



	Experiment title: Unravelling the thallium speciation in pyrite: which is the role of As? Arsenic speciation by XAS techniques in (Tl, As)-bearing pyrite	Experiment number: 08-01-1046
Beamline: BM08	Date of experiment: from: 19/07/2017 to: 22/07/2017	Date of report: 01/03/2018
Shifts: 8	Local contact(s): Giovanni Orazio Lepore	<i>Received at ESRF:</i>
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Report:

Since only 9 among the 18 requested shifts were accorded for the experiment, our measurement strategy was reviewed accordingly. X-ray Absorption Spectroscopy (XAS) measurements were then performed at both the As-*K* edge (11867 eV) and at the Tl *L*₃ edge (12658 eV) 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 11667-12850 eV for As and 12458-13206 eV for Tl. In order to reduce the thermal damping of the signal and to prevent possible beam-induced redox reactions, all samples were measured in vacuum at 80 K. Spectra were collected in both fluorescence and transmission mode.

Studied samples were:

- i) three natural pyrite samples from ores of the southern Apuan Alps; all pyrite samples were measured at the As *K*-edge and one of them at both As *K*- and at Tl *L*₃-edge,
- ii) one limonite sample, originated from the alteration of pyrite deposits, measured at both As *K* and at Tl *L*₃ edge,
- iii) seven standards of As bearing minerals measured at the As *K*-edge only: skutterudite (CoAs₃), protochabournéite (As³⁺ sulfide), arsenopyrite (FeAsS), adamite (Zn₂AsO₄OH), orpiment (As₂S₃), As₂O₃, As₂O₅ (hydrated).

Samples of set i) and ii) 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 fluorescence emission. For measurements at the Tl *L*₃ edge, given the presence of the As fluorescence emission ($K\alpha_1 = 10543$ eV) which almost superimposes on Tl emission line ($L\alpha_1 = 10269$ eV), spectra were then collected with a Ga filter (K-edge = 10367 eV) associated with a 40 μ m Al filter. The Ga filter was prepared in the laboratories of the “Dipartimento di Scienze della Terra, Università di Pisa” by depositing Ga₂O₃ on various layers of teflon filters to obtain a thickness equivalent to 80 μ m of Ga₂O₃ which should absorb ~ 80% of fluorescence emission above Ga K-edge. A minimum of ten spectra was collected for each sample. Samples of set iii) were measured in transmission mode.

Tl *L*₃ edge results

The XANES spectrum of the pyrite sample (CDR6) indicates that Tl in pyrite is present as Tl(I), showing a single absorption peak, typical of Tl monovalent compounds (*e.g.* Biagioni et al., 2017 and references

therein); EXAFS fit results (see Table 1, together with pyrite samples measured in exp. 08-01-1016) indicate that Tl has a first coordination shell constituted by S atoms with an average Tl-S distance of 3.19(3) Å.

Table 1- EXAFS fit results on pyrite (Tl L3-edge)

	Path	CN	R(Å)	σ^2 (Å ²)
SEN	Tl-S	3(1)	3.12(5)	0.02(1)
	FOR5	Tl-S	2.0(3)	2.97(5)
CDR6	Tl-S	6(1)	3.19(3)	0.037(6)
	Protochabournéite	Tl-S	6(1)	3.25(2)
	Tl-S	3(1)	3.50(2)	//

R is the path length, σ =Debye-Waller factor.

In all the pyrite samples Tl-S distance is typical of Tl with low coordination number (CN), as testified by the comparison with protochabournéite where Tl is present in two sites, bonding 9 S atoms with an average Tl-S distance of ~3.39 Å.

The limonite sample resembles those measured in rust scales from water pipes in exp. 08-01-1016 (Biagioni et al., 2017); despite the high noise prevents us from doing a more accurate analysis, it is possible to say that also in this case Tl is bonded to O with a distance of 2.26(5) Å, typical of Tl(III) in 6-fold coordination.

As K-edge results

Measurements at the As K-edge were, as suggested by the review panel, focused on the XANES region. Preliminary results show that in all the sample there is a high variability in As speciation.

Table 2- Linear combination fit (LCF) of pyrite samples (As K-edge), all As standards were used for the fit

	Protochabournéite (As ³⁺ sulfide)	Arsenopyrite (As ⁻)	Adamite (As ⁵⁺ : arsenate)
SEN	0.78	0.21	0.04
CDR6	0.17	0.82	0.04
FOR	0.12	0.76	0.13

Despite the measurements were taken in vacuum, there was no way to avoid the partial oxidation of As into As⁵⁺ in sample FOR. It is reasonable to think indeed that all the “arsenate” contributions in pyrite highlighted by the LCF are due to the oxidation of As during the preparation of the pellets.

However, since As is always present as both As⁻ and As³⁺, collected data confirm that the hypothesis of a substitution mechanism such $Tl^+ + As^{3+} = 2Fe^{2+}$, the main aim of the experiment, could be possible in the studied systems.

As for the limonite sample, it was possible to notice that As is present only as As(V) and bonded to oxygen. Indeed both the edge position and EXAFS results (As-O=1.70 Å) are compatible with the presence of As as arsenate.

All the assigned shifts were used during the experiment and it was possible to collect a large amount of data. The Tl signal results however extremely attenuated, with the XAS signal dominated by the background (due to the emission of Fe and As).

References

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.