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Abstract

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.

Mineralogical, chemical extractions and X-ray spectroscopy (i.e. XPS, and synchrotron-based XAS) evidences have shown that $As^{III}-O$ species are dominant in the geothermal precipitates dominantly comprised of the Mg-rich trioctahedral smectite, with minor contributions of As^V-O and $As^{III}-S$ species. This is the first documented arsenic-bearing smectites, and is shown to be resistant to rigorous chemical leaching.

Based on phyllosilicate synthesis experiments, the timing of arsenic uptake can provide insights on the crystallographic location of arsenic in phyllosilicates. Initial $As^{3+}-Si$ 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.

Sorption of $As^{3+}-Si$ aqueous complexes are thus responsible for the simultaneous uptake of dissolve arsenite and silica in geothermal fluids using poorly crystalline inorganic sorbents (e.g. schwertmannite). However, the retrieval of useable silicates from spent geothermal brine is beset by the accumulation of arsenic in the retrieved materials as Ca-As-Si phases.

I. Introduction

The Philippines and Japan are two of the largest users of geothermal energy resources (Fig. 1). It is often vaguely touted that geothermal energy exploitation is the most environment-friendly amongst the electricity generating schemes (e.g. nuclear, coal and oil). The environmental impacts of geothermal energy exploitation range from ground disturbances (e.g. landslides), gas emissions, noise pollution and contamination by handling of solid and liquid geothermal wastes that contains trace amounts of toxic trace elements (e.g. particularly arsenic).

Arsenic is naturally abundant in the geothermal environment. Surprisingly, there has been no reported serious contamination of areas surrounding active geothermal fields and power plants. This implies that natural attenuation of dissolved arsenic takes place in the geothermal environment.

The mobility of arsenic in the geothermal environment would be influenced by its aqueous species distribution and its affinity to available mineralogical hosts. Sulphide minerals are the commonly known mineralogical hosts for arsenic in the geothermal environment. However, its stability under surface oxidizing conditions is limited and would eventually release arsenic upon dissolution. Fe-oxyhydroxides are capable of taking up dissolved arsenic in the natural environment such that it has become popular in remediation studies. However, it is only selective to arsenate species (As^{5+}) and would require oxidation of dissolved arsenite species (As^{3+}) which are more dominant in the geothermal environment. The mobility of arsenite species is enhanced due to its slow rate of oxidation to arsenate and subsequent sorption to Fe-oxyhydroxides. Even if the oxidation of arsenite takes place, dissolved silica which is also abundant in the geothermal environment would compete with arsenate for sorption sites in Fe-oxyhydroxides.

Clay minerals although common in geothermal systems have not been attributed to influence arsenic mobility in the geothermal environment. This misconception arises from sorption experiments that have used crystalline phyllosilicates *ex situ* added to arsenic contaminated sites. In this study, mineralogical, chemical, spectroscopic evidences complemented by synthesis experiments would show that *in situ* formed mineralogical hosts particularly phyllosilicates (i.e. clay minerals) influence the mobility of arsenic in the geothermal environment.

II. Materials and Methods

Geothermal precipitates both natural and from geothermal power plants from the Philippines and Japan have been collected to assess arsenic distribution in the geothermal environment. Bulk sample characterization was done using petrography, X-ray Diffraction, X-ray Fluorescence and Fourier-Transform Infrared Spectroscopy with an Attenuated Total Reflection cell. Scanning Electron Microscopy fitted with Energy Dispersive Spectrometry was used in microscopic imaging and micro-analyses. Selective chemical extractions complemented by Inductively Coupled Plasma Mass Spectrometry were used to determine arsenic concentrations in the geothermal precipitates. X-ray Photon Spectroscopy was also done to probe surfaces of geothermal precipitates and to detect small amounts of discrete phase. Synchrotron-based X-ray Absorption Spectroscopy, its XANES and EXAFS, was used to probe arsenic oxidation states and coordination environments.

Synthesis experiments were conducted to validate hypotheses on mechanisms of arsenic uptake in the naturally-occurring arsenic-bearing smectites found in a northwestern Japan geothermal field. The experiments also provided a venue to duplicate these natural attenuation processes occurring in the geothermal environment to determine their applicability in the remediation of arsenic-contaminated sites.

III. Discussions and Conclusions

The geothermal environment is a geochemically dynamic environment where the variations in pH, redox and temperature greatly affect the stability of aqueous ligands present. Arsenic complexes dominance and stabilities are greatly influenced by these physicochemical variations, and thus their affinity with mineralogical hosts. At reducing conditions in low temperature environments, they tend to precipitate as arsenic sulphides or associated with iron sulphides. At higher temperatures and reducing conditions, they are stable as $\text{H}_3\text{As}^{\text{III}}\text{O}_3$ aqueous species which do not have a certain affinity to documented mineralogical host in the literature. At low temperature oxidizing conditions typical of the surface environment, arsenate aqueous species (e.g. $\text{H}_2\text{As}^{\text{V}}\text{O}_4^-$ and HAsO_4^{2-}) dominate and have the greatest affinity for sorption unto Fe-oxyhydroxides.

Sulphide minerals are sparingly stable under oxidizing surface conditions. Fe-sulphides, however, tend to form Fe-oxyhydroxides during its oxidative dissolution. If arsenite species are simultaneously oxidized to arsenate, these iron phases will be able to control the mobility of arsenic in the geothermal environment and implement natural attenuation of arsenic in the geothermal environment. However, these can be considered as short-term sinks in the fate of arsenic in the geothermal environment. During the ageing and crystallization of Fe-oxyhydroxides to more stable phases (e.g. goethite), arsenic could be released into solution and resume its lability in the aqueous phase. The current focus of most researches lies in the short-term fate of arsenic, and thus the long-term fate of arsenic in the geothermal environment is still largely unknown.

In the study areas in Japan and the Philippines, amorphous silica and a smectite were found to uptake arsenic stably. Their resistance to rigorous leaching in either highly alkaline or highly acidic solution suggests that they must be structurally incorporated, especially in the smectite found in Japan. X-ray spectroscopy has further shown that the arsenic is dominantly in the form of $\text{As}^{\text{III}}\text{-O}$ species and only minor contributions from both $\text{As}^{\text{V}}\text{-O}$ and $\text{As}^{\text{III}}\text{-S}$ forms. The potential of the clay to uptake arsenic was further investigated in synthesis experiments designed to determine the mechanism involved. Both co-precipitation with smectites through initial $\text{As}^{\text{III}}\text{-Si}$ complexation, and sorption to precursory poorly crystalline phyllosilicates was able to uptake arsenic in large amounts and offers significant stability.

Despite difficulties in characterizing the poorly crystalline synthesized phyllosilicates, the timing of arsenic uptake based on coprecipitation and sorption experiments provide insights on the possible crystallographic location of arsenic in the phyllosilicate structure. Arsenic uptake through initial complexation with dissolved silica would suggest incorporation into the tetrahedral structure, and would also support its affinity with amorphous silica in the natural environment. Initial adsorption with a poorly crystalline phyllosilicate and later incorporation would more favorably enable it to substitute into octahedral sites (i.e. Mg^{2+}) rather than the tetrahedral sites. In both cases of uptake, it is implied that arsenic can go into the phyllosilicate structure with the *in situ* formed mineralogical hosts similar to the documented arsenic-bearing smectite.

In the retrieval of useful silicates from geothermal fluids, arsenic accumulation in the SACS-derived materials could have been due to the $\text{As}^{\text{III}}\text{-Si}$ relation mentioned earlier. Even in sorption with the inorganic sorbents, the presence of the $\text{As}^{\text{III}}\text{-Si}$ complex could be the likely scenario in the simultaneous uptake of As and Si from geothermal fluids. This would imply that retrieval of useable materials from the geothermal fluid is beset by accumulation of arsenic in the SACS-retrieved materials. However, the potential stability of arsenic in the Ca-Si-As solids would enable their use in non-environmentally crucial applications (e.g. cement admixtures).

On an environmental standpoint, this would mean that the long-term fate of arsenic in the geothermal environment is influenced by dissolved silica. It is quite logical since sulphide minerals are not as common and as stable as silicate minerals. The mechanisms involved in the uptake of arsenic in silicates (i.e. particularly phyllosilicates) could be beneficial for wastewater treatment technology and in the remediation of arsenic-contaminated sites.

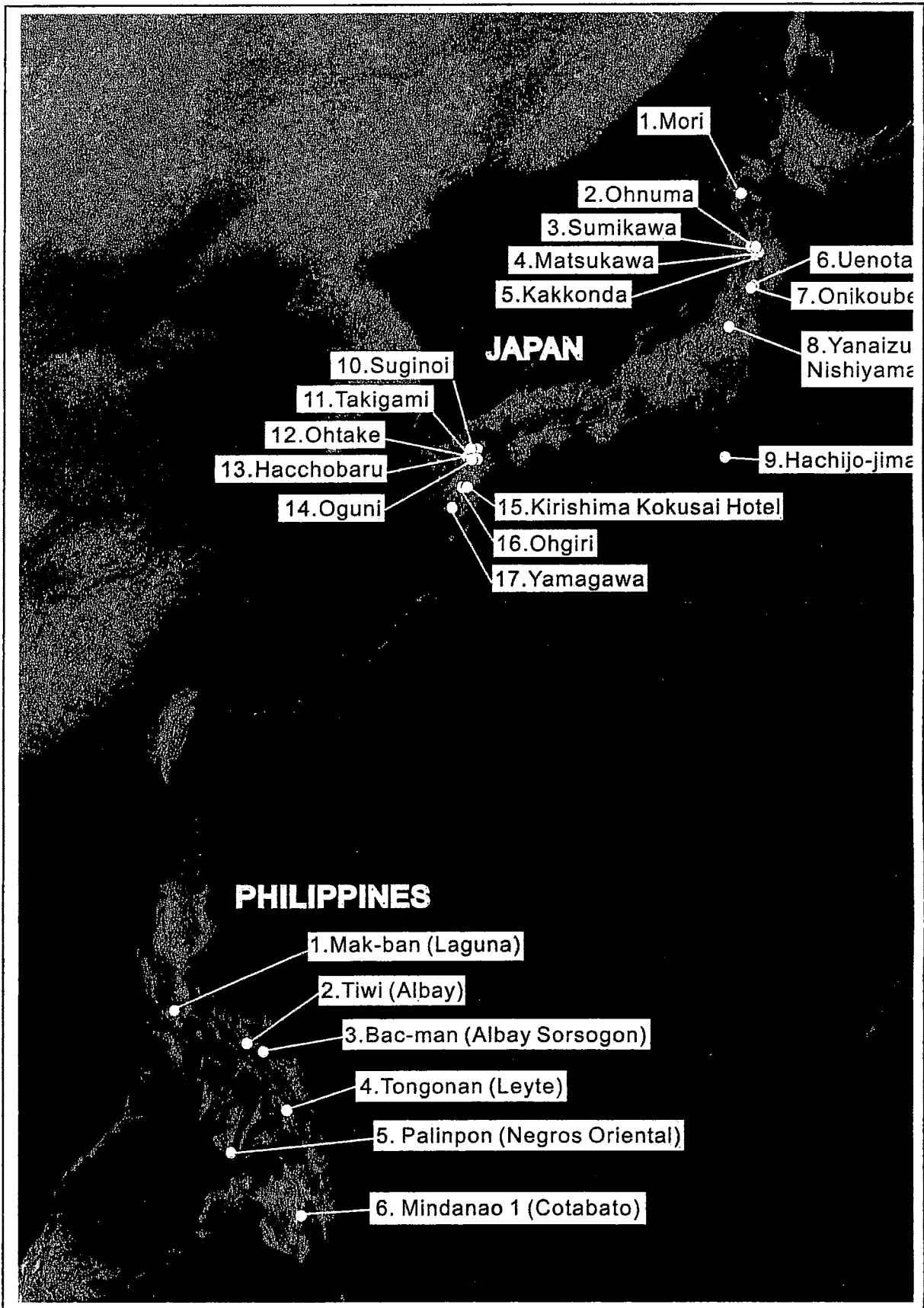


Figure 1. The distribution of geothermal fields in the Philippines and Japan which are exploited for the generation of electricity.

学位論文審査結果の要旨

提出学位論文について各審査委員が個別審査を行うとともに、平成18年2月10日開催の口頭発表を踏まえて、同日開催の論文審査委員会にて検討し、以下の通り判定した。

本論文は、地熱水環境におけるヒ素の挙動を解明し、廃水中のヒ素の回収や地熱発電所の配管から出るスケールの安全な処分方法を開発するための基礎研究であり、その要点は次の通りである。

フィリピンルソン島や秋田県にある地熱発電所で、ヒ素を比較的高濃度に含む熱水の配管から出るスケールを精緻に調べた結果、配管を通過する間にヒ素は自然に浄化され、生成されたスケール中に取り込まれていた。逐次選択抽出法を適用してこれらのスケール中のヒ素の分配を定量的に調べたところ、フィリピンのスケールでは非晶質シリカに、秋田県のスケールでは三八面体型スメクタイトに分配され、特に後者のヒ素はフッ酸で処理を施さなければ抽出できないほど強固に構造内に組み込まれていた。放射光を利用したXAS分析やEXAFSの分析の結果、固体中のヒ素は3価で三八面体型スメクタイトの構造内に取り込まれており、通常の熱水環境下で認められるような硫化物として存在するものは僅かであった。また、スケールの生成環境を模擬した合成・吸着実験の結果、三八面体型スメクタイトや非晶質シリカの生成時にヒ素が存在している場合にのみ、構造内に強固に取り込まれることが判明した。

以上のように、本研究は熱水環境におけるヒ素の挙動の理解や、その安全な処理・処分のための技術開発に大きく貢献するものであり、本論文は博士（理学）の学位に十分値すると判断される。