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Cycling of Ca and Mg in a Sandstone Aquifer: Evidence from Ca and Mg Isotopes of Groundwater with Different Ages

XIAO-WEI JIANG

China University of Geosciences, Beijing

In basins with fresh groundwater, evolution from Ca-Mg-HCO_3-dominated groundwater in the recharge area to Na-HCO_3-dominated groundwater in the discharge area is widespread. Unfortunately, the mechanisms causing releasing and removing of Ca and Mg in the critical zone remain underexplored. In this study, we investigate mechanisms of Ca and Mg cycling in a sandstone aquifer in the Ordos Basin, NW China by employing Ca and Mg isotopes of groundwater spanning in age from ~10 years to ~10, 000 years.

In the recharge area where groundwater is young (~10 years) and dominated by Ca and Mg in cation, their Ca/Na molar ratio and Mg/Ca molar ratio are much lower than those of HAc leachate of sandstone, indicating that the majority of Ca and Mg released by silicate and calcite dissolution has been removed by clay formation. Mg isotopes reveals that Mg is removed by incorporating into the structure of neo-formed clays like montmorillonite, whereas Ca isotopes reveals that Ca is removed by adsorption onto neo-formed montmorillonite.

In the discharge area where groundwater is old (~1000 to ~10, 000 years) and dominated by Na, groundwater has low Ca/Na and Mg/Ca molar ratios. However, the depth of sampling wells determines the relative age and concentrations of SO_4. For groundwater in the shallow part of the discharge area with age below 8000 years and SO_4/Ca molar ratio below 1, Mg isotopes reveals that Mg is removed by adsorption onto the surface of clays like montmorillonite, whereas Ca isotopes revealed that Ca is removed by adsorption as well as cation exchange. For groundwater in the deep part of the discharge area with age above 8000 years and SO_4/Ca molar ratio above 1, Mg isotopes reveals that Mg is removed by superposition of cation exchange and adsorption, however, although cation exchange has contribution to Ca removal, the Ca isotopic signature is mainly controlled by gypsum dissolution.

To sum up, by collecting groundwater samples with contrasting ages and using metal isotopes, this study enhances understanding of Ca and Mg cycling in the critical zone.