



Geochemistry of arsenic and other trace elements in a volcanic aquifer system of Kumamoto Area, Japan

Shahadat Hossain (1), Takahiro Hosono (2), and Jun Shimada (1)

(1) Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto-Shi, 860-8555, Japan (sahedmc@yahoo.com, jshimada@sci.kumamoto-u.ac.jp), (2) Priority Organization for Innovation and Excellence, Kumamoto University, 2-39-1 Kurokami, Kumamoto-Shi, 860-8555, Japan (hosono@kumamoto-u.ac.jp)

Total arsenic (As), As(III) species, dissolved organic carbon (DOC), methane (CH₄), sulfur isotope ratios of sulfate ($\delta^{34}\text{SSO}_4$), major ions and trace elements were measured in groundwater collected from boreholes and wells along the flow lines of western margins of Kumamoto basin, at central part of Kyushu island in southern Japan. Kumamoto city is considered as the largest groundwater city in Japan. 100% people of this city depends on groundwater for their drinking purpose.

In this study, we used trace elements data and $\delta^{34}\text{SSO}_4$ values to better understand the processes that are likely controlling mobilization of As in this area. Arsenic concentrations ranges from 1 to 60.6 $\mu\text{g/L}$. High concentrations were found in both shallow and deep aquifers. The aquifers are composed of Quaternary volcanic (pyroclastic) flow deposits. In both aquifers, groundwaters evolve along the down flow gradient from oxidizing conditions of recharge area to the reducing conditions of stagnant area of Kumamoto plain. 40% samples from the Kumamoto plain area exceed the maximum permissible limit of Japan drinking water quality standard (10 $\mu\text{g/L}$). In the reducing groundwater, As(III) constitutes typically more, however; 50% samples dominated with As(III) and 50% samples dominated with As(V) species. High As concentrations occur in anaerobic stagnant groundwaters from this plain area with high dissolved Fe, Mn, moderately dissolved HCO₃, PO₄, DOC and with very low concentrations of NO₃ and SO₄ suggesting the reducing condition of subsurface aquifer. Moderately positive correlation between As and dissolved Fe, Mn and strong negative correlation between As(III)/As(V) ratio and V, Cr and U reflect the dependence of As concentration on the reductive process.

The wide range of $\delta^{34}\text{SSO}_4$ values (6.8 to 36.1‰) indicate that sulfur is undergoing redox cycling. Highly enriched values suggesting the process was probably mediated by microbial activity. It also be noted from positive values of sulfur isotopes that sulfate was not originated from oxidation process of pyrite. A weak correlation was observed between $\delta^{34}\text{SSO}_4$ values and total As contents when all the samples were considered. Although, there is evidence for sulfate reduction, however; it is less clear about co-precipitation or sequester of As with Fe and Sulfide ion.

It is evident that As distribution in subsurface geological media is not controlled by single solid phase. Probably, dissolution-desorption from different phases contributes to the total As in groundwater. The data are consistent with the possibility that microbial mediated reactions and reductive dissolution of Fe-oxyhydroxides are the important processes to mobilize arsenic in this area. The combination of slow flow of groundwater and the younger age of aquifer sediments are also considered potentially important causes for the high dissolved As concentrations in groundwater as the sediments have not been well flushed since burial.