Origin of mercury in the groundwater in Hirakata City, northeastern Osaka Prefecture

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Thirty one groundwaters contained excess mercury of standardvalue(0.5ppb) among the 4513 groundwaters monitored by Osaka Prefecture. Most of those were found in the northeastern part of Osaka(Hirakata and Shijo-nawate cities) and along the active Ikoma Fault system(Osaka Prefecture,2009). The mercury was plausibly geogenic, however, the source was not clear. This study was planned to reveal the origin of mercury using its stable isotopes.
The groundwater was sampled from 15 shallow dug wells and tube wells <10m depth in July 2015-in November in Hirakata city. The water level was 1~2m from the ground. After analyzing major chemistry and total mercury concentration, the groundwater highly containing mercury were selected to determine the mercury isotope ratios. The total mercury concentration was measured by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), the methyl mercury concentration was measured by Gas Chromatography- Atomic Fluorescence Spectrometry(GC-AFS), and the mercury isotope ratio was measured by Multi-Collector Inductively Coupled Plasma Spectrometry(MC-ICP/MS) attached with hydride generation system.
Major chemistry of the studied groundwaters were Ca^{2+}-HCO_3^- and Na-Cl- SO_4+NO_3types. Mercury concentrations were less than the standard value, while the maximum concentration was 133ppt. The mercury concentrations of groundwater from the same wells varied largely, relationship to season and /or precipitation. For one of the case, the groundwaters containing the lower mercury(90ppt) with the higher SO_4^{2-} than that containing higher mercury(133ppt). For the other case, the higher mercury containing groundwater(86ppt) containing higher Ca^{2+} and HCO_3^- than the low-mercury groundwater(59ppt). When the groundwaters taken from two wells, within 20m distance contained 55ppt mercury(well depth >5m) and 2.0ppt(2~3m depth). These observations suggest that the mercury in the groundwater >5m depth in diluted by infiltrating water from the surface around the wells. Therefore, mercury was not contaminated from the source on the ground surface. The most of mercury was in inorganic form, and mono-methyl mercury was less than 1% except one groundwater containing extremely low-mercury. Thus, the mercury does not relate to human activities or bio-chemical reaction.
The mercury isotope ratio is effective to specify origin. The mercury isotope ratio is influenced by bio-chemical fractionation, and many researchs have been done for the bioaccumulation processes (e.g. Blum 2013). While, less studies have reported for the behavior of mercury in the crust using stable isotopes. Although only two groundwaters were analyzed, the present study in the first report on the mercury isotope ratio of shallow groundwaters but not hydrothermal water. δ^{202}Hg of groundwater was -0.65‰~-0.85‰. Many mercury mines are known in the Kii Peninsula and Shikoku Island. Takeuchi(2011) reported that δ^{202}Hg of sinnabars from Niu-mine was -0.68±0.12(‰), Yamato mercury mine was -0.19±0.36(‰), and Mizui mine was -0.51±0.47(‰). The isotope ratios of syudied groundwaters were close to those values, indicating the similar origins of those mercuries. When cinnabar is precipitated from hydrothermal one liquid, isotope fractionation occur to concentrate heavier mercury in the cinnabar. If so, slightly smallen δ^{202}Hg of the studied groundwaters than those of the cinnabars from the Kii Peninsula and Shikoku would suggests more pristine isotope composition of the fluid from the deep crust. Mercury isotope study will be useful to trace the fluids from the deep in relation to the regional tectonics.

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