



	Experiment title: Probing thallium in pyrite using high-resolution X-ray absorption spectroscopy: towards an improved assessment and management of critical-metal georesources	Experiment number: ES 1126
Beamline: BM16	Date of experiment: from: 01/06/2022 to: 07/06/2022	Date of report: 03/09/2023
Shifts: 18	Local contact(s): Mauro Rovezzi	<i>Received at ESRF:</i>
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Report:

Experimental strategy and conditions:

The main objective of this pioneering experiment were to explore thallium redox and structural state in pyrite which is the main host of this important trace metal in nature. This goal has been reached by taking advantage of *i*) the recent HERFD-XAS device for dilute samples at the upgraded FAME-UHD beamline that overcomes the resolution and detection limitations of existing studies, and *ii*) the availability at our disposal of a good collection of representative well-characterized natural Tl-rich pyrite samples from key types of hydrothermal ore deposits.

Experiments were performed at BM16 beamline. XAS spectra were collected at the Tl L₃ edge (~12.66 keV) from pellets of natural mineral powders placed in a liquid He cryostat (10-15 K) to avoid beam-induced damage for redox-sensitive Tl and As and increase the signal-to-noise ratio. The beamline optics incorporated a Si(220) double-crystal monochromator with sagittal focusing (~200×100 μm at the sample), Rh-coated mirror for harmonic rejection, and five Si(555) crystals placed in a Roland circle geometry (Bragg angle 74.11°), enabling a gain by a factor of 4-5 compared to nominal resolution (natural width is 5.6 eV at Tl L₃-edge). HR-XANES and EXAFS spectra were recorded using a Ketec mono-element detector. Acquisition times per sample varied from 4-6 hours (for Tl concentrations of >1000 ppm) to more than half a day (for Tl concentrations of several 100s ppm); the final spectra represent the sum of energy-calibrated individual scans.

Major results:

The use of the HR device greatly improves both energy resolution and signal-to-noise ratio thereby demonstrating both the necessity of such an approach as well as the general feasibility of this study for natural pyrite samples (Fig. 1). However, among them, only the most concentrated ones (700-3000 ppm Tl) could be explored for the XANES part; the signal for less concentrated samples yet remained too noisy even after many hours of acquisition. Similarly, no EXAFS spectra were found to be exploitable for any of the samples, due to the elevated spectral noise. Its exact origin could not be identified during this particular experiment.

Despite these difficulties, decent quality HR-XANES spectra could have been obtained for 4 representative Tl-rich pyrite samples from gold epithermal deposits in Bulgaria and Italy, along with a number of different reference compounds ranging from native Tl and sulfarsenides to oxides and sulfates. The pyrite XANES spectra are all similar among them within the spectral resolution, suggesting a similar Tl environment, at least in rather concentrated samples investigated here. Remarkably, none of the reference compounds matches the pyrite spectra (Fig. 2a). This is an important indication that Tl is present in a “dissolved” (i.e., substitution) state in the pyrite structure and does not form discrete sulfide or sulfarsenide solid phases known in nature.

The XANES spectra of the natural pyrites were compared with those calculated by the FDNMES code using DFT-optimized pyrite structures with Tl alternatively substituting for Fe or S in their respective crystallographic sites (Fig. 2b). Neither of the calculated spectrum matches those of natural pyrite samples. This, yet preliminary, finding indicates that the Tl structural position in pyrite is more complex than a simple

stoichiometric substitution. The Tl environment is very likely to be related to the presence of arsenic with which Tl was found to be positively correlated evidenced by both XRF and LA-ICPMS analyses of our pyrite samples. Work is currently in progress to explore, using DFT calculations, different possible Tl substitution and clustering models with As in the pyrite structure and to compare their theoretical XANES spectra with those recorded in our experiment.

Next steps and broader perspectives:

The logic continuation of this promising project will be to improve the signal-to-noise ratio to allow exploitable spectra acquisition at lower concentration levels (<100 ppm Tl) for natural samples, which will be complemented by synthetic Tl-bearing pyrite samples prepared at controlled laboratory conditions. The synchrotron work will be combined with a careful characterization of both types of samples using micro/nano analytical lab techniques (EPMA, LA-ICPMS, TEM and SEM). Both structural and thermodynamic models will help to establish the Tl speciation and major hydrothermal fluid parameters (T, P, redox, S and As activity, pH) controlling its incorporation in pyrite and its association with other critical metals (e.g., Au). The combined naturalistic, spectroscopic and physical-chemistry approach, being developed in this work, will open the door for studies of various critical metals in pyrite and other major minerals that are the major hosts of their economic resources on Earth.

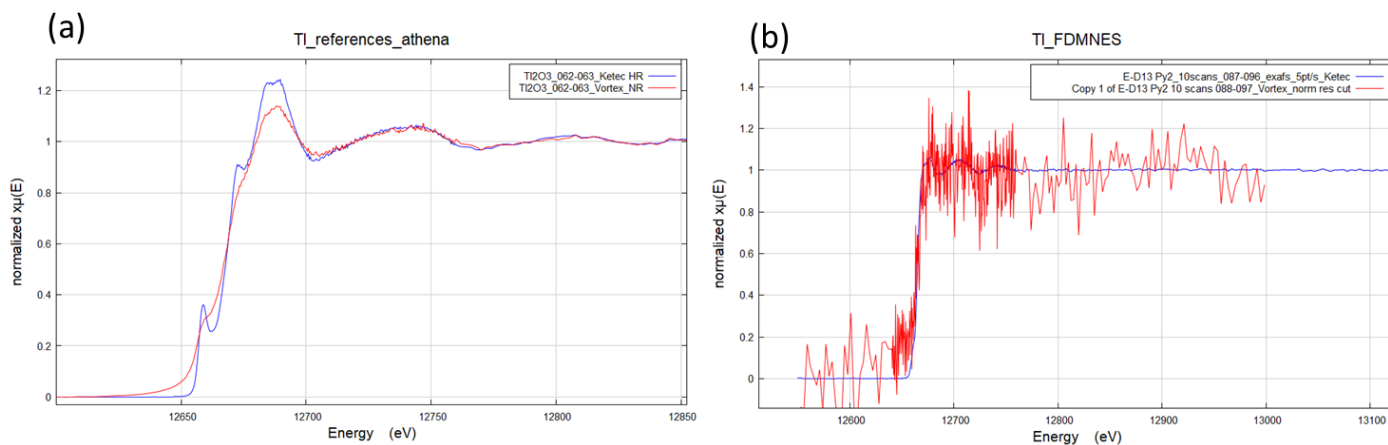


Fig.1 Comparison of Tl K-edge XANES spectra recorded in HR mode (blue curves, HR, Ketec detector) and in classical total fluorescence yield mode (red curves, NR, Vortex detector) for **(a)** a reference compound (Tl_2O_3) and **(b)** a natural pyrite with 1000 ppm Tl. The improvement in resolution in HR mode is just spectacular.

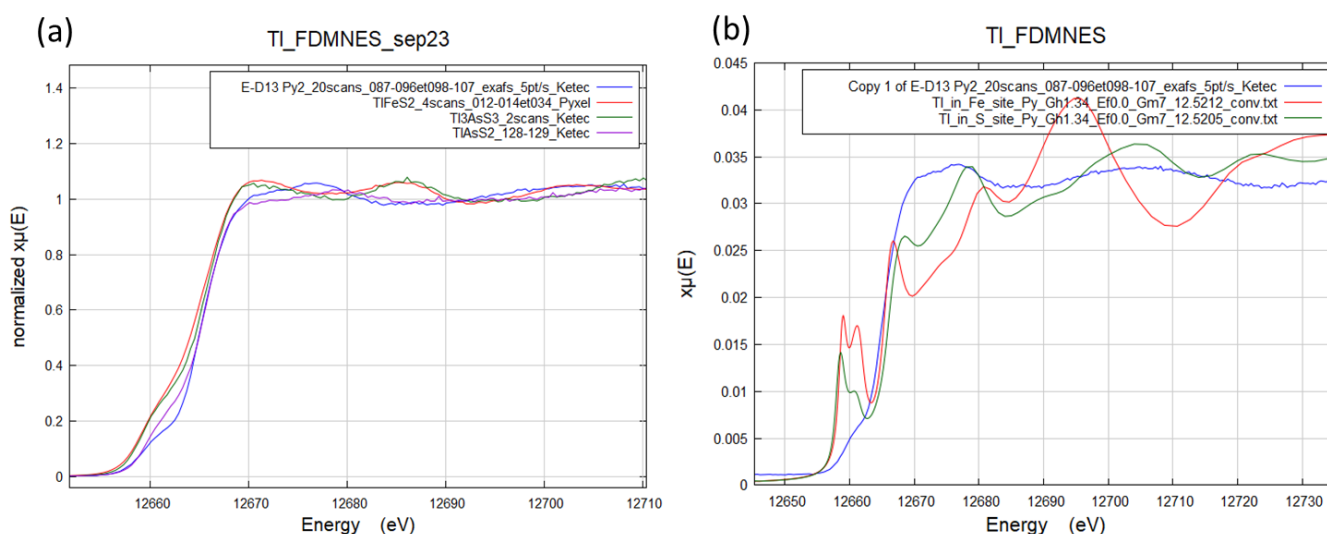


Fig. 2 (a) Comparison of HR-XANES spectra of a representative natural Tl-rich pyrite sample from the Elshitsa epithermal deposit (Bulgaria) and selected common Tl sulfarsenide minerals. The pyrite spectrum is distinctly different, both in pre-edge and main edge features from those and other common Tl minerals. **(b)** Comparison of the same pyrite spectrum with FDMNES-calculated spectra for Tl substitution in the Fe and S sites of the FeS_2 structure. Again, the experimental spectrum is different, suggesting a different (possibly multiple) Tl structural environment in pyrite.