

**Experiment title:**

XAS study of arsenic incorporation in hydrotalcite-like sulphates

Experiment**number:**

08-01-773

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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 members of the hydrotalcite group of minerals. These minerals, and their synthetic counterparts, have remarkable technological properties as catalysts and ionic exchangers. The phases of specific interest here are glaucocerinite, $(\text{Zn,Cu})_5\text{Al}_3(\text{OH})_{16}(\text{SO}_4)_{1.5}\cdot 9\text{H}_2\text{O}$, and similar sulphates (zincowoodwardite), found as secondary minerals at some mine sites. It was shown that they can contain As up to several units % wt., and therefore can act as controls of the mobility of this dangerous contaminant. A first hypothesis is that As is present as oxyanion (most probably as arsenate) in substitution of $(\text{SO}_4)^{2-}$ in the interstitial anionic layer; a second hypothesis is that As is adsorbed onto specific surface sites of the brucite-like octahedral layer. Clarification of these aspects will be of great importance to better understand the environmental significance of glaucocerinite and similar phases at mine sites, their potential applicability in remediation tasks, and to extend our knowledge of the remarkable properties of these compounds.

Experiment

A total of 11 samples (4 natural and 7 synthetic) were analyzed by X-ray absorption spectroscopy at the As K edge (11867 eV). Natural samples had been collected in the Baccu Locci mine area (Sardinia, Italy). Table 1 reports their composition. The spectra of a number of standard compounds (As_2O_3 , As_2O_5 , Cu_3AsS_4) were also acquired. Both samples and standards were prepared at the beamline weighing the amount expected to give the optimal absorbance (~ 10-25 mg depending on the material). This amount was then mixed with ~ 50 mg of cellulose and prepared as a pressed pellet. Acquisition was attempted both in transmission and in fluorescence geometries with a photodiode or a 13-element fluorescence detector. For natural samples, and for synthetic H3-1, H3-3, SG-10, the edge jump in the transmission spectrum was too weak, suggesting a low quality of the spectrum: for these samples, the fluorescence spectra were considered. 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 samples. 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. To achieve a better signal to noise ratio, the chamber was cooled with liquid nitrogen down to about

85° K. For each sample, at least two spectra were acquired and averaged to improve counting statistics.

Table 1

| Sample | Origin | Mineralogy (XRD) | Chemical formula |
|------------|-----------|---|---|
| Glauco1b | natural | glaucozerinite | $(\text{Zn}+\text{Cu})_6\text{Al}_3(\text{SO}_4(1.5)+\text{AsO}_4(0.28))_{1.79}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| Glauco2-6 | natural | zincowoodwardite (+ quartz, plumbojarosite) | $(\text{Zn}+\text{Cu})_{5.6}\text{Al}_3(\text{SO}_4(1.3)+\text{AsO}_4(0.15))_{1.46}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| Glauco2 | natural | zincowoodwardite | $(\text{Zn}+\text{Cu})_{6.8}\text{Al}_3(\text{SO}_4(1.35)+\text{AsO}_4(0.56))_{1.92}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| Glauco 2-7 | natural | zincowoodwardite | $(\text{Zn}+\text{Cu})_{6.5}\text{Al}_3(\text{SO}_4(0.38)+\text{AsO}_4(0.19))_{0.58}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| H2A | synthetic | honessite | $\text{Ni}_6\text{Fe}_{2.4}(\text{SO}_4(0.22)\text{AsO}_4(0.76))_{0.98}(\text{OH})_n\cdot m(\text{H}_2\text{O})$ |
| H3-1 | synthetic | honessite | $\text{Ni}_6\text{Fe}_{1.7}(\text{SO}_4(0.7)\text{AsO}_4(0.13))_{0.83}(\text{OH})_n\cdot m(\text{H}_2\text{O})$ |
| H3-3 | synthetic | honessite | $\text{Ni}_6\text{Fe}_{1.85}(\text{SO}_4(0.63)\text{AsO}_4(0.46))_{1.08}(\text{OH})_n\cdot m(\text{H}_2\text{O})$ |
| H3-4 | synthetic | As-honessite | $\text{Ni}_6\text{Fe}_{3.3}(\text{AsO}_4)_{1.21}(\text{OH})_n\cdot m(\text{H}_2\text{O})$ |
| SGA-13 | synthetic | zincowoodwardite | $(\text{Zn})_{8.4}\text{Al}_3(\text{SO}_4(0.36)+\text{AsO}_4(1.23))_{1.59}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| SGA-6 | synthetic | glaucozerinite (?) | $(\text{Zn})_{8.4}\text{Al}_3(\text{SO}_4(0.36)+\text{AsO}_4(1.23))_{1.59}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |
| SG-10 | synthetic | zincowoodwardite | $(\text{Zn})_{8.3}\text{Al}_3(\text{SO}_4(1.33)+\text{AsO}_4(0.43))_{1.76}(\text{OH})_n\cdot m\text{H}_2\text{O}$ |

Results

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. The most striking feature is the presence, in all natural samples, of a double peak in the edge region (Fig. 1).

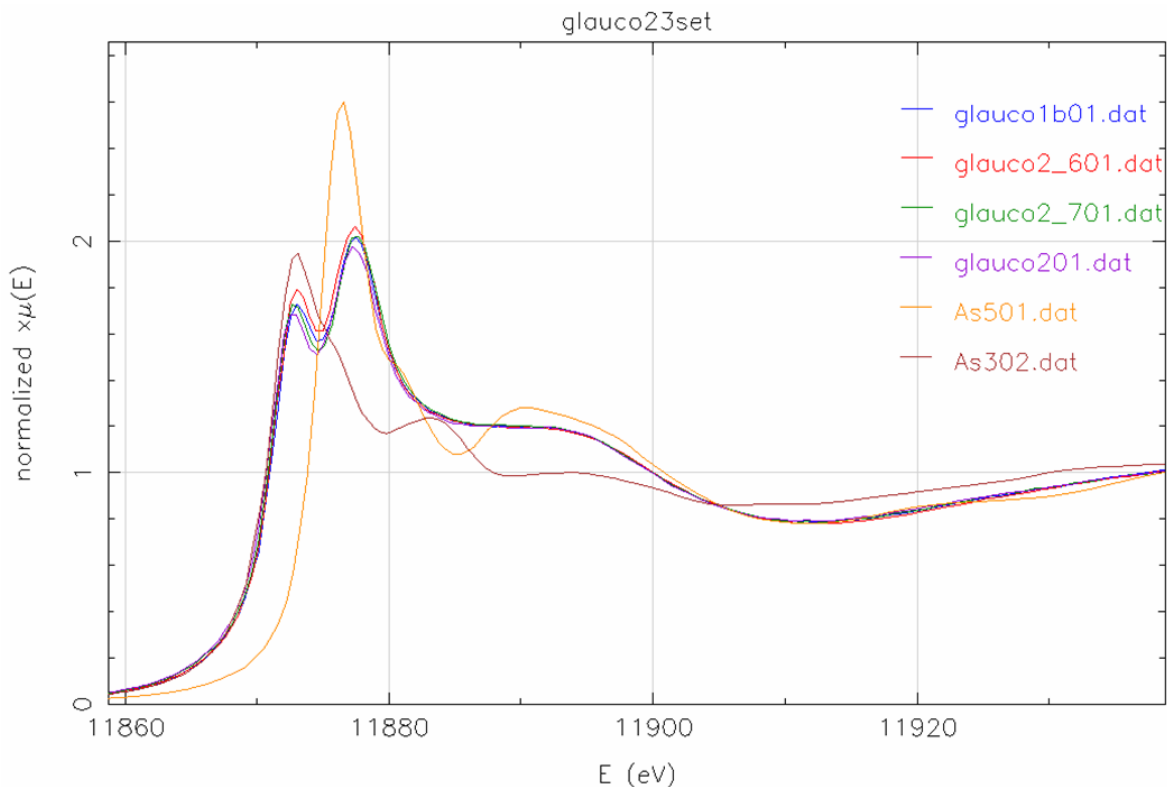


Figure 1: Natural samples X-ray absorption spectra at the As K edge (11867 eV).

By comparison with reference compound spectra, this double peak suggests the occurrence of As in two distinct valence states, III and V. This unexpected finding is very important for a correct modelization of the geochemical behaviour of As in the Bacu Locci system. The synthetic samples (in agreement with synthesis conditions) show evidence of As (V) only (Fig. 2 – only two samples shown for clarity).

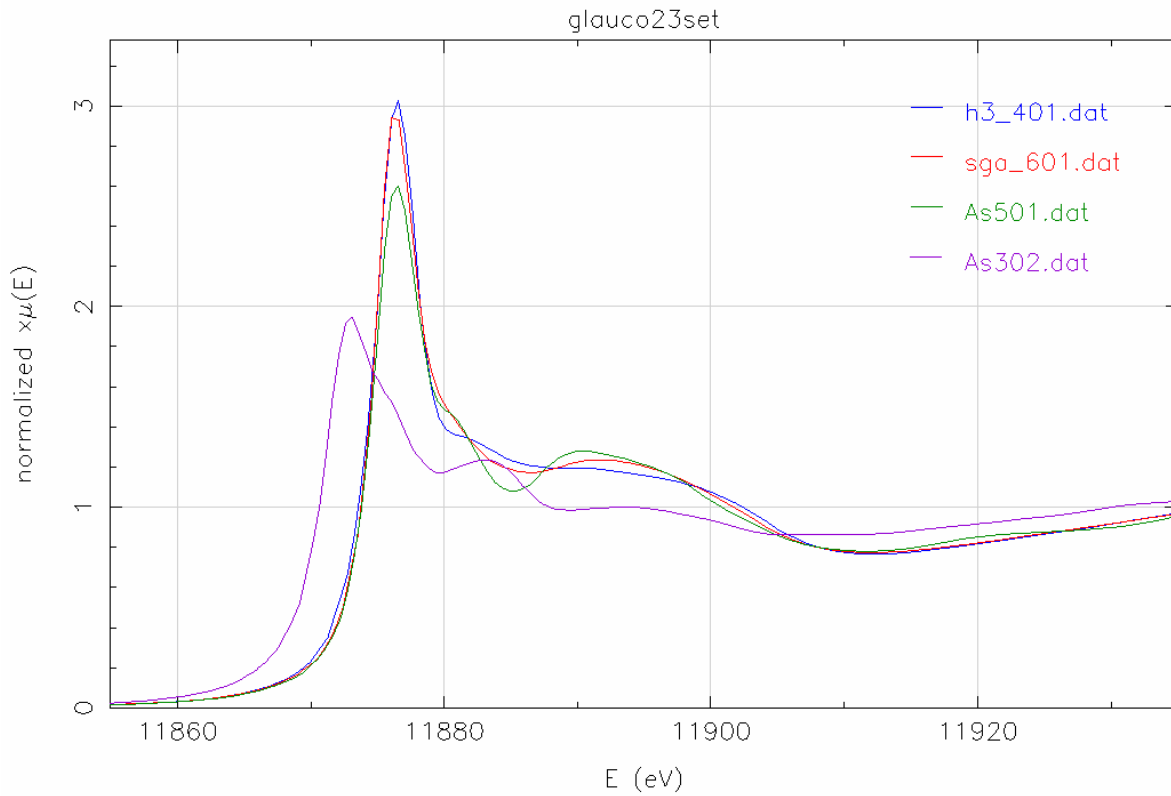


Figure 2: Synthetic samples X-ray absorption spectra at the As K edge (11867 eV).