



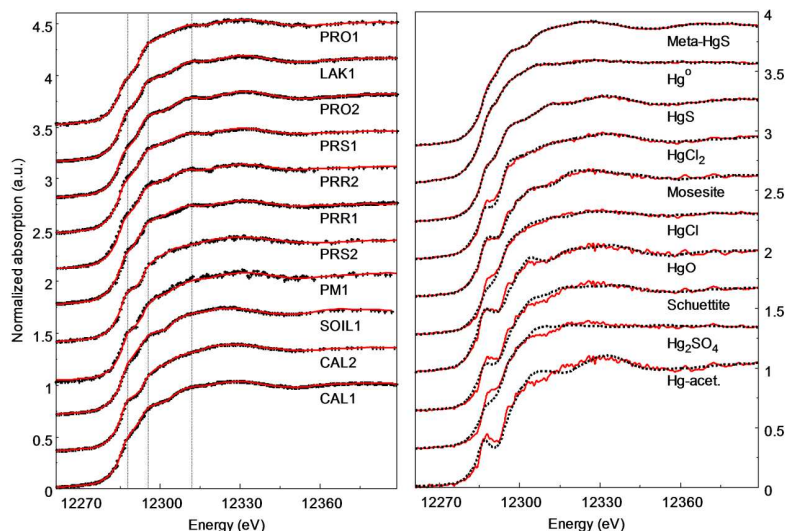
	<b>Experiment title:</b> Speciation of mercury in the mining district of Monte Amiata (Italy)	<b>Experiment number:</b> EC-910
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 23-11-2011 to: 28-11-2011	<b>Date of report:</b> 7-11-2014
<b>Shifts:</b> 15	<b>Local contact(s):</b> Jesus Ivan Da Silva Gonzalez	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Prof. Marco Benvenuti, Earth Science Dept., University of Firenze Dr. Fabrizio Bardelli, Institut des Sciences de la Terre, University of Grenoble Alpes Prof. Pierfranco Lattanzi, Dept. of Chemistry, University of Cagliari Dr. Francesco Di benedetto, Earth Science Dept., University of Firenze Prof. Pilario Costagliola, Earth Science Dept., University of Firenze Dr. Valentina Rimondi, Earth Science Dept., University of Firenze		

## Report:

*In this study, XAS analysis was used to identify Hg speciation in samples collected from the Mt. Amiata Hg district (southern Tuscany, Italy). Mining activity in this area ceased in the 1980s, but abandoned mine wastes continue to release Hg into the downstream environment, where Hg is actively methylated (Rimondi et al., 2012). A previous speciation study was conducted in this area by application of Sequential Chemical Extractions (SCE) (Malferrari et al., 2011); however, investigations combining XAS and SCE have not been previously conducted. In this study, a comprehensive set of samples collected in and around the Mt. Amiata area were analyzed, including 1) mine waste calcines and soils, 2) suspended particulate matter in stream waters, 3) stream sediments, and 4) pre-industrial (pre-dating mining) stream sediments. Speciation of Hg was identified in materials representing both the source of Hg to the environment (calcine and soil in the mining area), and downstream sites with Hg contamination (lake and stream sediment). Moreover, the present-day speciation of Hg in the mining area was evaluated by analysis of suspended particulate matter in stream water, while sediment deposited in pre-industrial times provided the local pre-mining background.*

XAS measurements were conducted at the beamline BM25 (SPLINE) at the Hg L<sub>III</sub>-edge (12284 eV) using pseudo channel-cut type monochromator with two fixed Si(111) crystals and Rh-coated mirrors. Spectra were collected at room temperature in fluorescence yield mode using a 13-element solid state (Si(Li)) detector (e2v Scientific Instruments). Al-filters of suitable thickness were used to attenuate the strong fluorescence signal from the matrix, especially from Fe. Depending on the concentration of Hg, two or three consecutive scans were acquired to improve statistics. Portions of the same samples used for chemical characterization were newly ground for synchrotron analysis in an agate mortar, then mixed and homogenized with cellulose, and finally pressed into a pellet. This procedure should ensure a homogenous distribution of Hg in the analyzed samples. Several Hg reference compounds were chosen on the basis of the knowledge of the likely mineralogy of the studied area. Spectra for these compounds (Fig. 2) were acquired in transmission mode using ionization chambers. The set of reference compounds included natural and synthetic compounds: Hg<sub>2</sub>Cl<sub>2</sub> (calomel), HgCl<sub>2</sub> (Hg(II) chloride), Hg<sub>2</sub>SO<sub>4</sub> (Hg sulphate), HgO (Hg oxide), HgS<sub>red</sub> (cinnabar, hexagonal), HgS<sub>black</sub> (metacinnabar, isometric), Hg<sub>2</sub>NCl<sub>0.5</sub>(SO<sub>4</sub>)<sub>0.3</sub>(MoO<sub>4</sub>)<sub>0.1</sub>(CO<sub>3</sub>)<sub>0.1</sub>·H<sub>2</sub>O (Hg<sub>mos</sub>; mosesite),

and  $\text{Hg}_3(\text{SO}_4)_2$  ( $\text{Hg}_{\text{sch}}$ ; schuetteite). In addition, a  $\text{Hg}^0$  (metallic Hg) reference spectrum, prepared embedding a fine emulsion of elemental Hg in epoxy resin, was simultaneously acquired at each energy scan for accurate energy calibration. Principal Component Analysis (PCA) and Least Combination Fitting (LCF) were applied to the XANES spectra to obtain quantitative information on the sample speciation. PCA allows determining the minimum number of components necessary to reconstruct an experimental spectrum and to identify the best candidates among a set of reference compounds through a procedure called "target transformation" (TT). LCF consists in a weighted linear combination of the reference standards suggested by PCA able to reconstruct a given experimental spectrum. Therefore, provided that the set of reference compounds is sufficiently representative, LCF can reveal the relative amounts of the main compounds present in the samples. The precision of the fractions obtained from LCF was previously estimated to be between 10 and 20% of the total Hg, and strongly depends on the signal to noise ratio and on possible errors in the calibration and normalization procedure. Fractions present in amounts  $<10\%$  were neglected since these amounts were comparable to the error associated with this technique, and because they were found to improve the fits negligibly. PCA and LCF were performed using the SIXPACK and IFEFFIT packages, respectively (Ravel and Newville, 2005; Webb, 2005). PCA indicates that two Hg species were generally responsible for the spectral features, while six components were necessary to satisfactorily reconstruct all samples spectra. TT applied to the set of reference compounds, indicated that the statistical indicators undergo to a steep increase including standard compounds beside the first six ranked by increasing values of the above statistical indicators:  $\text{HgS}_{\text{red}}$ ,  $\text{Hg}^0$ ,  $\text{HgS}_{\text{black}}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgCl}_2$ , and  $\text{Hg}_{\text{mos}}$ . The TT curves are shown in the right panel of **Fig. 1**, superimposed with the corresponding spectra of the standards. LCF results (**Fig. 1** and **Table 1**) indicate that  $\text{Hg}_{\text{sulphides}}$  ( $\text{HgS}_{\text{red}}$  and  $\text{HgS}_{\text{black}}$ ) were the most common Hg compound present in the samples ( $\geq 60\%$  in all samples, with the exception of PRS2), Metallic Hg ( $\text{Hg}^0$ ) is one of the main Hg compounds in both present-day stream sediments (PRS), and recent sediments (PRR), where it accounts for a large fraction of the all Hg compounds, ranging from 22 to 40%. Another important Hg mineral is mosesite, which was found in about half of the samples. The results obtained during the experiment EC-910 suggest that, due to the proximity of Hg mines to the urban center of Abbadia San Salvatore, the influence of other anthropogenic activities is a key factor determining Hg speciation. The results have been published on Chemical Geology (Rimondi et al., 2014).



**Fig. 1.** Left panel: XANES spectra of the samples (points) and LCF curves superimposed (red solid lines). The vertical dashed lines highlight some of the main spectral features. Right panel: XANES spectra of the Hg reference compounds (dotted lines) with Target Transform (TT) curves superimposed (thicker red lines).

Sample	$\text{HgS}_{\text{(red)}}$	$\text{HgS}_{\text{(black)}}$	$\text{Hg}_2\text{Cl}_2$	$\text{HgCl}_2$	$\text{Hg}_{\text{mos}}$	$\text{Hg}^0$
CAL1	40	60	--	--	--	--
CAL2	21	37	--	--	42	--
SOIL1	--	100	--	--	--	--
PRR1	60	--	--	--	--	40
PRR2	67	--	--	--	--	32
PRS1	63	--	--	--	--	37
PRS2	20	--	--	22	36	22
PRO2	100	--	--	--	--	--
PRO1	61	--	39	--	--	--
LAK1	76	24	--	--	--	--
PM1	60	20	--	--	20	--

**Table 1.** Hg fractions derived from LCF.

## References

- Rimondi, V., Bardelli, F., Benvenuti, M., Costagliola, P., Gray, J.E., Lattanzi, P., 2014. Chem. Geo. 380 110–118.  
 Rimondi, V., Gray, J.E., Costagliola, P., Vaselli, O., Lattanzi, P., 2012. Sci. Total Environ. 414, 318–327.  
 Malferrari, D., Brigatti, M.F., Elmi, C., Laurora, A., 2011. Neus Jb Miner. Abh. 188, 65–74.  
 Ravel, B., Newville, M., 2005. J. Synchrotron Radiat. 12, 537–541.  
 Webb, S.M., 2005. Phys. Scr. T115, 1011–1014.