

A study on adsorption mechanism of organoarsenic compounds onto ferrihydrite

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The inorganic arsenic compounds are cause of groundwater pollution in the world. In addition, organoarsenic compounds also have potential of the water pollution. It is important to know the adsorption structures of arsenic compounds to understand the migration of arsenic compounds in environments. In this study, adsorption structures of methyl and phenyl substituted organoarsenic compounds onto ferrihydrite, one of the most active adsorbents for anions in nature, were studied by the extended X-ray absorption fine structure (EXAFS) measurement and density functional theory (DFT) calculations.

Methylarsonic acid (MMA), dimethylarsenic acid (DMA), phenylarsonic acid (PAA), and diphenylarsinic acid (DPAA) were adsorbed on ferrihydrite at 25 °C, pH 4 and 7. As K-edge EXAFS spectra of organoarsenic solution and adsorbed on ferrihydrite samples were collected by BL01B1 at SPring-8 and BL-12C at KEK Photon Factory (PF).

The EXAFS spectra suggest that all organoarsenic compounds treated in this study form inner-sphere complexes with ferrihydrite regardless of bulky functional groups. The interaction energy analysis using DFT calculations indicate that the steric hindrance between organoarsenic compounds and surface functional groups of ferrihydrite dominate the adsorption structures and adsorption amounts.

Internal ²³⁸U-²³⁰Th isochron method for dating young basaltic eruptions

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Dating of young (Late Pleistocene to Holocene) volcanic eruption gives valuable information in volcanology, environmentology, and archaeology. Although several geochronological methods such as ⁴⁰Ar/³⁹Ar, (U-Th)/He, and ¹⁴C, and U-series disequilibrium, have been applied for dating, there exist many analytical limitations in these methods especially for young basaltic volcanics.

This study demonstrates the applicability of ²³⁸U-²³⁰Th internal isochron methods for the determination of eruption age from young basaltic volcanics using chemically-separated groundmass phases. Groundmass phases of basaltic lava collected from Laguneta volcano, El Salvador, were separated into several fractions with different magnetic susceptibility, followed by leaching in hydrochloric acid solution. Hydrochloric acid solution congruently dissolves olivine, titanomagnetite, and phosphorous-bearing minerals; incongruently dissolves anorthite-rich plagioclase; and does not dissolve augite, albite-rich plagioclase, and alkali-feldspars in the examined groundmass phases. During acid leaching, the range of (²³⁸U/²³²Th) increased from 0.2 (unleached groundmass fractions) to 1.8 (leachates and residues). No, or little, preferential leaching between U and Th occurs by the acid-leaching treatment. Thus, the linear regression line obtained by leachate, residue, and unleached groundmass fractions can be regarded as an isochron, the slope of which indicates the eruption age. The ²³⁸U-²³⁰Th internal isochron age for two individual samples gave an identical value within the error. Using all the fractions from two samples, the most precise ²³⁸U-²³⁰Th isochron age was determined as 14 ± 1 ka (2σ). This age agrees with the degassing-induced external ²³⁸U-²³⁰Th isochron age obtained by whole rock samples when the error is considered. This study also revealed that acid-leaching preferentially fractionates Ra/Th because of incongruent dissolution of plagioclase. Thus, ²³⁰Th-²²⁶Ra isotope systematics cannot be used for acid-leached samples. The significance of this study lies in the development of precise geochronological method for any type of volcanics which erupted between ~3 and ~300 ky.