12C/2007G663

Oxidation states of arsenic in pyrites

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Introduction

Arsenic has several oxidation states. In aqueous and aerobic environment, As is present as 3+ and 5+, adsorbed on Fe hydroxides [1]. In highly reducing environment, As is present by substituting S in sulfide minerals e.g. arsenopyrite. Pyrite is a common sulfide mineral which commonly occurs in sedimentary rocks. We have interests to the As elution from such sulfides in aqueous environment. Here, As speciation analysis of pyrites was carried out.

Experimental

Pyrite samples were collected from the Hishikari epithermal gold deposit (Kagoshima Pref., Japan) and Saint Lucia mine, Peru. The Hishikari pyrites (sample A & B) were small crystals hosted by quartz, collected from the auriferous quartz veins. Their polished surfaces were directly analyzed with a 0.1mm x 0.1mm X-ray beam. Coarse grains of pyrite from Peru (sample P) were pulverized and resultant powder intact was used for analysis.

XANES spectra at the As K-edge were taken in the fluorescence mode with 19 SSD using station BL-12C at KEK-PF. A Si(111) double crystal was used to monochromate X-ray. K-edge spectra of As were calibrated with reference to the peak top of As_2O_3 fixed at 11865 eV. All experimental procedures were performed at ambient temperature and pressure.

Results and Discussion

Resultant XANES spectra were shown in Fig. 1 Peak top energies of FeAsS, $KAsO_2$, and KH_2AsO_4 were shown as gray lines in Fig. 1. The peak top of sample P is between those of FeAsS and $KAsO_2$, which indicates presence of As^{3+} pyrite by substituting Fe [$(Fe,As)S_2$] as reported recently [2] in contrast to the common substitution of S as [$Fe(As,S)_2$]. The presence of As^{5+} was indicated for samples A and B, though further experiments were needed to check the influence of the oxidation during sample preparation.

A hydrothermal experiment using a drilled sediment which consists of hemipelagic mudstones demonstrates that As is released to the experimental fluids from the sediments according to a heating to 350 degree Celsius as well as alkali metal elements [3]. A similar elemental behavior was detected by us in the three active fault zone collected in the Taiwan Chelungpu-fault Drilling Project [4]. Pyrites is a plausible candidate to control the As leaching from such sediment rocks to fluid phases in hydrothermal condition.

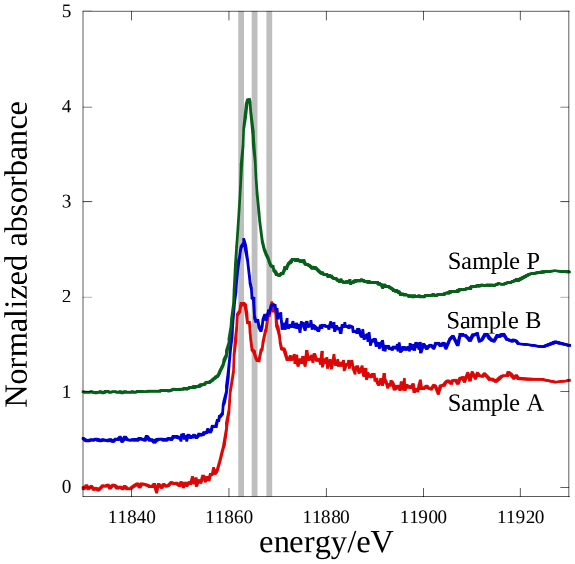

Fig. 1. As XANES spectra of pyrites. Oxidation states of As (1-, 3+, and 5+) were indicated with gray lines from peak tops of FeAsS, $KAsO_2$, and KH_2AsO_4, respectively.

Acknowledgments This research was supported in part by “Global Environment Research Fund by Ministry of the Environment Japan” RF-084 and by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientists (B), No. 21740392, 2009.

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