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Investigating basalt weathering in the Icelandic highlands with Ca and C isotopes

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High riverine HCO_3^- fluxes from basaltic landscapes are widely interpreted as evidence that basalt weathers significantly faster than granite and that basaltic regions are atmospheric CO_2 hot spots, which disproportionately regulate long-term global climate. The weathering of basaltic glass, as well as mechanical erosion by glaciers, may accelerate chemical weathering rates and thus CO_2 drawdown, but controls on the geochemistry of basaltic rivers remain debated. To address this problem, we investigated the calcium and carbon isotope ($\delta^{44/40}Ca$ and $\delta^{13}C_{DIC}$) geochemistry of rivers draining the glaciated highlands of central Iceland. Here, large sediment-laden rivers drain ice caps that have formed on top of young, glassy basalt. The highlands also experience vigorous hydrothermal activity leading to the precipitation of a suite of alteration minerals, as well as widespread groundwater discharge. We report high-precision $\delta^{44/40}Ca$ values for rivers, hyaloclastites, palagonites, basaltic glass, and suspended sediment leachates and digests. We also measured riverine $\delta^{13}C_{DIC}$ values, which are sensitive to mixing between silicate and carbonate weathering but not secondary silicate mineral formation. Riverine $\delta^{44/40}Ca$ values are at least 0.20‰ higher than those for bulk basalt and primary basaltic minerals. Nearly all riverine $\delta^{44/40}Ca$ and $\delta^{13}C_{DIC}$ values define a mixing line between calcite and groundwater. Unlike lowland rivers draining crystalline basalt, highland rivers show little evidence for the weathering of basalt and glass by atmospheric CO_2. We find that high Ca^{2+} and HCO_3^- concentrations mostly reflect groundwater inputs and likely trace carbonate mineral weathering, with smaller contributions from surficial basaltic glass weathering by atmospheric CO_2.