


Experiment title:

XAS study of arsenic in glaucocerinite, a hydrated sulphate of the hydrotalcite-like group of minerals

Experiment
number:

08-01-745

Beamline:

BM-08

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Shifts:
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Report:

Introduction

The aim of this experiment was to investigate the chemical and structural state of As in both natural and synthetic As-bearing glaucocerinite samples $[(\text{Zn,Cu})_5\text{Al}_3(\text{OH})_{16}(\text{SO}_4)_{1.5} \cdot 9\text{H}_2\text{O}]$ by X-ray Absorption Spectroscopy. In particular the purpose of this short preliminary test at the GILDA beamline was to examine the possibility to acquire meaningful As spectra; in fact, since the mineral glaucocerinite contains very high Zn concentrations, the strong fluorescence Zn peak would rapidly lead to detector saturation, preventing acquisition of the As peak. Expedients to avoid detector saturation caused by Zn, and still obtain a good As signal, needed to be tested.

Materials for this preliminary experiment included: 1) a standard of As_2O_5 from GILDA; 2) a natural crystalline As-bearing glaucocerinite from Baccu Locci mine (Sardinia); 3) a natural amorphous As-bearing phase (likely amorphous glaucocerinite) from Baccu Locci mine (Sardinia). Table 1 reports Zn and As concentrations for the two natural samples, and the name used for the experiment at the beamline.

Table 1. Analysed samples description

Material	Sample name	Zn (wt. %)	As (wt. %)
Natural crystalline As-bearing glaucocerinite	Glaucocerinite1 Glaucocerinite1b	23	1.5
Natural amorphous As-bearing glaucocerinite	Glaucocerinite2	23	2.7

Experiment

Samples for XAS were prepared at the beamline weighing the amount of natural glaucocerinite expected to give the optimal absorbance (~ 23 mg). This amount was then mixed with ~ 50 mg of cellulose and prepared as a pressed pellet. A second pellet was prepared for the crystalline sample (labelled as Glaucocerinite1b) after the first acquisitions, because of the low homogeneity of the first pellet prepared (Glaucocerinite1). The spectra were collected at the As K edge (11867 eV). Acquisition was attempted both in transmission and in fluorescence geometries with a photodiode or the 13-element fluorescence detector. The Figure 1 reports the absorption coefficient measured in transmission geometry ($\mu = \log(I_0/I_t)$) which is too poor to be used. A test of fluorescence acquisition with a photodiode gave too noisy data. The best results were obtained using the multidetector in fluorescence geometry (Fig. 2). To avoid detector saturation, attenuation of the Zn signal needed to be achieved. For this reason the detector was positioned as farthest as possible from the sample. Therefore As signal attenuation and a significant instrumental noise was expected.

Nevertheless, as illustrated in detail ahead, a good quality of As signal was obtained, thanks to the significant As concentration in the samples. Because of time limitation, spectra were acquired at room temperature in order to speed up sample handling; this attenuates the structural signal due to thermal noise. Scans were repeated respectively once for Glaucocerinite1, 4 times for Glaucocerinite1b (Glaucocerinite1b-0101, 0102, 0103, 0104), and 3 times for Glaucocerinite2 (Glaucocerinite2-0101, 0102, 0103). Each scan took about 2 hours.

Results

Upon inspection of the raw data, it appears that in several spectra there is one or more significant background jump. This results from the fact that, at the time of the experiment, ring refilling was performed frequently (topping-up mode). In fluorescence acquisition normalization with respect to I_0 cannot remove the step(s) due to re-injection, probably owing to modification in the optics and/or flux background. Only one scan for each sample resulted jump-free, and they have been used in this preliminary analysis. Data collection across injection should be avoided in the next experiments as resulting in a waste of time.

A detailed interpretation of the results is currently under way. However, from a first inspection, it can be said that the quality of some spectra is quite good (Figures 3 and 4), especially considering that they were acquired at room temperature; in this sense, the experiment can be regarded as successful, and gives useful indications for continuation of the study. Investigation of the structural state of arsenic in this type of material by means of XAS appears to be feasible, provided that the used material (samples and standards) has an As concentration at least of the same order of magnitude (~ 1 wt. %) of the samples tested in this experiment. A higher quality of spectra and the possibility to enhance the next neighbour shell signal is expected from collection at liquid nitrogen temperature.

