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CALCIUM AND STRONTIUM ISOTOPIC CHARACTERIZATION OF SURFACE WATERS IN A SMALL BASALTIC WATERSHED (MASSIF CENTRAL, FRANCE)

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Introduction: The chemical weathering of rocks is one of the essential processes in the geochemical cycling of elements because during this process at the earth's surface, rocks and primary minerals are transformed into solutes and secondary minerals, which form soils and sediments. In most countries, human activities also impact the cycle of dissolved species in catchments. We present here a series of calcium isotopes in surface waters draining a basaltic catchment in the Massif Central (France). These data will be interpreted by coupling measurements of $\delta^{44}\text{Ca}$ isotope ratio in waters, rocks, sediments and soils, together with Sr isotopes on the same media. Coupling Ca and Sr isotopes may permit an examination of the relationships of these isotope systematics as Ca and Sr, and K and Rb may behave similarly during weathering of such silicate rocks.

Materials and methods: Main bedrocks in the volcanic zone (11 to 2.5 Ma) are basanites (SiO_2 : 41-45%, $\text{Na}_2\text{O} + \text{K}_2\text{O} < 5\%$) and a ground mass of clinopyroxene and plagioclase. Surrounding rocks are feldspatic basalts (SiO_2 : 46-49%, $\text{Na}_2\text{O} + \text{K}_2\text{O} < 5\%$). The main phase in these basalts is plagioclase with hypersthene and olivine. The Sr isotopes were analysed using a Finnigan MAT 262 after chemical separation and $^{44/40}\text{Ca}$ isotopic ratios were measured by double spike method on the same TIMS and normalized to seawater.

Sr and Ca isotopes in river waters: The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the riverwater increase from the headwaters to the outlet and the Sr isotope ratios and Cl content exhibits a good relationship. These relationships imply the existence of a first component with low Cl content and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and a component with high Cl content and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These two components have been related to rock weathering and to addition of fertilizers from land. Once the correction for atmospheric contribution for any element Z in the river water being done ($\text{Cl}_{\text{river}} \times Z / \text{Cl}_{\text{rainwater}}$), the anthropogenic correction was done in the same way considering that all the residual Cl after the atmospheric correction derives from anthropogenic input, the ultimate correction leads to all the samples having zero Cl content. Applying the dual correction to all river water shows a good relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ values in the water resulting from weathering ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{WRI}}$) and the bedrock ($R^2 = 0.70$), reflecting different degrees of weathering.

The $\delta^{44}\text{Ca}$ of the riverwater is ranging between -1.18 to -0.95‰, close to that of basanite bedrock ($\delta^{44}\text{Ca} = -0.94 \pm 0.05\%$, $n = 7$), without any relationship with the Cl content or the distance to the headwaters. The dual correction applied to Ca highlighted that between 24 and 81% of Ca in the river water can be related to anthropogenic inputs and conversely, between 13 and 69% of Ca can be related to weathering. But such inputs seems to have no influence on the Ca isotopic signature of the river water since its $\delta^{44}\text{Ca}$ remains close to that of bedrocks. Coupling $\delta^{44}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{WRI}}$ in the surface water draining the volcanic area confirm the influence of weathering on the Sr isotopes and not on the Ca isotopes.