

Seasonal variations of dissolved Ge:Si ratios in streams from the Aso caldera, Kyushu, Japan

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Volcanic island arcs display the highest silicate weathering rates on Earth. In these environments, hydrothermal fluids act as an additional source of acids for weathering reactions. The hydrothermal influence on riverine dissolved weathering fluxes remains poorly constrained. High Ge:Si ratio values in rivers have been attributed to hydrothermal inputs to rivers. Here we assess the seasonal variability of the dissolved Ge:Si ratio in a volcanic hydrothermal region. We analysed hydrothermal spring, groundwater, river water and rainwater samples from the Aso caldera, Japan, collected in 2014-16 across five seasons. The hydrothermal springs exhibited high Ge:Si ratios (0.2-19.5 $\mu\text{mol/mol}$). Similar values (0.2-25.5 $\mu\text{mol/mol}$) were found in rivers with low Cl:SO₄ and high SO₄:Na ratios, arguing for hydrothermal inputs. In contrast, lower Ge:Si values were measured in groundwater (0.1-1.3 $\mu\text{mol/mol}$) and rainwater (0.2 $\mu\text{mol/mol}$). The Ge:Si ratio in hydrothermal springs, groundwater and rainwater did not vary significantly between sampling seasons and years. In contrast, the Ge:Si ratio of hydrothermally-impacted rivers was systematically lower in the wet seasons. This suggests dilution of the hydrothermal signal. Our results demonstrate a seasonal influence on the Ge:Si ratio in rivers receiving hydrothermal inputs. Estimates of the hydrothermal input to weathering fluxes which does not account for this variability may be biased.