

地熱水環境におけるヒ素の移動性の鉱物学的・地球化学的研究
Mineralogical and Geochemical Constraints in Arsenic Mobility in the Geothermal Environment

環境動態講座 3 年 Environmental Dynamics, 3st year

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The mobility of arsenic in the geothermal environment is influenced by the affinity of arsenic aqueous species to the dominant mineralogical host, and the potential stability of the mineralogical host under prevailing surface environment geochemical conditions.

Aqueous arsenite species (e.g. $\text{H}_3\text{AsO}_3(\text{aq})$ and H_2AsO_3^-) are more dominant in high temperature geothermal fluids ($T > 90^\circ\text{C}$) while at lower temperatures ($T < 70^\circ\text{C}$) As-S species dominate. This is consistent with the observed mineralogy of high temperature geothermal precipitates ($T > 100^\circ\text{C}$) where As-sulphide minerals are not present. However, the only possible mineralogical hosts in geothermal precipitates are amorphous silica and the Mg-rich smectite. Mineralogical, chemical extractions and X-ray spectroscopy (i.e. XPS, and synchrotron-based XAS) evidences have shown that $\text{As}^{\text{III}}\text{-O}$ species are dominant in the geothermal precipitates dominantly comprised of the Mg-rich trioctahedral smectite, with minor contributions of $\text{As}^{\text{V}}\text{-O}$ and $\text{As}^{\text{III}}\text{-S}$ species. This is the first documented arsenic-bearing smectites, and is shown to be resistant to rigorous chemical leaching.

The formation of As-sulphide minerals occurs during the cooling of geothermal fluids upon contact with the atmosphere. However, dissolved sulphide oxidizes quickly that only a small amount of minerals are formed. Upon contact with oxidizing surface and ground waters, the sulphide minerals (e.g. pyrite) are weathered to form Fe-oxyhydroxides which can host arsenate species.

Based on phyllosilicate synthesis experiments, the timing of arsenic uptake can provide insights on the crystallographic location of arsenic in phyllosilicates. Initial $\text{As}^{3+}\text{-Si}$ complexation prior to precipitation of the phyllosilicate implies incorporation into the tetrahedral structure. Adsorption to precursory poorly crystalline Mg-silicate phases would most favorably enable As^{3+} to substitute into octahedral sites instead of the tetrahedral sites. In both cases, arsenic is incorporated through the formation of *in situ* mineralogical hosts.

This is also broadly consistent with results from *in situ* and laboratory experiments suggesting that the *ex situ* addition of crystalline sorbents would not take up dissolved arsenic. Sorption of $\text{As}^{3+}\text{-Si}$ aqueous complexes are thus responsible for the simultaneous uptake of dissolved arsenite and silica in geothermal fluids using poorly crystalline inorganic sorbents (e.g. schwertmannite).

The retrieval of useable silicates from spent geothermal brine is beset by the accumulation of arsenic in the retrieved materials as Ca-Si-As-phases. These are relatively stable and resistant to chemical leaching which may find use in non-environmentally crucial applications (e.g. silica admixtures).