

FAME-BM30B CRG Beam Time - exp
EV 43 - Local contact Isabelle Kieffer

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Experiment report

Introduction

The semi-conductor industry is a fast paced activity sector producing increasingly sophisticated consumer products that are typically short lived. This industry relies heavily on the use of rare metals (e.g. Ga, Tl, In, Sb...). As a consequence, environmental exposure to these metals due to increased mining and/or disposal is becoming a genuine concern. In this context, thallium, a highly sought-after metal for industrial applications, is of particular interest because of serious toxic effects to humans and the environment that exceed those of lead or mercury (e.g. 1, 2). A comprehensive knowledge of the mechanisms governing the environmental mobility of thallium and its associated transformation and ecotoxicity is a pre-requisite to any sound disposal/treatment strategy. The speciation of Tl is of course a major, if not the most important parameter in identifying these mechanisms. However, such determination are complicated by the low concentrations of Tl used in the products, and thus the low levels released in the environment. Then, besides contaminated industrial environments, which are typically not available for a field study, the possibilities of studying the eco-dynamic and eco-toxicological effects of Thallium, under conditions warranting meaningful speciation analyses, are limited to sites that are naturally exposed to "high" concentrations of this metal.

The site at Jas Roux (Hautes Alpes, France) is a site of choice because of its unique mineralogy including rare thallium sulfide minerals like pierrotite ($\text{TlSb}_3\text{As}_2\text{S}_8$) routhierite ($\text{Tl}(\text{Cu},\text{Ag})(\text{Hg},\text{Zn})_2(\text{As},\text{Sb})_2\text{S}_6$) or chabourneite ($(\text{Tl}, \text{Pb})_{23}(\text{Sb},\text{As})_{91}\text{S}_{147}$). These minerals are present on a little cliff from 2170 to 2300 m elevation. Alteration and erosion caused the release of this metal and its transfer to the soil down the primary rock (see figure 1). This unique natural site is the perfect opportunity to monitor speciation changes during the environmental transfer, and especially modification of the redox state from the more mobile Tl(I) to Tl(III) (e.g. 1, 3). Nevertheless, the most valuable lesson to be learnt is the pathway(s) by which thallium is transferred into plant material, i.e., to put it in public health perspective, the mechanism(s) by which this documented toxic element enters the food chain via plants.

Experimental details

A first field experiment was conducted at the Jas Roux site. Re-crystallized minerals formed by weathering of the primary minerals were sampled ('red weathered minerals'). Along two toposequences, 6 spots located at the top (under the cliff), the middle and the bottom (river) were chosen for collecting soil samples (top 10 centimeters) and plant material (see Fig. 1). ICP-MS chemical analyses revealed that the concentration of Tl at the top of the toposequence varies from 85 to 324 ppm (table 1). At the bottom of the toposequence the concentration of Tl was much lower and always below 20 ppm. The transfer from soil to plant was confirmed for all sites, including those with low Tl concentration at the bottom of the toposequence. The Tl content in plants varied as a function of the soil content but also as a function of the plant species. For *Festuca violacea* species the Tl concentration varies from few ppm (dry mass) to 95 ppm in the upper part and from 20 to 304 ppm in the root part. Therefore these samples were on top of the priority list during the XANES session.

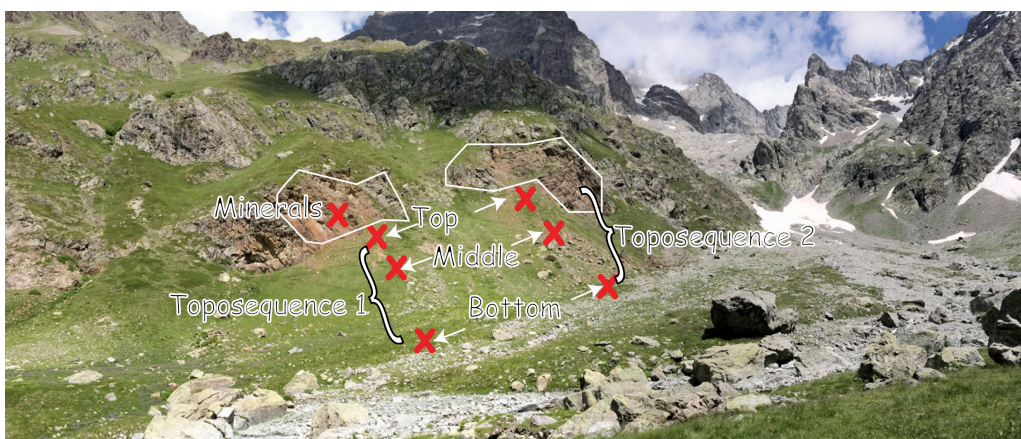


Figure 1: sampling site

Table 1: concentration of Tl and major elements from the studied samples.

Name	Description	Al mg/kg	S mg/kg	Ca mg/kg	Mn mg/kg	Fe mg/kg	Tl mg/kg	Pb mg/kg
Mineral samples (soil and rock from the cliff)								
Soil A1	Soil: top of toposequence 1	8 555	4 330	1 595	2 466	48 790	324	274
Soil A2	Soil: top of toposequence 2	2 756	1 525	1 085	1195	27 320	85,7	19,9
Soil A1-Bottom	Soil: at the bottom of toposequence 1	13 735	Nd.	2 305	741	17 930	16,3	41,0
Minerals from cliff	Red weathered sample Ca, Fe and S rich	570	244 300	63 800	10	627	65	118
Plant samples								
<i>Festuca violacea</i>)	Top of toposequence 2							
	Root part	479		192 782	441	1 438	304,7	7,9
	Upper/Aerial part	53		66 589	0,049	6,6	94,9	0,9
<i>Festuca violacea</i>	Top of toposequence 1							
	Root part	562		396 434	473	5 235	129,5	5,1
	Upper/Aerial part	81		69 371	2 214	2 091	83,3	0,8
<i>Festuca violacea</i>	Bottom of toposequence 2							
	Root part	71		116 203	4 466	2 373	20,3	
	Upper/Aerial part	27		83 397	855	9 896	6,2	

XANES spectra were performed at the thallium LIII edge on the FAME beamline (BM30b) from the 21th to the 28th of January 2014. Due to the low concentrations, the 30 elements fluorescence detector was used. All samples were analyzed at low temperature (Helium cryostat) in order to prevent beam damage and preserve samples. The counting time was extremely high up to 10 hours for the upper part of the plant samples.

We have to mention that not technical problems occurred during the session whether on the Fame beamline or from the ring.

All the samples were brought back to our home institution at the end of this experiment.

Main results

First, reference compounds of thallium with different oxidation states and different atoms in the first atomic shell were analyzed (Figure 1) from sulfide to oxides as well as organo-metallic compounds like thallium-acetate. The energy shift from Tl^{1+} and Tl^{3+} can be quantified from our data. The maxima of the derivative curve indicates that for Tl^{1+} the value varies from 12 666,2 to 12 666,5 eV and that for Tl^{3+} it varies from 12 667,5 to 12 669,7 eV. The case of 'red weathered' minerals that can be considered as one source term of thallium to soil is interesting since the value is at 12 668,6 eV. This intermediate value can be due to a mixture between Tl^{1+} and Tl^{3+} . It is also worth noting that the spectrum of the weathered minerals is very close to the Tl-Jarosite (jarosite = $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) sample (Dutrizac et al, 2005) for which Tl is mainly under Tl^{1+} with possible presence of Tl(III) as iron substitution.

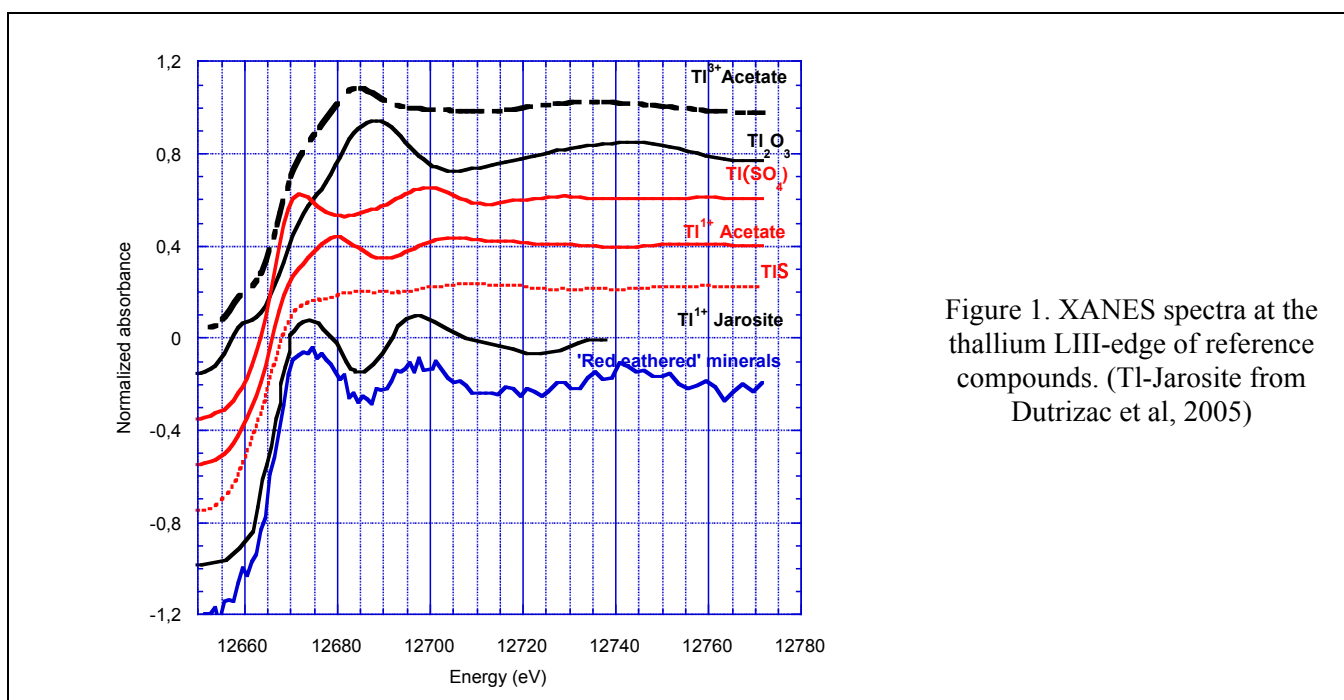


Figure 1. XANES spectra at the thallium LIII-edge of reference compounds. (Tl-Jarosite from Dutrizac et al, 2005)

The session was a great opportunity to better address the detection limit on the Fame beamline for thallium. It is clear that the fluorescence yield for the LIII edge is generally lower than for the K edge and then the detection limit was lower than what was obtained for other elements at the K edge (arsenic for instance). All soil samples at the top of the toposequences were concentrated enough to perform XANES analysis. Even if the matrix was fluorescing due to major elements, the energy of the L emission lines of the Tl were at much higher energy compared to those from the matrix. Then the detector resolution was good enough to avoid contribution of the fluorescence from the matrix in the Tl XANES spectra. So even at 80 ppm it was possible to obtain data with a signal to noise ratio high enough to be considered in the analysis. Unfortunately the soil samples at the bottom of the toposequence (16 ppm) were not concentrated enough as it can be seen on the next figure.

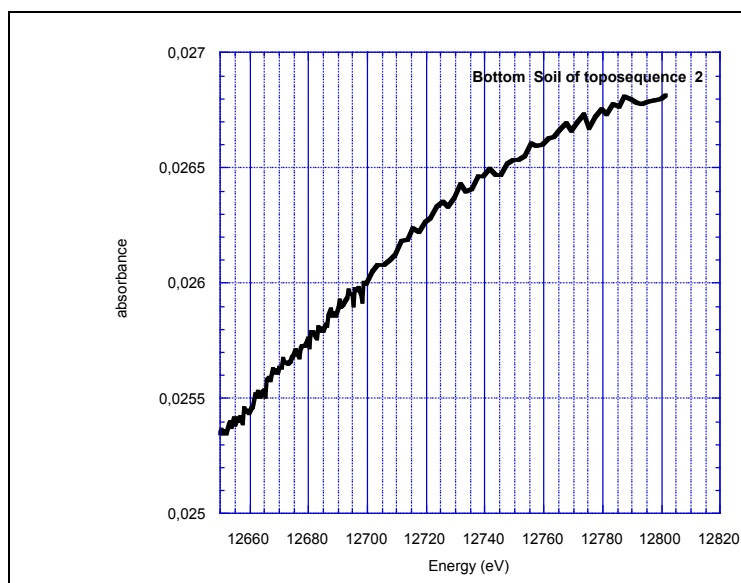


Figure 2: 'XANES' spectrum for the bottom soil

In the case of the plant samples the root part was concentrated enough. However in the case of the leaves and upper part, the signal was much more noisy. Then for the *Festuca* upper part, from the top of the toposequences 1 & 2 (94 and 86 ppm respectively) the counting time was up to 10 hours. For the plant at the bottom, whether for the root (20 ppm) or the upper part (6pp), the signal was too noisy to be useful. We therefore consider that the detection limit for Ti in plant is about 50 ppm \pm 30 %.

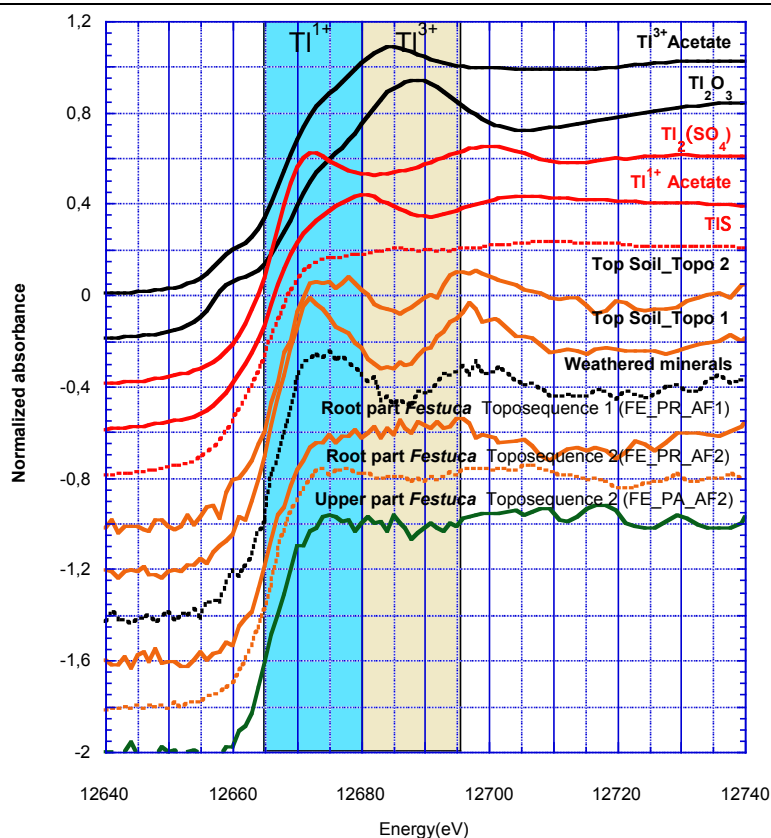


Figure 3 : Comparison of the XANES spectra of reference compounds with Soils and plants.

A rough analysis of the XANES features enables to discriminate between soil and plant XANES spectra (figure 3). In the case of soils as well as weathered minerals we can clearly determine a strong contribution of

Tl¹⁺ redox state. However for the plant XANES spectra whether for the root or the upper part, spectra are more 'featureless'. This first indicates a modification of the thallium speciation from the soil to the plant.

The comparison between the XANES of the two top-soil samples indicates that the position and intensity of the 'white' line is slightly modified (figure 4A). Between both spectra the position and intensity of the main white line (12672 eV) decrease in intensity and is shifted to higher energy from Toposequence 1 to 2. If we consider the spectrum of the 'red weathered' minerals as the main source of thallium for the soils, it is clear that an increase proportion of thallium sulfide (primary rock minerals) can decrease the intensity of the white line (figure 4 C). However an increase proportion of Tl(III) (acetate or Tl₂O₃) will lead to both a shift of the position in energy (Figure 4D) as well as a decrease in intensity. Therefore it is likely that the difference between both soils can be due to different fractions of Tl(I) and Tl(III).

The spectra of the upper and the root parts of the *festuca* samples exhibit less significant differences (Figure 4B).

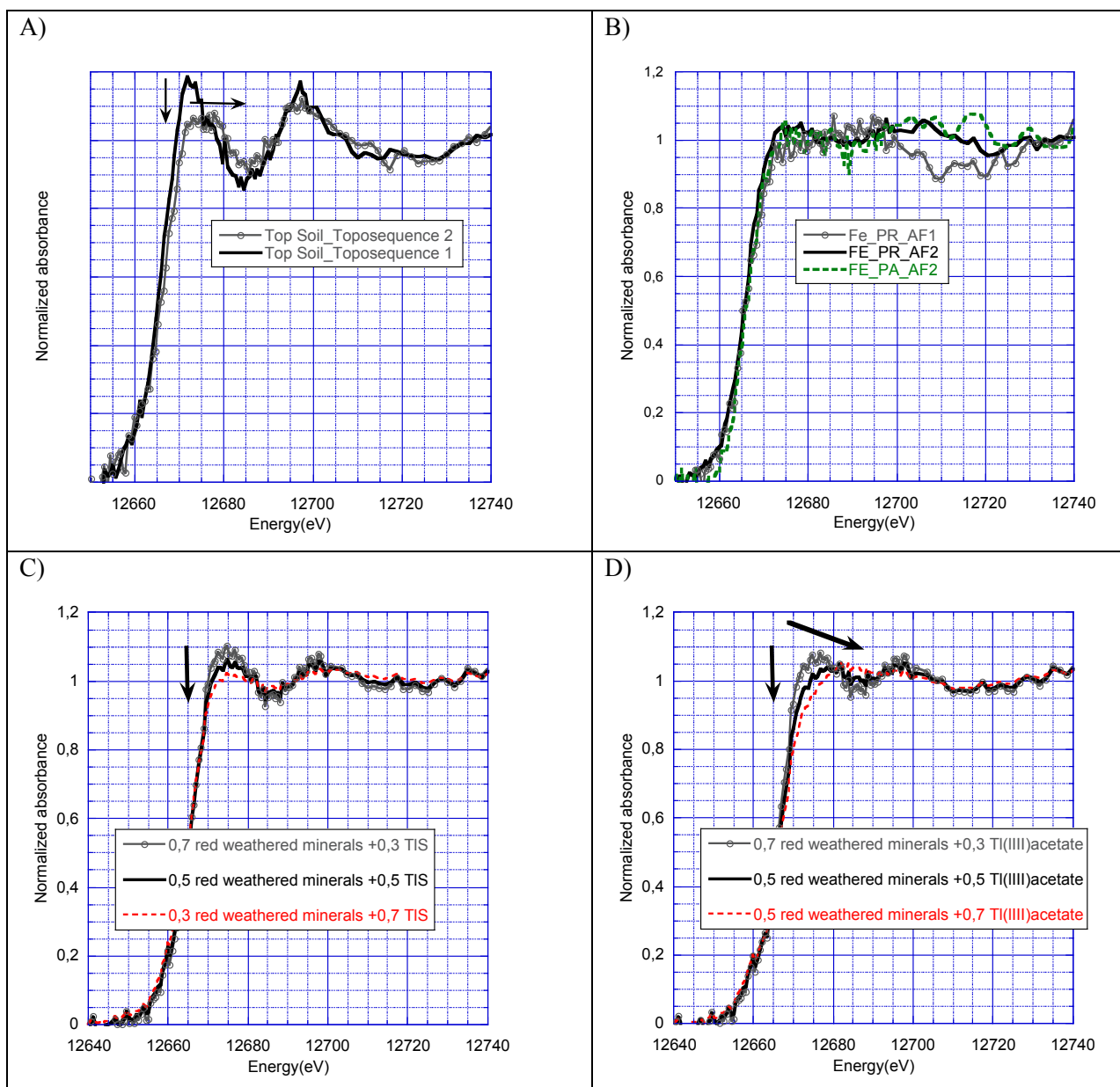


Figure 4: comparison the Tl-LIII edge XANES spectra A) for soil samples B) plant samples C) effect of the proportion of red weathered minerals and TIS, D) or Tl(III) acetate on the XANES spectra.

A more quantitative analysis was performed using linear combination of spectra from reference compounds. The reference compounds database included TlS , Tl^{+1} _jarosite, Tl^{+1} acetate, $\text{Tl}_2(\text{SO}_4)$, Tl_2O_3 , Tl^{3+} acetate, red weathered minerals from the cliff of Jas Roux that can be considered as one source of Tl in soils (XRD results indicated the presence of iron sulfate jarosite). The fits were performed with three components at maximum.

Table 2: Results of the fits using linear combination (values are in proportion)

	TlS	Tl^{+1} jarosite	Red weathered minerals	Tl^{+1} acetate	Tl_2SO_4	Tl_2O_3	Tl^{3+} acetate	Residue
Top Soil _toposequence2	0,00	0,00	0,59	0,00	0,22	0,00	0,19	0,0466
Top Soil _toposequence1	0,00	0,00	0,66	0,00	0,34	0,00	0,00	0,1162
FE_PR_AF1 = Root part <i>Festuca</i> Toposequence 1	0,01	0,00	0,58	0,00	0,00	0,41	0,00	0,0631
FE_PR_AF2 = Root part <i>Festuca</i> Toposequence 2	0,00	0,00	0,43	0,28	0,12	0,00	0,17	0,0431
FE_PA_AF2 = Upper part <i>Festuca</i> Toposequence 2	0,00	0,00	0,39	0,00	0,20	0,00	0,41	0,1477

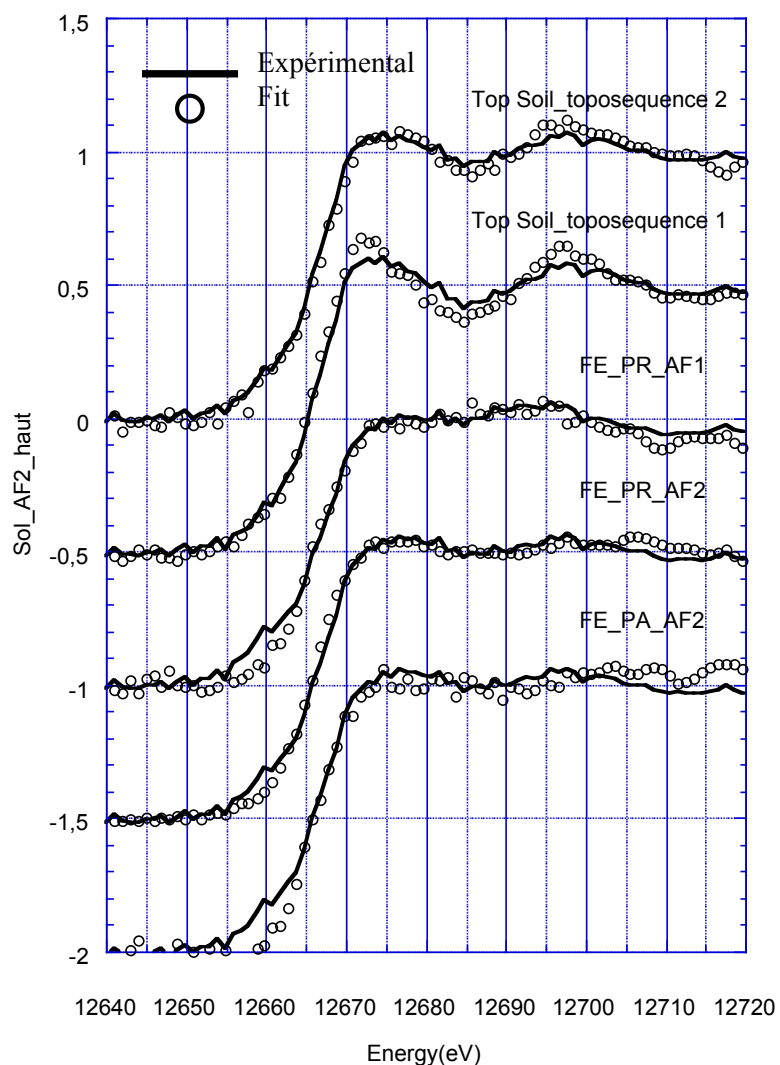


Figure 5 : results of linear combination fits.

The results indicate that the major contribution in soils comes from the weathered minerals. This is not surprising since top soils are just below the little cliff with Tl rich primary minerals. The XANES spectrum of 'red weathered minerals' is very similar to the Tl-Jarosite mineral spectrum. It is worth indicating that the rock weathering leads to the formation of amorphous iron oxyhydroxide but also to jarosite. X-ray diffraction of the 'red' weathered minerals confirmed the presence of jarosite. Then this result suggests that iron phase play an important role in the fixation of thallium. It is also interesting to note that thallium sulfate contribution is significant. This is also not so surprising since primary minerals are composed by thallium sulfide phases that can be transformed to thallium sulfate upon weathering / oxidation. The main difference between both top-soil spectra is the occurrence of a Tl(III) contribution on top of toposequence 2. From our database, it is difficult to conclude whether the Tl(III) phase corresponds to an organometallic or to an other more inorganic phase. A larger set of reference compound in our XANES database would help better defining the exact speciation.

In the case of plants it is worth noting that the contribution of 'red weathered' minerals is still high in the root parts. This clearly indicates that even if we did good plants washings, it is almost impossible to fully remove soil fraction associated to plants. Even in the upper part for which small particles can be transported from the altered cliff and deposited on the leaves. The most interesting result in the case of plant is that a high contribution of Tl(III) species occurs. This oxidation of thallium from soil to plant suggests an active chemical effect of plants or micro-organisms from the rhizosphere. Even if the determination of Tl redox state within plants has been poorly investigated, this result differs from the literature since for instance Nolan et al, 2004, and Scheckel et al 2004, found that thallium was 95 % under the Tl(I) form in the upper and root part of the Tl hyper accumulator *Iberis intermedia*. However bio-oxidation of Tl(I) to Tl(III) has been observed by Twining et al (2003) using fresh water plankton communities.

We also used top-soil spectra as reference compounds to fit plant spectra. However it appeared that they do not contribute statistically to the spectra of root and the inorganic part of the spectra was better adjusted using the weathered minerals.

Our first results are very promising. This is one of **the first times** that the **evolution of thallium speciation** during a soil-plant transfer for non – hyper-accumulating plant was determined. The partial oxidation in plant is of high concern since it has been observed that Tl(III) is 50 000 more toxic than Tl(I) (8).

However since the counting was very high **it was not possible to scan enough samples to obtain more generic conclusion**. More over based on our first results we need to **increase the number of reference compounds** from our database to better determine Thallium speciation.

References

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