The Occurrence and Speciation of Arsenic in Serpentinites in Northern Vermont, USA

Lijie NIU1, Keiko HATTORI2, Yoshio TAKASHASHI2 & Peter C RYAN3
1 Dept. of Earth Sciences, University of Ottawa, Ottawa, Ontario, Canada (*khattori@uottawa.ca)
2 Dept. of Earth and Planetary Systems Science, Hiroshima University, Higashi-Hiroshima, Japan
3 Dept. of Geology, Middlebury College, Middlebury, Vermont, U.S.A.

ABSTRACT

High concentrations of As are reported in ground waters and bedrocks in many parts of New England (Ayotte, et al. 2003). Ryan et al. (2009) reported that hydrous ultramafic rocks contain high concentrations of As (up to 4-49 ppm in serpentinites and 1-110 ppm in talc-magnesite rocks) in northern Vermont. Altered ultramafic rocks are common in the Appalachians in New England. We investigated the occurrence of As in serpentinites from northern Vermont (103-450 ppm As in bulk rocks). This study includes the examination of polished thin sections, electron probe microanalysis (EPMA) of minerals, acid leaching of mineral separates, as well as X-ray absorption fine structure (XAFS) study of As in the mineral separates. EPMA and micro-XAFS analyses showed that antigorite is the major host of As. In the phosphate leaching experiments, 20 to 30% of As is dissolved, suggesting that this fraction is probably adsorbed on antigorite. It is suggested that As in the local ground water may be equilibrium with the adsorbed As - XANES spectra at As K-edge showed that As is predominantly As(III) in the serpentinite samples. EXAFS spectra show that the As has a tetrahedral coordination, indicating that As is in the Si-site of antigorite. EPMA data indicate a positive correlation between Fe and As abundances, which can be explained by the charge compensation effect: Fe(III) as Fe(III) + As(III) = Mg(II) + Si(IV) in antigorite. Our earlier study of serpentines in north western Himalayas show that As (V) is fixed in serpentines by replacing Si(IV) in antigorite (Hattori, et al. 2005). The results of these studies suggest that hydrous ultramafic rocks are capable of fixing both As(III) and As(V) in serpentinite crystal structure, and the speciation of As in serpentinites is controlled by the oxidation state of As in the hydrating fluids.

BACKGROUND and OBJECTIVES

Arsenic is well known for its toxic potential and has caused health problems in many regions in the world. It ubiquitously present in the earth crust and may enter human or live stocks diets through drinking water, as well as fruits and vegetables that are grown on As-rich soil. Ryan et al. (2009) showed that ground water in the areas underlain by ultramafic rocks in Vermont contain high concentration of As. We investigated the host phase of As, oxidation state of As, and local atomic structure of As in serpentinites in order to understand incorporation process of As in the rock and the source of high concentration of As in groundwater.

METHODS

Serpentinite samples were collected from the northern Vermont, USA, where As is high in ground water. Concentration of As reached as high as 330 ppm in groundwater, and over 1000 ppm in some rocks. X-ray fluorescence (XRF) images show the boundaries between antigorite and Fe oxides of sample. Large grains of Fe oxides have Crip-splined cones rimmed by magnetite. Red color corresponds to higher concentration of elements. The locations for micro-XAFS with 5 μm beam are shown with open circles.

RESULTS and DISCUSSION

The results show that antigorite has higher As concentration than Fe oxides. EPMA also shows high conc of As in antigorite (up to 1300 ppm). Electron probe micro-analysis (EPMA) - Micro X-ray absorption analysis - Acid leaching followed by ICP-AES and ICP-MS analysis - X-ray diffraction (XRD) analysis - Synchrotron-based X-ray absorption analysis

CONCLUSIONS

Arsenic in serpentinites is mostly As(III). The coordination number of As calculated from extended XAFS spectra is ~ 4, suggesting that As occupies the Si site of antigorite. Approximately ~ 30% of As in serpentinites is adsorbed on the surface of antigorite. High concentrations of As in groundwaters in the area are explained by the resorption of As from the surface antigorite and the release of As during the alteration of serpentinites to talc-carbonate rocks.

REFERENCES


ACKNOWLEDGEMENTS

The study is supported by a Discovery Grant to KH from the Natural Science and Engineering Research Council of Canada and a grant-in-aid for scientific research to YT from Japan Society for the Promotion of Science.