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

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ABSTRACT

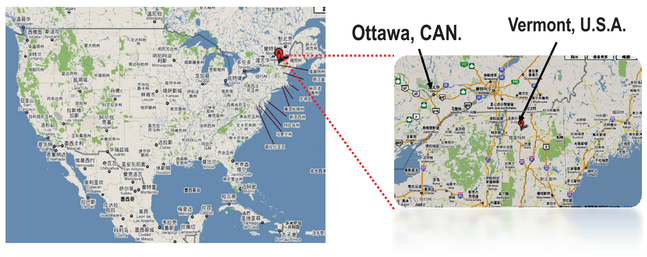
High concentrations of As are reported in ground waters and bedrocks in many parts of New England (Ayotte, et al. 2003). Ryan et al. (2009) reported that hydrated ultramafic rocks contain high concentrations of As (up to 449 ppm in serpentinites and 1,100 ppm in talc-magnesite rocks) in northern Vermont. Altered ultramafic rocks are common in the Appalachians in New England. We investigated the occurrence of As in representative 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 the As is predominantly As(III) in our serpentinite samples. EXAFS spectra shows 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 serpentinites in north western Himalayas show that As (V) is fixed in serpentinites by replacing Si(IV) in antigorite (Hattori,et al. 2005). The results of these studies suggest that hydrating ultramafic rocks are capable of fixing both As(III) and As(V) in serpentine crystal structure, and the speciation of As in serpentinites is controlled by the oxidation state of As in the hydrating fluids.

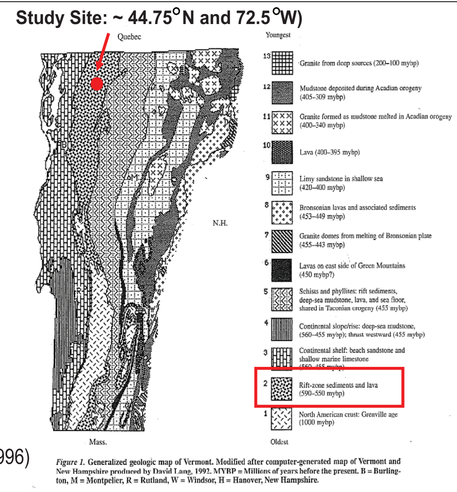
BACKGROUND and OBJECTIVES

Arsenic is well known for its potent toxicity and has caused health problems in many regions in the world. It is 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.s

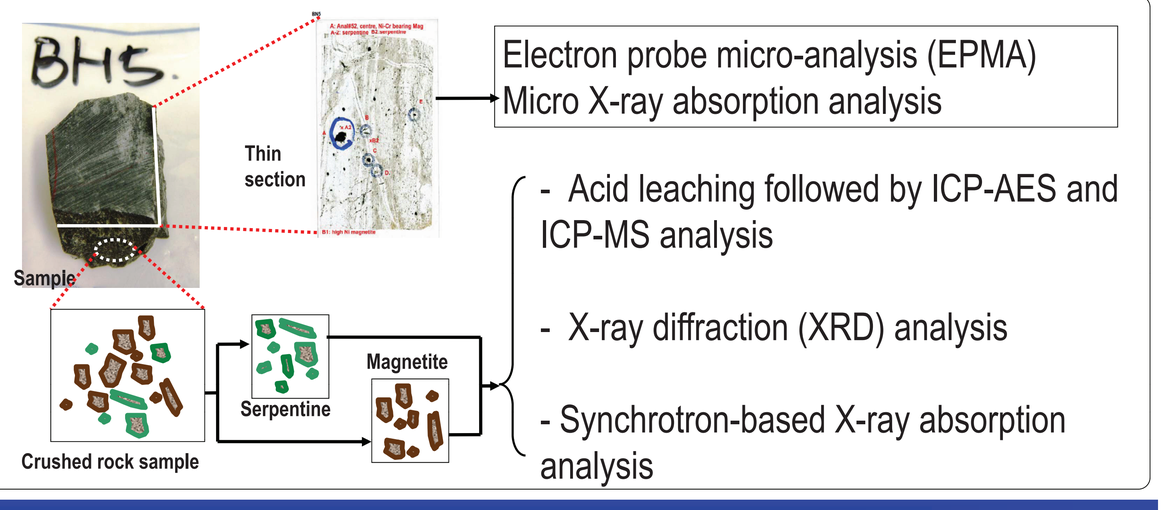
METHODS

Serpentinite samples were collected from the northern Vermont, USA, where As is high in ground water. Concentration of As reached as high as 300 ppb in groundwater, and over 1000 ppm in some rocks.

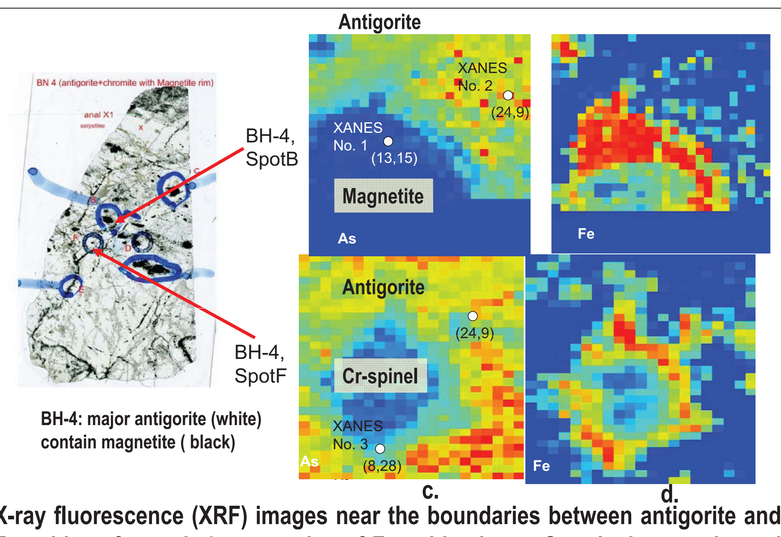




(Dolan,1996)



RESULTS and DISCUSSION

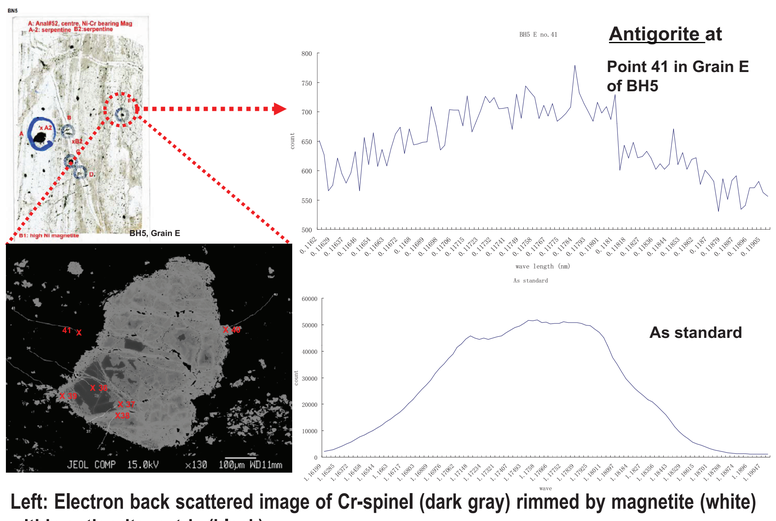


BH-4: major antigorite (white) contain magnetite (black)

X-ray fluorescence (XRF) images near the boundaries between antigorite and Fe oxides of sample Large grains of Fe oxides have Cr-spinel cores 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.

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).

EPMA analysis shows that the contents of As in Cr-spinel and Fe oxides are below the detection limits of ~ 100 ppm. These minerals did not show a AsKα peak, whereas antigorite shows a positive peak.



Left: Electron back scattered image of Cr-spinel (dark gray) rimmed by magnetite (white) within antigorite matrix (black).
Right: Kα peak of As on antigorite compared to that of As standard.

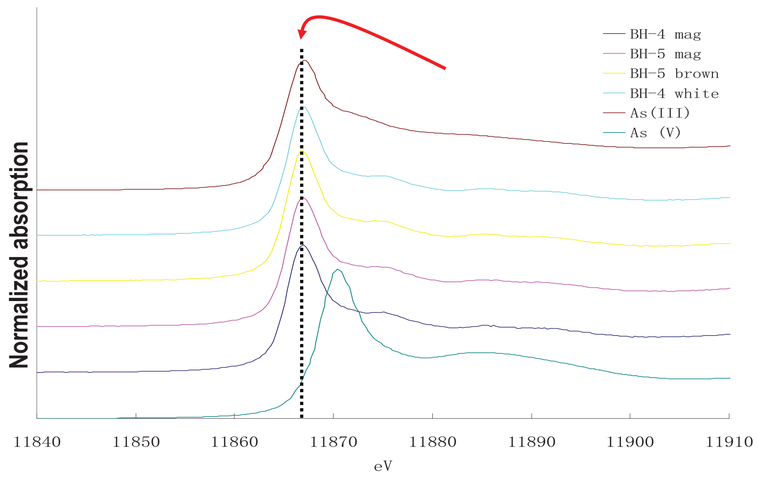


Fig. 4 XAFS analysis of bulk rock sample. The valence states of different samples were compared to As(III) and As(V) standards. The vertical line indicated the absorption peak of As(III).

The major As specie presented in the samples is As (III) in serpentine.

Table 1. Leaching experiment results.

Leaching solution	Elements	Concentration (ppm) BH-4	Concentration (ppm) BH-5
NaH_2PO_4 (1.0 M)	Ca	1490	< D.L.
	Mg	45800	47000
	Al	133	469
	Si	13400	22700
	Mn	574	441
	Fe	368	1400
	As	108	135
HF/HNO_3 (Total)	As	357	756

Two sources of As leached by phosphate solution; As adsorbed on antigorite and As incorporated in carbonates (mainly magnesite). Considering high Mg/Si in the solution and low (< 100 ppm) As concentration in magne-site determined by EPMA (< 100 ppm), As in the phosphate leaching solution is mainly from As adsorbed on antigorite.

Arsenic fraction adsorbed on antigorite estimated from leaching experiments by phosphate solution is 20-30%. The fraction may regulate As concentration in groundwater through the adsorption-desorption reaction, since As in other host phase may be minimal. Another fraction (70-80%) may be incorporated in the structure of antigorite. The average local structure of As in antigorite is estimated from EXAFS as shown in Fig. 4 and Table 2.

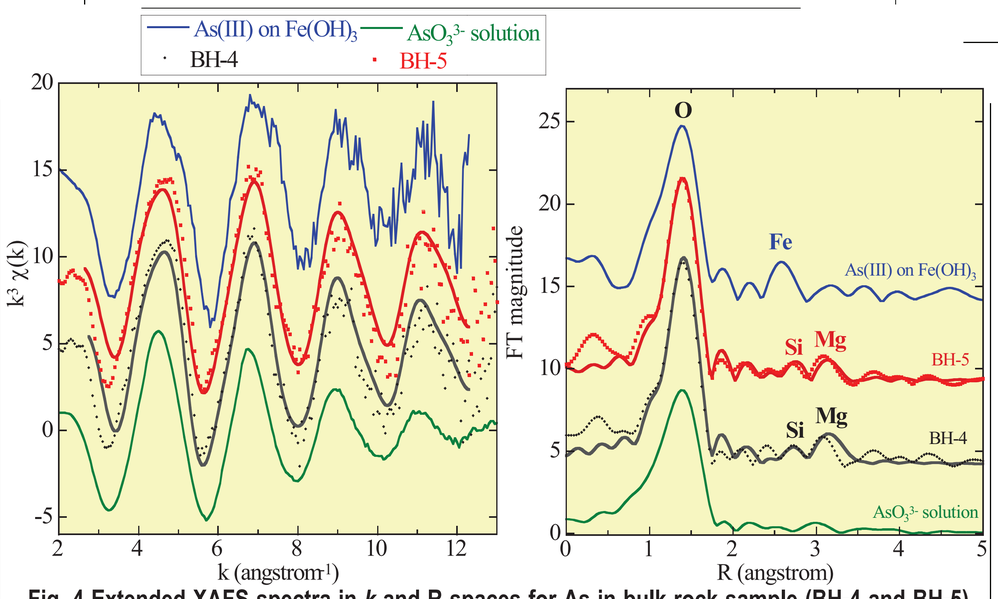


Fig. 4 Extended XAFS spectra in *k* and R spaces for As in bulk rock sample (BH-4 and BH-5), As(III) solution, and As(III) adsorbed on $Fe(OH)_3$. Simulation results using FEFF parameters were also shown for BH-4 and BH-5.

Table 2. EXAFS parameters for BH-4 and BH-5.

	Shell	R (Å)	CN	DW (Å)	ΔE (eV)
BH-4	As-O	1.780±0.009	4.0±0.5	0.070±0.016	8.9±2.0
	As-Si	3.204±0.070	0.6±0.1	0.075*	
	As-Mg	3.491±0.031	1.9±0.9	0.075*	
BH-5	As-O	1.775±0.009	3.9±0.5	0.069±0.016	8.0±2.0
	As-Si	3.188±0.062	0.7±0.6	0.075*	
	As-Mg	3.484±0.032	1.8±0.9	0.075*	

Coordination number (CN) and the distances between As and O indicate that As(III) has a tetrahedral coordination in antigorite. Peaks of second and third shells in R space in BH-4 and BH-5 are weaker than that that of As on $Fe(OH)_3$, suggesting that Fe is not significant in the shells. The calculated distances for As-O, As-Si, and As-Mg are longer than Si-O (1.65-1.65 Å), Si-Si (3.0-3.1 Å) and Si-Mg (3.4 Å) of antigorite. The As-O bonding is distorted compared with Si-O tetrahedra, but the second and third shells are similar to those of As-free antigorite.

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 of antigorite and the release of As during the alteration of serpentinites to talc-carbonate rocks.

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