

Controls of $\delta^{13}\text{C}_{\text{DIC}}$ of Stream and Spring Waters in Sandstone and Carbonate-rock Catchments in Korea

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Stream and spring waters both in sandstone and carbonate-rock catchments in Korea were sampled on a biweekly basis for 7 months, and $\delta^{13}\text{C}_{\text{DIC}}$ and geochemical parameters including water temperature, pH, Eh, EC, DO, and TDS were measured to constrain mechanism controlling $\delta^{13}\text{C}_{\text{DIC}}$ of stream and spring waters. In sandstone catchment, stream water shows $\delta^{13}\text{C}_{\text{DIC}}$ value of -7.3‰ in average and negative correlation of $\delta^{13}\text{C}_{\text{DIC}}$ with water temperature and Eh; spring water emerging from steep sandstone slope shows -3.8‰ in average; and spring water emerging from soil shows -18.0‰ in average. In carbonate-rock catchment stream water shows $\delta^{13}\text{C}_{\text{DIC}}$ value of -8.0‰ in average; spring water shows -10.5‰ in average.

The negative correlation of $\delta^{13}\text{C}_{\text{DIC}}$ in stream water of sandstone catchment with water temperature suggests that water temperature is a main factor controlling $\delta^{13}\text{C}_{\text{DIC}}$ in stream water of sandstone catchment. $\delta^{13}\text{C}_{\text{DIC}}$ value of -3.8‰ in spring water emerging from steep sandstone slope might be resulted from CO_2 exchange between atmosphere and groundwater, and soil-derived CO_2 might have influenced little on the variation of $\delta^{13}\text{C}_{\text{DIC}}$ of spring water in sandstone catchment as indicated by much lower value of $\delta^{13}\text{C}_{\text{DIC}}$ in soil-derived spring water nearby (-18.0‰).

Positive correlation between $\delta^{13}\text{C}_{\text{DIC}}$ and EC, and slightly lower $\delta^{13}\text{C}_{\text{DIC}}$ value in stream water of carbonate-rock catchment than in stream water of sandstone catchment suggest that the dissolution of carbonate rocks has contributed to the increase in the $\delta^{13}\text{C}_{\text{DIC}}$ value; however, dissolution of carbonate rocks did not contribute substantially to the increase in the $\delta^{13}\text{C}_{\text{DIC}}$ value of stream water in carbonate-rock catchment. Instead, the CO_2 exchange between water and atmosphere with subsequent fractionation of carbon isotope in $\text{CO}_{2(\text{g})}$, $\text{CO}_{2(\text{aq})}$, $\text{CO}_{2(\text{HCO}_3^-)}$ is a main factor controlling $\delta^{13}\text{C}_{\text{DIC}}$ value in carbonate-rock catchment. $\delta^{13}\text{C}_{\text{DIC}}$ value of -10.5‰ in spring water emerging from carbonate rock suggests that soil-derived CO_2 had a considerable effect on the lowering of the $\delta^{13}\text{C}_{\text{DIC}}$ value of groundwater in carbonate-rock catchment.

Investigation of the $\delta^{13}\text{C}_{\text{DIC}}$ value of stream and spring waters in sandstone and carbonate-rock catchments shows that the CO_2 exchange between atmosphere and water and the subsequent fractionation of carbon isotope among carbonate species in water were the main factor controlling the $\delta^{13}\text{C}_{\text{DIC}}$ value of stream and spring waters. The increase in the $\delta^{13}\text{C}_{\text{DIC}}$ value of stream and spring waters in carbonate-rock catchment by the dissolution of carbonate rocks was not substantial. Metabolism of aquatic biota influenced little on the variation of $\delta^{13}\text{C}_{\text{DIC}}$ value of waters.

Keywords: Controlling factors of $\delta^{13}\text{C}_{\text{DIC}}$; geochemical parameters; stream and spring waters; sandstone and carbonate-rock catchments