# Examining the role of organic compounds and secondary minerals on Ga/Al fractionation in the Critical Zone

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Aluminum (Al) is a major component of primary and secondary minerals in the Critical Zone and is responsible for biogeochemical processes such soil acidification and stabilization of soil organic matter. Quantifying and tracing Al cycling has been limited because it is monoisotopic. Gallium (Ga) may be an effective geochemical tracer for Al because of their similar chemical properties. It is imperative to characterize the proceses that fractionatate Ga/Al ratios, particularly from organic compounds and secondary minerals.

To investigate the extent of Ga/Al fractionation during weathering and phase partitioning, we measured Ga and Al in regolith profiles ≥7 m profiles at six Critical Zone Observatoies: Boulder Creek, Calhoun, Luquillo, Southern Sierra, and Shale Hills. Contemporary climatic conditions and lithologies strongly varied among CZOs. Using a sequential extraction, we found organic + exchangeable Ga/Al ratios ranged between 0.002 – 0.013 mmol $mol^{-1}$ and averaged 0.002 ± 0.001 mmol $mol^{-1}$. Secondary oxyhydroxide Ga/Al ratios ranged between 0.2 – 211.8 mmol $mol^{-1}$ and averaged 7.3 ± 4.3 mmol $mol^{-1}$. Thus, organic compounds preferentially retained Al while secondary oxyhydroxides preferentially accumualted Ga across CZOS.

To confirm the preferential complexation of Al relative to Ga, we conducted batch reactor weathering experiments using fresh rock from Luquillo CZO and a reference kaolinite. Based on obtained results, the effect of low molecular weight organic ligands such as citrate decreased Ga/Al below the average solid phase proportion of 0.10 mmol $mol^{-1}$. However, The effect catechol showed minimal Al complexation, causing the Ga/Al to increase to 0.5 mol $mol^{-1}$. We conclude that organic compounds can preferentially retain Al relative Ga, potentially leading to greater sorption or leaching of Al. Further investigations into Ga/Al ratios are warranted.