ESRF	**Experiment title:** Study of unsaturated Fe coordination associated to crystalline silica and silica glasses with health relevance	**Experiment number**: CH-3929
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Report:

The present experiment has been realised with the aim of assessing the redox properties and the speciation of Fe, associated to crystalline silica and volcanic silica glasses, in relation to its potential relationship with the human health (risks under occupational exposure) and with the environment. The undertaken study was carried out by X-ray Absorption Spectroscopy (XAS) at the Fe K edge, with focus on the three main regions of the spectrum: pre-edge, XANES and EXAFS.

The two considered case studies were investigated by analysing two distinct sets of samples:

1) samples belonging to the industrial manufacturing of the so-called "artificial stone", i.e. conglomerates of mainly quartz, silicates and carbonates, artificially assembled through epoxy resins;

2) volcanic ashes, sampled after Mt Etna (Sicily, Italy) eruptive events in the period 2012-2014.

The two sets of samples required own experimental set up, and will be separately reported here below.

A) *Artificial stone*

Risks to the human helath by artificial stones under occupational exposure are fostered only when the stones are polished. In this refining procedure, quartz rich particulate is created and suspended in the air. Accordingly, we selected samples of the pristine stone (as reference sample), of the microcrystalline powders obtained from dry polishing, and of the microcrystalline powders obtained from wet polishing. The stone aliquotes were cut in the form of ~2x1.5x0.2 cm parallelepipeds, whereas the loose polishing powders were stabilised as pellets, after opportune mixing with cellulose.

On the whole, 4 complete series (stone / dry powders / wet powders) out of seven available were deeply investigated. The samples exhibited a wide range of Fe-contents, non of which, however, allowing to operate in the Transmission mode. Accordingly, the Fluorescence mode was chosen, involving the use of a multielement Ge detector. All spectra were registered at room temperature, and in air (without the use of a pre-evacuated chamber). The good brilliance of the beamline, in fact, allowed to minimise the peak-to-noise ratio. The use of the multielement Ge detector was also fundamental for the investigation of the stone samples. Although being assembled by very fine microcrystalline powders, in fact, these samples often contain larger crystals (used to confer the "natural" look to the material), so intense Bragg peaks could mask the XAS detection. In this case, Bragg peaks were observed in at maximum two out of the 12 channels of the Fluorescence detector.

Preliminary results can be summarised as follows:

1) apparent changes from the original state (that in the stone samples) are always observed in polishing dusts;
2) at least in one case, the process of change of state is associated to an inlet of additional Fe from sources external to the stone,
3) during the wet polishing a systematic contamination by elemental/metallic Fe is produced: this could be due to the erosion of the surfaces of the polishing media (usually made of hardened steel) (Fig. 1a, b);
4) a frequent change of the redox state of the Fe, i.e. the balance between Fe^0, Fe(II) and Fe(III), is found associated to the different polishing procedures (Fig. 1c);
5) results can be only seldom generalised to all samples, thus confirming the high variability of the physical chemical features of the artificial stone.

According to these results, the experiment can be considered fully successful in highlighting the changes of Fe redox properties and speciation, during the processing of the artificial stone. Further and deeper analyses on the collected data, as well as on new materials from this industrial sector, will allow to ascertain and quantify the observed trends.

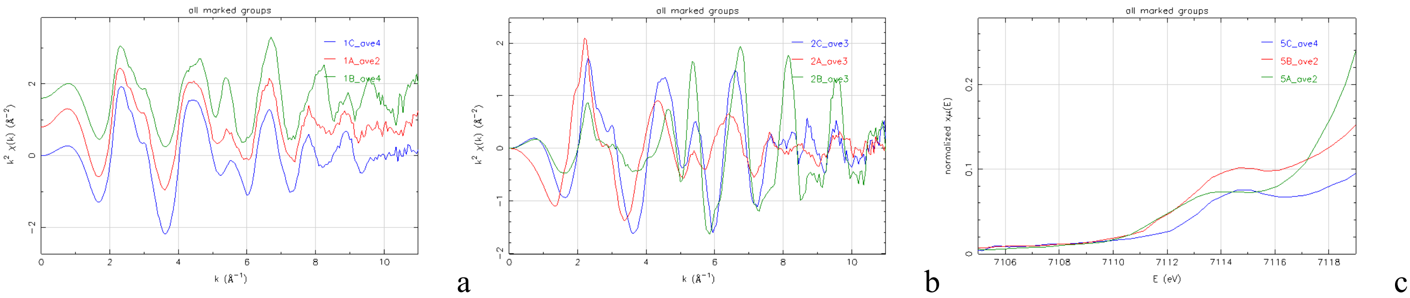

Figure 1 – EXAFS on the "1" (a) and "2" (b) series highlighting the Fe0 contamination in the "b" wet polished samples; change of the redox state of Fe in the pre-edge region of the "5" series (c).

B) *Volcanic ashes*

The samples selected for the experiment belong to different volcanic events, and were collected in a very wide region around the volcano, in the Province and in the urban area of Catania. All samples consists of brown-to-black ashes made of a large amount of glass, associated to variable amounts of crystalline phases, including plagioclases and clinopyroxenes. All samples exhibit a variable particle size, ranging from submillimetric to very fine particles. Laboratory analyses (SEM/EDS + XRF) revealed an average Fe content of ~ 10 wt%, variably distributed between the glassy and the crystalline matrices. Accordingly, all samples were analysed as pressed pellets of the opportune mix between cellulose and volcanic ash. Moreover, the use of the Transmission mode of XAS was allowed, using two ionising chambers before and after the sample. All spectra were registered at room temperature and in air (*vide supra*). Due to the high transmissivity of the pellets, a reference Fe foil were put between the second and a third ionising chambers, in order to allow the precise calibration of the pre-edge energy. This was just qualitative in the case of the artificial stone samples. Concerning the samples, three different kind of samples were provided: raw volcanic ashes, leached ashes (performing a tretament with distilled water) and samples subdivided by granulometry in classes.

Preliminary results can be summarised as follows:

1) there's a general homogeneity of the spectral results; this holds true for pre-edge, XANES and EXAFS regions. In other words, Fe speciation appears as almost constant irrespectively of the source (specific eruption) or of the place (of sampling);
2) all samples contains both Fe(II) and Fe(III) in a complex speciation, where most of the Fe is supposed to enter the glassy phase (Fig. 2a);

3) samples can be divided in two groups: those without changes after leaching or granulometric subdivision, and those exhibiting some (small) change;
4) the observed change mainly refer to the change of the redox balance, i.e. ratio between Fe(II and Fe(III), and only slightly with EXAFS (Fig. 2b, c). Thus, the appearance/disappearance of an additive Fe-bearing phase is attributed of the observed changes.

In comparison with already obtained TEM observations (revelaing the presence of magnesioferrite nanoparticles) and EPR investigations (revealing the presence of diluted Fe(III), magnetic Fe minerals, and superparamagnetic Fe nanoparticles), a comprehensive and quantitative view of the obtained data is in progress, and it will be correlated mainly with the environmental threaths that conspicuous coverage of agricultural soils by volcanic ashes in the region could bring.

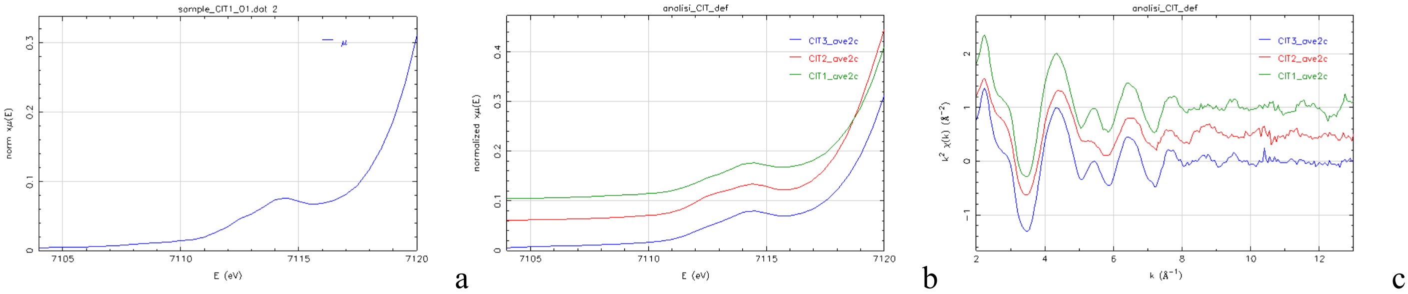

Figure 2 – pre-edge region of an exemplare ash sample (a); comparison of pre-edge (b) and EXAFS (c) spectra of three samples (raw, leached, granulometry subdivided).