the formation of clay minerals or carbonate versus silicate rock weathering [5,6].

In this study, we report Ca stable isotopic compositions for micro-drilled samples ($n = 11$) of a hand-specimen sized spheroidally weathered ~ 2.37 Ga old diabase from southern India. The $^{44}\text{Ca}/^{40}\text{Ca}$ values of these samples were determined by a Thermo Fischer Triton Plus Thermal Ionisation Mass Spectrometer (TIMS) using a ^{43}Ca - ^{48}Ca double spike. The $^{44}\text{Ca}/^{40}\text{Ca}$ values of the weathered samples range from 0.42‰ to 0.84‰ (w.r.t. SRM915a) whereas the unweathered (UW) diabase shows a $^{44}\text{Ca}/^{40}\text{Ca}$ value of 0.65‰. The variation in $^{44}\text{Ca}/^{40}\text{Ca}$ in the weathered samples is significantly higher than the external reproducibility of our measurements ($< 0.1\%$ based on multiple measurements of Ca isotopic standards SRM 915a, SRM 915b and seawater (NASS-6)).

The samples with lower $^{44}\text{Ca}/^{40}\text{Ca}$ show higher values of chemical index of alteration (CIA), Al/Ca and Sr/Ca than the UW diabase while samples having higher $^{44}\text{Ca}/^{40}\text{Ca}$ show lower CIA, Al/Ca and Sr/Ca than the UW diabase. The weathered sample having the lowest $^{44}\text{Ca}/^{40}\text{Ca}$ exhibits the highest value of europium anomaly (Eu/Eu*) and possibly reflects the $^{44}\text{Ca}/^{40}\text{Ca}$ of plagioclase in the diabase and is consistent with reported values of $^{44}\text{Ca}/^{40}\text{Ca}$ of plagioclase [7]. We also measured the $^{44}\text{Ca}/^{40}\text{Ca}$ of clinopyroxene from the San Carlos peridotite and our result (1.05) is consistent with published values of the same [3]. Using the above-mentioned end member compositions of $^{44}\text{Ca}/^{40}\text{Ca}$ for plagioclase and clinopyroxene and their Sr/Ca and Al/Ca values, based on published data for these minerals from the southern Indian dykes (Sahoo and Balakrishnan, 1994), we demonstrate that the $^{44}\text{Ca}/^{40}\text{Ca}$, Sr/Ca and Al/Ca values of the weathered samples can be explained by varying proportions of residual clinopyroxene (20-65%) and plagioclase (80-35%) in the weathered rock. This study demonstrates that selective weathering of major rock-forming minerals in nature can result in significant variation in $^{44}\text{Ca}/^{40}\text{Ca}$ in weathered rocks and has implications for understanding the $^{44}\text{Ca}/^{40}\text{Ca}$ variability in rivers.

References: [1] Amini et al., 2009, Geost. Geoanal. Res., 33, 231-247; [2] He et al., 2017, Geost. Geoanal. Res., 41 (2), 283-302; [3] Huang et al., 2010, Earth. Planet. Sci. Lett., 292, 337-344; [4] Kang et al., 2016, Geochim. Cosmochim. Acta, 174, 335-344; [5] Hindshaw et al., 2013, Earth. Planet. Sci. Lett., 374, 173-184; [6] Jacobsen et al., 2015, Earth. Planet. Sci. Lett., 416, 132-142; [7] Ryu et al., 2011, Geochim. Cosmochim. Acta, 75 (20), 6004-6026