

## Experiment Report Form



	<b>Experiment title:</b> From pyrite ores to drinking water: changes in Tl speciation by XAS techniques. A case study from Northern Tuscany, Italy.	<b>Experiment number:</b> 08-01-1016
<b>Beamline:</b>	<b>Date of experiment:</b> from: 13/07/2016 to: 18/07/2016	<b>Date of report:</b> 07/06/2016
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### Report:

X-ray Absorption Spectroscopy (XAS) measurements at the Tl- $L_3$  edge (12658 eV) were performed at the LISA beamline (BM-08, d'Acapito et al., 2016) at the European Synchrotron Radiation Facility (ESRF, Grenoble – France). Spectra were acquired in the energy range 12458-13206 eV. In order to reduce the thermal damping of the signal and to prevent possible beam-induced redox reactions, all samples were measured at 80 K. Spectra were collected in both fluorescence and transmission mode. A Se (Se  $K$ -edge=12657.8 eV) reference was placed before a third ionization chamber, allowing to acquire a spectrum simultaneously with each measurement on the samples and thus accurately calibrate the energy.

Studied samples were:

- i) a series of rust scales samples from different segments of the aqueduct pipeline serving the village of Valdicastello and the town of Pietrasanta, northern Tuscany, Italy. The water leachate, the residual solid fraction, and the salts obtained evaporating the leachate were also measured.
- ii) a sample of the solid deposit coming from the *Molini di Sant'Anna* water spring (smsa).
- iii) two natural pyrite samples from ores of the southern Apuan Alps and a protochabournéite standard.
- iv) a sample of Tl-bearing alum-K.

Results on set of samples i) have already been published (Biagioni et al., 2017). Here is the abstract:

*Following the detection of a severe thallium contamination of the drinkable water from the public distribution system of Valdicastello Carducci-Pietrasanta (northern Tuscany, Italy), and the identification of the source of contamination in the Molini di Sant'Anna spring (average Tl content  $\approx 15 \mu\text{g L}^{-1}$ ), the replacement of the contaminated water with a virtually Tl-free one ( $\text{Tl} < 0.10 \mu\text{g L}^{-1}$ ) caused*

*an increase in Tl concentration in the drinkable water. This suggested that the pipeline interior had become a secondary source of Tl contamination, promoting its mineralogical and geochemical study. Rust scales samples taken from several pipeline segments, as well as leaching products obtained from these samples, were investigated through scanning electron microscopy, X-ray fluorescence chemical analyses, inductively coupled plasma – mass spectrometry, X-ray diffraction, and X-ray absorption spectroscopy. Thallium-rich rust scales (up to 5.3 wt% Tl) have been found only in pipeline samples taken downstream the water treatment plant, whereas the sample taken upstream contains much less Tl ( $\sim 90 \mu\text{g g}^{-1}$ ). The Tl-rich nature of such scales is related to the occurrence of nano- and micro-spherules of  $\text{Tl}_2\text{O}_3$  and less abundant nanocrystalline  $\mu\text{m}$ -sized encrustations of  $\text{TlCl}$ . Leaching experiments on Tl-rich rust scales indicate that a fraction of the available Tl is easily dissolved in tap water; X-ray absorption spectroscopy suggests that monovalent thallium occurs in water equilibrated with the rust scales, probably related to the dissolution of  $\text{TlCl}$  encrustations. Therefore, Tl dissolved as  $\text{Tl}^+$  only in the water from the Molini di Sant'Anna spring was partially removed through oxidative precipitation of  $\text{Tl}_2\text{O}_3$  and precipitation of  $\text{TlCl}$ . This highlights the critical role played by the addition of chlorine-based oxidants in water treatment plants that could favour the deposition of Tl-rich coatings within the pipelines, giving rise to unexpected secondary sources of contamination.*

Samples of set ii), iii) and iv) were measured in fluorescence mode by means of a 12-elements solid state (high purity Germanium) detector. Suitable filters were used for fluorescence measurements in order to attenuate for Fe and As fluorescence emission on sample sets ii) and iii): these samples, bearing significant As amounts, showed indeed strong As fluorescence emission ( $K\alpha_1 = 10543 \text{ eV}$ ) which almost superimposes on Tl emission line ( $L\alpha_1 = 10269 \text{ eV}$ ). Spectra were then collected with a Ga filter (K-edge =  $10367 \text{ eV}$ ) associated with a  $40 \mu\text{m}$  Al filter. The Ga filter was prepared by depositing  $\text{Ga}_2\text{O}_3$  on various layers of teflon filters to obtain a thickness equivalent to  $80 \mu\text{m}$  of  $\text{Ga}_2\text{O}_3$  which should absorb  $\sim 80\%$  of fluorescence emission above Ga K-edge. A minimum of ten spectra was collected for each sample.

All the samples of sets ii), iii) and iv) show single absorption peaks in the XANES region, typical of monovalent Tl.

The EXAFS of sample smsa indicates first-shell coordination corresponding to a highly coordinated Tl(I)-O site; it was not possible to observe contributions from coordination shells higher than the first.

EXAFS fit results on Pyrite samples indicate that Tl in the analysed pyrite samples has a first coordination shell constituted by S atoms with Tl-S distances typical of Tl with low coordination number.

Results on sample of set iv) are in agreement with the presence of Tl at the K site of Alum-(K).

All the assigned shifts were used during the experiment and it was possible to collect a big amount of data. Despite the low Tl concentration on many samples and the difficult measurement conditions, namely the overlap of As  $K\alpha_1$  and Tl  $L\alpha_1$  emission lines, the quality of collected data is very good and it has already helped to get to one of the two main aims of the proposal (“*determination of Tl phases in Fe oxyhydroxides scales lining the drinking water pipes in order to assess Tl availability in drinking waters*”). Data on mineral phases from ores of southern Apuan Alps will be useful in reaching the other aim of the proposal (i.e. determining “*the speciation of Tl in natural pyrite from southern Apuan Alps in order to assess Tl origin and availability in natural deposits*”).

*Biagioni, C., D'Orazio, M., Lepore, G. O., d'Acapito, F., & Vezzoni, S., (2017). Thallium-rich rust scales in drinkable water distribution systems: A case study from northern Tuscany, Italy. Science of the Total Environment, 587, 491-501.*

*d'Acapito, F., Trapananti, A. and Puri, A., (2016). LISA: the Italian CRG beamline for x-ray Absorption Spectroscopy at ESRF. Journal of Physics: Conference Series 712, 012021.*