





**Experiment title:** Structural studies of the X-phase during the process of light induced alteration of arsenic sulfide ( $\text{As}_4\text{S}_4$ ) polymorphs to pararealgar

**Experiment number:**  
08-02-198

**Beamline:**

**Date of experiment:**

from: 15-7-00 to: 17-7-00

**Date of report:**

30-8-00

**Shifts:**

6

**Local contact(s):**

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*Received at ESRF:*

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## Report:

The red mineral realgar ( $\text{As}_4\text{S}_4$ ) as well as the polymorph  $\beta$ -phase ( $\beta\text{-As}_4\text{S}_4$ ) undergoes a change in colour and molecular structure under light exposure, producing pararealgar (yellow). As realgar is well known to be used as red pigment during Renaissance, it is important to characterise such transformation, especially in view of the fact that the presence of pararealgar in some Renaissance valuable painting has already been reported in the literature (Corbeil & Helwig, 1995).

During the light induced transformation from realgar (or  $\beta$ -phase) to pararealgar a precursor is formed, called  $\chi$ -phase, (Douglas et al., 1992; Bonazzi et al., 1996; Trentelman et al., 1996) whose structure is presently unknown.

Zoppi (1999) performed a detailed powder X-ray Diffraction (PXRD) study on the light induced alteration of  $\text{As}_4\text{S}_4$  by means of a laboratory source. However, due to severe peak overlap no information could be extracted on the structure of the  $\chi$ -phase. Moreover several other problems, related to the experimental conditions used, added complexity to the matter. In particular, noticeable peak broadening was observed during the transformation, which was possibly due to stratification of the sample under study (i.e. the uppermost portion of powder was more irradiated than the lower layers) or to anisotropic peak broadening.

In the aim of obtaining higher resolution data on this transformation, we performed powder XRD experiments at the GILDA beamline. The samples were prepared as finely ground powder in 200 mm thick glassy capillary in order to get a homogeneous light exposure throughout all the sample. Two set of experiments were performed, starting from realgar and from the  $\beta$ -phase. Each sample has been illuminated by a 150 W halogen lamp equipped with optical fibres and filtered by a 550 nm long-wavelength pass filter. After each illumination, XRD powder spectra were recorded by means of a image plate with an X-ray beam wavelength of 0.8822 Å. The X-ray wavelength has been calibrated against a  $\text{LaB}_6$  standard. Thanks to the high resolution of the apparatus used we were able to separate some of the peaks of the phases involved in the transformation.

The experimental data are now under examination.

References:

- Bonazzi P., Menchetti S., Pratesi G., Muniz-miranda M., Sbrana G. (1996) light-induced variations in realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub>: X-ray diffraction and Raman studies, *Amer. Mineral.*, **81**, 874–880.
- Corbeil M.C., Helwig K., (1995) An occurrence of pararealgar as an original or altered artist's pigment. *Stud. Conserv.*, **40**, 133–138
- Douglass D.L., Shing C., Wang G. (1992) The light induced alteration of realgar to pararealgar. *Amer. Mineral.*, **77**, 1266–1274.
- Trentelman K., Stodulsky L., Wang G. (1992) Characterisation of pararealgar and other light-induced transformation products from realgar by Raman microspectroscopy. *Anal. Chem.*, **68**, 1755–1761.
- Zoppi M. (1998) Alterazione indotta dalla luce sul minerale realgar: un'applicazione del metodo Rietveld. Tesi di laurea, Dipartimento di Scienze della Terra, Università di Firenze.

