ESRF	**Experiment title:** Investigation of As speciation in biocalcite from travertines of the natural laboratory of Carletti spring system	**Experiment number**: 08-01-1083
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Report:

Introduction and experimental details

The aim of the experiment dealt with the characterisation, in terms of redox speciation and of local structural environment, of arsenic in solid samples pertaining to the so-called Carletti spring system. This system, part of the Bullicame spring area (Viterbo, Italy), consists of a spring pool where water emerges at 57.2 °C, and some pools, at variable distance from the spring. The farthest pool is linked to the spring by a 120 m long channel, where travertine encrustation develops at different decreasing temperature values, and in contact with an abundant presence of biofilm, produced by a variegate and stratified microbioma.

Two kinds of sample were investigated:

- Rock samples, consisting of travertine encrustations, variably interconnected to biofilm. These samples were prepared under a conventional procedure: powders were gently hand milled, then dispersed in cellulose, and finally pressed up to 3.5 – 5 tons, to obtain a self supporting pellet. 27 rock samples were investigated (see Table 1).
- Campaign suspended particulate (SP) samples; these samples were provided as cellulose filters obtained by filtering the waters from the channel at different distances from the spring (i.e. at different equilibration temperatures). Filtration continued until the filter was fully packed by dusts. 6 SP samples were investigated (see Table 1).
- Laboratory SP samples; these samples were prepared as the previous batch, to elucidate kinetic of calcite formation and As trapping at different times on sampled water at spring source (interval 1 hour – 9 days). 7 Laboratory SP samples were investigated (see Table 1).

Experimental investigation proceeded by standard operation of X-ray Absorption Spectroscopy under Fluorescence mode (max. As- content of the order of 300 mg/kg). Samples were put in an evacated chamber, and frozen down to 80 K, to avoid undesired as species interconversion under the beam. A standard reference (i.e. GaAs, was used as reference for energy calibration in a second chamber, located after the first one. No

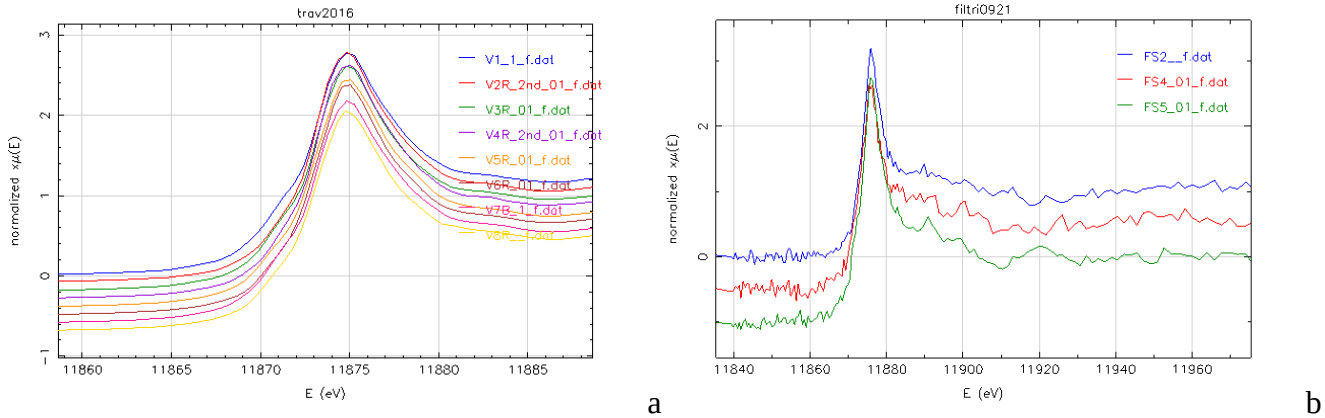
particular experimental criticalities occurred. All the samples were successfully investigated as well as a set of relevant standards. During the experiment, a couple of beam failures occurred, with a total of 2-3 hours of lost beamtime. At the beginning of the experiment, during the set up of the beamline parameters for the experiment, the beam was found misaligned with respect of the front end slits, and the re-alignement, operated in accordance with the staff of the control room, lasted 4 hours. In the whole, we estimate 1 shift of lost beamtime. Nevertheless, we were able, as previously stated, to complete all the planned measurements.

TABLE 1 List of the investigated samples

label	site	description	absorber	type	label	site	description	absorber	type
V1	1	Rock	Pellet	A	**FM2sup**	2	SP	Filter	C
V2R	2	Red rock	Pellet	A	**FM2fon**	2	SP	Filter	C
V3R	3	Red rock	Pellet	A	**FM4**	4	SP	Filter	C
V4R	4	Red rock	Pellet	A	**FM6**	6	SP	Filter	C
V5R	5	Red rock	Pellet	A	**Syn4.1**	4	Artificial encrustation	Pellet	A
V6R	6	Red rock	Pellet	A	**Syn4.2**	4	Artificial encrustation	Pellet	A
V7B	7	Rock	Pellet	A	**Syn4.3**	4	Artificial encrustation	Pellet	A
V8B	8	Rock	Pellet	A	**PS1**	1	Lab SP - tq	Filter	B
V2G	2	Green rock	Pellet	A	**PS2**	1	Lab SP – 1h	Filter	B
V3G	3	Green rock	Pellet	A	**PS3**	1	Lab SP – 2h	Filter	B
V4G	4	Green rock	Pellet	A	**PS4**	1	Lab SP – 1g	Filter	B
V5G	5	Green rock	Pellet	A	**PS5**	1	Lab SP – 2g	Filter	B
V6G	6	Green rock	Pellet	A	**PS6**	1	Lab SP – 9g	Filter	A
V7G	7	Green rock	Pellet	A	**PS7**	1	Lab SP- 9g f	Filter	A
V8G	8	Green rock	Pellet	A	***V3bis***	*3*	*Gessi pareti ext*	Pellet	A
TC2G	2	Green rock	Pellet	A	***V7bis***	*7*	*Gessi pareti ext*	Pellet	A
TC7G	7	Green rock	Pellet	A	***Zit1***		*Sedimento sup. acqua*	Pellet	A
TC2R	2	Green rock	Pellet	A	***Zit2***		*Sedimento sup. acqua*	Pellet	A
TC7B	7	Rock	Pellet	A	***Vulc***		*Vulcanite Vico*	Pellet	A
FS2	2	SP	Filter	B					
FS7	7	SP	Filter	B					

Preliminary view of the obtained results

The whole dataset can be divide into three parts: samples exhibiting an high-quality spectrum, where both XANES and EXAFS provide significant insights (A samples in Table 1, Fig. 1a), samples for which the registration of As was enough to get a noisy but well detectable spectrum (only a noisy edge jump and XANES is in this case available, B samples in Table 1, Fig. 1b) and samples that fell below the minimum detection limit of the technique under the adopted set up (C samples in the Table 1).



a b

Figure 1 – Exemplar spectra of a) A samples (red travertine series) and of b) B samples (campaign filters)

Focussing preliminarly on B and C samples, we noticed that only fully packed filters receive amount of matter, and trapped detectable As. These samples will be the object of a further beamtime request at beamlines focussed on the detection of ultra trace contaminants in the environment.

Coming to the A samples, the largest part of the dataset, they share almost common features:

1) A prevailing +5 redox state; As(III) is however always present (Fig. 2)
2) The absence of further shells beyond the first one

3) A very short As-O distance (of the order of 1.68 Å).

Even if only minor changes are observed within the dataset, these allow to state that the As(V)/As(III) ratio is variable, with some samples slightly enriched in As(III). Also in these As(III) enriched samples As(V) is the main species. What appears preliminarly interesting, is that such travertines are sampled from places in contact with waters where the As speciation changes from a As(III) prevalence, at the pool, up to a As(V) prevalence, at the discharge pool. Only minor effects can be observed in relation to the presence of biofilm.

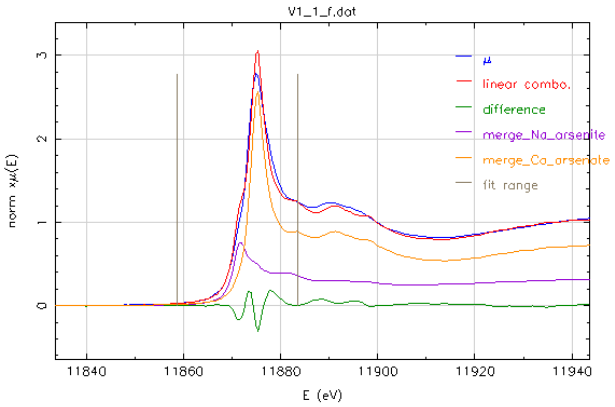


Figure 2 – example of a preliminary linear combination fit of the edge and white line region

Preliminary Conclusions

The preliminary bird's eye consideration of the obtained dataset allow to provide interesting links with the already available infromation on the system. In particular, we do expect that distribution coefficients of arsenic between solid and water samples will be very peculiar, tracing a possible active role of travertine in preferentially sorbing As(V). The role of the biofilm, and related organic matter in such a process, will be explored.