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Mineralogical approach in elucidation of contamination mechanism for toxic trace elements in the environment: Special reference to arsenic contamination in groundwater

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ABSTRACT

Mineralogy and mineral-microbe interactions play a significant role in the environmental contamination of toxic trace elements in groundwater and wetland ecosystems. This review has described the importance of use of TEM that is an essential tool to study the environmental mineralogy and mineral-microbe interactions. Biomineralization process that can advance the succession and evolution of biosphere on the earth has also been summarized briefly. This study explained the role of minerals to control the mechanism of adsorption, desorption, mobility and transport of toxic trace elements, especially arsenic (As) in the groundwater. Finally, this review has explored the evolution of As contamination in groundwater of the Quaternary age deposits including the Holocene and Pleistocene with special reference to groundwater of Bangladesh, West Bengal (India), Vietnam and Inner Mongolia (China).

1. Introduction

Contamination of toxic elements in land and water environments is one of the main problems of the 21st century for sustainable development of the world. Recent radioactive cesium (Cs) contamination over the wide area from a reactor at the Fukushima Daiichi nuclear power plant, which resulted from meltdown of fuel rods, has created a big problem (e.g., Yoshida and Takahashi, 2012; Blandford and Ahn, 2012). Mineralogy is one of the important research approaches; and it plays a very important role, especially in disclosing the mechanism of environmental contamination (e.g., Akai et al., 2004). Most important point is that mineralogy can precisely determine the chemical composition and crystal structure of the target solid material. The crystal structure of the minerals suggests the crystallochemical characteristics which are related to bonding and/or adsorption of toxic elements. Furthermore, mineralogy can elucidate the sites where toxic elements are embedded, and adsorbed on the surface or in the crystal structure. Furthermore, it also can elucidate under what conditions the toxic elements incorporated will be dissolved, released from or retained in minerals depending on the structure-related characteristics. Recently some studies have been published in the literature investigating the control of different types of mineralogy on the dissolution, mobility, transport and retention of toxic trace elements in the environment, especially in the groundwater systems (Bhattacharya et al., 1997; Nickson et al., 1998; Anawar et al., 2002, 2003; Akai et al., 2004, 2008 and references therein). However, a review synthesizing the previously published results that can focus the future stream of research has not yet been published. Therefore, the main objective of this review is to describe the mineralogical approach in elucidation of contamination mechanism for toxic trace elements in the environment with special reference to As contamination in groundwater.

2. TEM method in mineralogy

Mineralogical study is mainly using the Electron Microscopy (EM) since the early introduction of Transmission Electron Microscopy (TEM) methods to mineralogy in 1970s. Good review papers generally dealing with use of TEM in mineralogy have already been published (McLaren, 1991; Buseck, 1992; Putnis, 1992; Akai 1995, 2008; Lee, 2010). For geoscience interests, not always in atomic scales but unit cell scale information with EDS (Energy Dispersive) chemical data was enough in these days. This necessity was just fitted for the early day's TEM instruments' ability. Not only TEM but also Scanning Electron Microscopy (SEM) methods such as low vacuum SEM (Environmental SEM) and FESEM (Field Emission SEM) were also developed. TEM has advantage of disclosing not only inorganic solid materials but also bacteria and other materials. Mineral-microbe interaction has recently been known as one of the most important controlling factors for the environment in

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the Earth's surface (e.g., Banfield and Nealson, 1997). TEM method catches bacteria at the same time of small inorganic minerals (Barker et al., 1997). Out of two directly observable methods like TEM and SEM, TEM can disclose materials' structure and chemical composition from micrometer to nanometer sizes with Electron Diffraction.

High-resolution transmission electron microscopy (HRTEM) imaging principle is double Fourier Transform of the diffraction by crystalline materials: First Fourier Transform corresponds to electron diffraction (in reciprocal space), and second Fourier Transform of the diffraction (patterns) forms enlarged TEM image (real space). Such HRTEM image, structure image of the minerals, is formed by phase-contrast. This imaging is the results of interference of multibeams diffracted from the mineral crystals. Contrast in TEM images also comes from other factors like diffraction contrast, mass thickness contrast and phase contrast. The diffraction contrast is formed by aperture limitation, and mass thickness contrast corresponds to incoherent elastic scattering of electrons by the mineral samples. In order to take the best image, Sheltzer focus is selected, or conventionally through-focus images are taken and compared with the simulated images for precise interpretation.

TEM methods, largely developed, are closely related to development of specimen preparation techniques, such as ion thinning method (Barber, 1970). Ion beam thinning method is still widely used, because relatively wide area for electron transparent portion is formed. Ultramicrotomy was generally used for biological specimens. In the early days of TEM application to rock forming minerals, this ultramicrotomy was also applied to silicate with diamond knife and in some special cases, for example, weathered soil section containing both microbe and clay mineral, inorganic components, interplanetary dust or commet particle samples (Bradley and Brownlee, 1986; Stephan et al., 1994). Specimen preparation methods for rock forming minerals, and biomineralization and biomaterials are already reviewed by Konishi and Akai (1999) and Sasagawa and Akai (2000), respectively.

Recent development in HRTEM is Cs (Spherical Aberation) corrected STEM (Scanning TEM) imaging. It is aberration-corrected optics, atomic-resolution by HAADF (High Angle Annular Dark-Field)-STEM method. This technique uses high resolution Z-contrast, where atomic contrast is proportional to Z^2 (Z is the atomic number), and it opens a new era of nanotechnology (O'Keefe, 2008; Muller, 2009). Fig. 1 shows an example of imaging of single atoms by HAADF-STEM method; in the figure Th single atoms are found as white spots in amorphous metamict thorite ($ThSiO_4$). Another one is EBSD (Electron Back Scattering Diffraction) method, which is used for backscatter Kikuchi Patterns from polished samples of polycrystalline materials to obtain quantitative crystallographic orientations (Reddy et al., 1999; Watt et al., 2006). For specimen preparation recent development for TEM is FIB (Focussed Ion Beam) method, which is used just for specific site of the sample (Lee, 2010).

3. Mineral-microbe interaction

3.1. Environmental impact of mineral-microbe interaction

Recent image of the Earth is well understood with the concept of interaction between minerals and bacteria (microbes) (e.g., Banfield and Nealson, 1997; Dong and Lu, 2012). One of the two important branches is to study the gene analysis or modern biological approach in order to define the phylogenic position of the microbe. Phylogenic tree for bacteria relating to environmental problems was established based on 16S rDNA data; and recent one including 17 distinguished groups of bacteria is shown by Madigan et al. (2009).

3.2. Biomineralization

Biomineralization is defined as the process by which organisms form minerals under strict biological action (Watabe, 1997). Biomineralization, especially bacterial biomineralization is important due to the strong impact of its reactions onto the earth environment. This aspect is related to expansion of biosphere, for example, underground biosphere (Stevens, 1997; Amend and Teske, 2005)

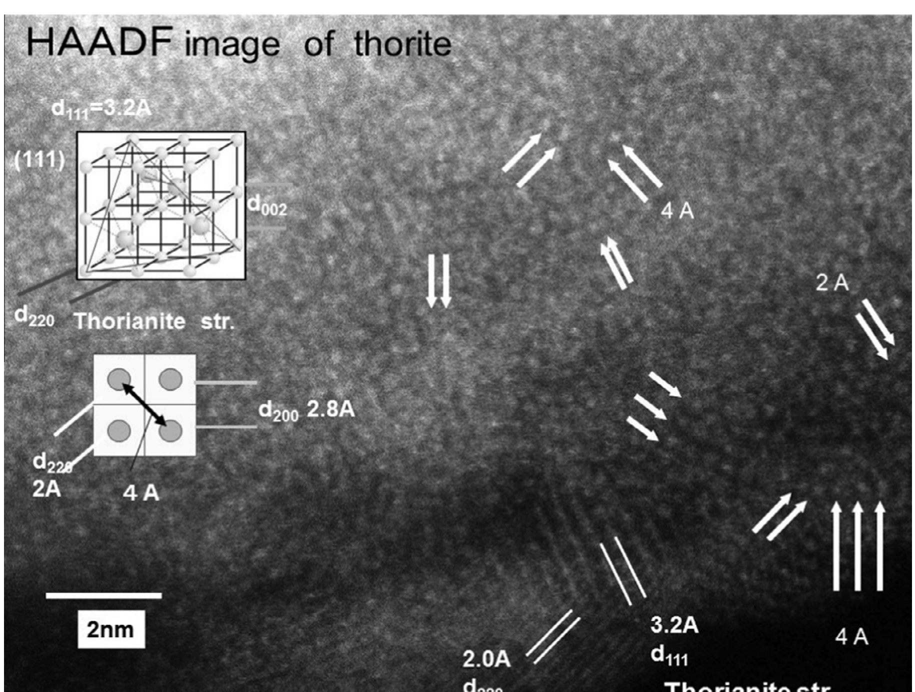

Fig. 1. HAADF-STEM image of thorite ($ThSiO_4$) from Ashizuri, Kochi, Japan. Th single atoms are found as scattered white spots in metamict (amorphous) structure of thorite which has partially recrystallized parts (thorianite ThO_2).