Structures and acidity constants of oxy- and thio- arsenite species in hydrothermal fluids: A first principle molecular dynamics study

MENGJIA HE[1], XIANDONG LIU[1]*, XIANCAI LU[1], CHI ZHANG[1], RUCHENG WANG[1]

[1] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210046, P. R. China

*Corresponding author. E-mail: xiandongliu@gmail.com

Arsenic commonly occurs in both low- and high-temperature conditions including aquifers, sedimentary rocks and hydrothermal ore deposits. It can readily combine with various metals (e.g., Cu/Ag/Au/Pb/Zn/PGE) to form As-containing mineral deposits. Meanwhile, Arsenic is well known for its acute toxicity to human health, from the use of As-bearing water. As usually bonds with oxygen and sulfur to form aqueous species, such as arsenites, arsenates, (oxy)thioarsenites and (oxy)thioarsenates. Thus, knowledge of arsenic speciation under various conditions is crucial for better understanding the behaviors of arsenic in nature.

In this study, the structures and acidity constants (pKa) of oxy- and thio- arsenites ($H_3AsS_xO_{3-x}$, x=0,1,2,3) are investigated using first principle molecular dynamics (FPMD) method. The results suggest that from ambient temperature to 573 K, $H_3AsS_xO_{3-x}$ have a trigonal pyramidal shape with As atom at the top of the pyramid. Moreover, the FPMD based vertical energy gap method was applied to calculate the acidity constants. Aqueous species distributions of $H_3AsS_xO_{3-x}$ versus pH are quantified at the three temperatures. As temperature increases, these pKa trends and comparisons for $H_3AsS_xO_{3-x}$ are also discussed.