

Ca isotope constraints on chemical weathering along the Middle Reaches of Yangtze River, China

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Understanding Ca isotope variability in groundwaters hosted in different lithologies could provide new insights into processes controlling the Ca isotope fluxes in the global Ca budget. Although there are abundant Ca isotope data from rivers, relatively few groundwater measurements have been reported [1]. We investigated two geographically close but lithologically different aquifer systems along the middle reaches of Yangtze, one of the world's largest rivers. The karst aquifer at Xiangxi River Basin (XRB) drains carbonate rocks and the Quaternary aquifer at Jiangnan Plain (JHP) drains mostly silicates. Ca isotopes in groundwater, along with hydrochemistry and Sr isotopes were measured in 27 samples. The dominant cations and anions are Ca, Mg, and HCO₃⁻. Most of the waters are oversaturated with respect to calcite and dolomite. Measured $\delta^{44/40}\text{Ca}$ values in XRB and JHP vary from -0.44 to -0.05‰ and -0.37 to +0.06‰ (versus BSE), respectively. The silicate aquifer generally has higher Ca concentrations and slightly heavier $\delta^{44/40}\text{Ca}$ values than the carbonate aquifer. Although the Ca isotope variations are small, there is a significant correlation between $\delta^{44/40}\text{Ca}$ and Mg/Ca. There is also a positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Mg/Sr ($R=0.72$, $P<0.01$). An endmember carbonate signature appears to be one of relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ (< 0.710), low $\delta^{44/40}\text{Ca} \approx -0.4\text{‰}$, and low Mg/Ca as might be expected. Carbonate hosted groundwaters with higher $\delta^{44/40}\text{Ca}$ also have higher Mg/Ca, suggesting that calcite precipitation has affected the Ca isotope signatures. Silicate hosted groundwaters have slightly higher $\delta^{44/40}\text{Ca}$ mostly between -0.20 and +0.06‰, similar to likely average values for the continental crust, and $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.7103 and 0.7118 are also close to the estimated average global riverine flux. Thus, our results suggest that although there are slight differences in source Ca isotope ratios for silicate and carbonate aquifers, calcite precipitation tends to narrow the differences so that average groundwater $\delta^{44/40}\text{Ca}$ values are close to BSE values.

[1] Fantle *et al.* (2014) *Earth-Sci. Rev.* **129**, 148-177.