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Philippe Négrel, Catherine Guerrot, Romain Millot, Emmanuelle Petelet-Giraud, Bullen Thomas. $^{44}/^{40}\text{Ca}$ and $^{87}/^{86}\text{Sr}$ isotopes as tracers of silicate weathering in small catchments of the Massif Central, France. EGU General Assembly 2013, Apr 2013, Vienne, Austria. pp. EGU2013-10951-1, 2013. hal-00773535

HAL Id: hal-00773535

<https://brgm.hal.science/hal-00773535>

Submitted on 14 Jan 2013

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$^{44/40}\text{Ca}$ and $^{87/86}\text{Sr}$ isotopes as tracers of silicate weathering in small catchments of the Massif Central, France

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We present calcium stable isotope and strontium radiogenic isotope data for soils and sediments developed on volcanic and igneous rocks forming small catchments in the Massif Central (France). Measurements of $^{44/40}\text{Ca}$ isotope ratios ($^{44/40}\text{Ca}$ measured by the double spike method on TIMS and normalized to the value for seawater Ca in delta units) in rocks, sediments and soils from silicate catchments (e.g. granite and basalts) together with $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios permit an examination of the relationships of these isotope systematics during weathering of silicate rocks. We have analysed the granite, weathered granite (arenite) and saprolite, sediment and soil overlying the granite on one hand and the basanite, sediment and soil overlying the basanite on the other.

The main bedrock in the volcanic zone (e.g. Allanche catchment) is 11 to 2.5 Ma basanite (nephelinitic to leucitic basalts) having SiO_2 between 41-45 wt. %, $\text{Na}_2\text{O} + \text{K}_2\text{O} < 5\%$, modal or normative nepheline or leucite and a ground mass of clinopyroxene and plagioclase. Surrounding rocks are feldspathic basalts having SiO_2 between 46-49 wt. %, $\text{Na}_2\text{O} + \text{K}_2\text{O} < 5\%$, normative nepheline, hypersthene and olivine, with plagioclase as the main crystalline phase. The granite massif (e.g. Margeride, 332 ± 12 Ma) consists of light and dark facies as a result of the fractional crystallisation of a crustal magma in a sub-horizontal laccolith, with leucogranites dated at 298 ± 2 Ma intruding this granite. The average mineral composition is 37% quartz, 30% oligoclase, 23% K-feldspar and 10% biotite (light facies) and 31% quartz, 30% andesine, 20% K-feldspar and 19% biotite (dark facies).

Sr isotope ratios in the arenite, sediment and soil diverge strongly from those in the granite bedrock and are positively correlated with Rb/Sr ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios both increase from the whole rock to the arenite, reflecting the weathering of low $^{87}\text{Sr}/^{86}\text{Sr}$, low Rb/Sr minerals such as plagioclase and apatite. Sediments collected on a river bank have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios greater than that of the arenite with values increasing in the sediment from the surface down to soil. The $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Rb/Sr variation observed in the volcanic area likewise confirms the weathering of low $^{87}\text{Sr}/^{86}\text{Sr}$, low Rb/Sr phases in the bedrock, and there is a linear increase in $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios from those in the sediment up to the values observed in the soils.

In the volcanic area, the basanite bedrock has $\delta^{44}\text{Ca} = -0.94 \pm 0.05\text{‰}$ ($n = 7$), while the soils and sediments have $^{44/40}\text{Ca}$ of -0.75 to -1.13‰ and -0.79 to -1.01‰, respectively. These results suggest that Ca isotopes are not strongly fractionated during weathering of the basalt. The granite whole-rock has $^{44/40}\text{Ca}$ of -1.29‰, while the soil and sediments have $^{44/40}\text{Ca}$ of -1.93 to -2.07‰ and -1.98 to -2.81‰, respectively, with values decreasing as the Ca content decreases. The $^{44/40}\text{Ca}$ ratios of arenite, soil and sediment are similar to or less than that of K-feldspar, reflecting complete loss of the relatively heavy Ca from plagioclase and apatite during weathering. Comparison of the $^{44/40}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios further revealed the role of mineralogical assemblage in sediments and soils, particularly for the lesser $^{44/40}\text{Ca}$ – greater $^{87}\text{Sr}/^{86}\text{Sr}$ samples, when compared to the bedrock.