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Secular change of stable carbon isotopic ratio in groundwater samples during their storage in laboratory

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Carbon isotope is a useful tracer in order to identify carbon sources and behavior in the fields of biogenic and geochemical processes. However, the isotopic change during the storage in sample bottles until the measurement sometimes occurs owing to carbon exchange between DIC and atmospheric CO_2, biogenic activity and/or carbonate mineral reactions (deposition and dissolution). The present study examined the secular change of carbon isotopic compositions, $^{13}C/^{12}C$ and $^{14}C/^{12}C$, of DIC in water samples.

The water samples examined are surface seawater (RICE-W01), hot spring water (RICE-W03: high salinity and high DIC, W04: high salinity and low DIC), shallow groundwater (RICW-W05: low salinity and low DIC), deep groundwater (RICE-W06: low salinity and low DIC), and RO water prepared by dissolving chemical regent (RICE-W07: low DIC, W08: high DIC). The carbon isotopic measurements were carried out on the samples which storage periods ware 860 days for W01, 560 days for W03-W06, and 480 days for W07 and W08.

Secular changes of $\delta^{13}C$ ranged from -5.4 ‰ to -0.2 ‰. The large isotopic change might be caused by decomposition of biogenic carbon in water samples, since the Keeling Plot showed the biogenic features of $\delta^{13}C$ of added carbon. The storage examination suggested that some water samples did not change the $\delta^{13}C$ values widely for years. The biogenic activity is prevented by regent addition to water samples. Commonly $HgCl_2$ or NaN_3 is used, but it is hard to use them for groundwater samples because sampling filed is not situated in the chemical controlled site. The present study confirmed that isotopic change reduced by NaOH instead of poisonous materials.

The materials of storage bottles are also influenced the secular isotopic change. The present study compared the $\delta^{13}C$ value and ^{14}C concentration among the glass, PAN plastic and PP plastic bottles. The $\delta^{13}C$ value was relatively constant for all bottles, while the ^{14}C concentration was clearly different. The contamination of modern carbon was detected for PP plastic bottle.

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