



## 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

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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  $\sim 2.37$  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  $^{43}\text{Ca}$ - $^{48}\text{Ca}$  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