

Proposal number of the experiment:

SI-1593

Title of the experiment:

Crystal Chemistry of Fe at the quartz surface

Authors

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Date of measurements at GILDA

18 shifts from December, 5 to December, 11 2007

Beam quality: excellent

no problems during experiments

Beamtime on other beamlines/facilities on the same research

No other beamtime asked/allocated on the same research

Introduction

Quartz and cristobalite, two of the most common crystalline silica polymorphs, induce relevant biological effects, being involved in the production of pulmonary affections (silicosis) and being considered relevant risk factors for lung cancer (**Goldsmith et al., 1986; Amandus et al., 1997; ACGIH, 2006**). As a consequence of this potential toxicity, the two crystalline silica polymorphs were labelled with the A2 (Suspected Human Carcinogen) notation by ACGIH, and their Threshold Limit Value (TLV) in the breathable dusts was lowered to 0.025 mg/m^3 .

In the industrial manufacturing of silica-bearing materials, many mechanical processes determine the breaking of crystals and the formation of new surfaces. These, in turn, are suspected to be the responsible of the pathogenicity of these mineral species. At present, the molecular bases of the silica health effects have not yet been clearly understood (**Fubini et al., 1995**). The mechanical breaking of the crystal structure and the formation of new surfaces can occur simultaneously with the partial poisoning of the fractures themselves by Fe and Al atoms.

The aim of this project is to gain a detailed characterisation of the Fe structural topology at the quartz surface: in particular, the definition of its valence state, number and geometry of coordination. In addition, the second coordination shell will be investigated, in order to understand if Fe is chemically bonded to the silica, or if the poisoning of the surface is only related to absorptive processes. The structural description of the Fe-doped silica surface requires an EXAFS investigation both in conventional and in total reflection modes.

Experiment

The experiment was divided in three parts: a) spectral characterisation of standards (powders), b) characterisation of pure quartz powders and quartz-bearing powders, c) characterisation of specific surfaces of large quartz crystals.

All spectra were collected at the Fe K-edge (7.112 KeV) in Transmission and Fluorescence modes (powders) and Total Reflection geometry (single crystals); fluorescence spectra were detected using a high-purity Ge solid-state detector. Spectra have been collected below the critical angle (0.25 deg at 7.200 KeV) for total external reflection, the sample being placed with the probe beam polarization parallel to the surface. Long runs and repeated spectra were necessary to improve the signal quality, due to the small amount of Fe involved (a partial or full covering of the surface is expected). This necessity was encountered during the spectral acquisition of crystal and of several powders, being nominally pure SiO₂.

The list of the analysed standards is shown in **Table 1**

sample		Sample	
FeO (WUSTITE)	T	FeCl ₃	T
Fe ₂ O ₃ (EMATITE)	T	Fe ₂ (SO ₄) ₃	T
FeC ₂ O ₄	T	Cu ₂ FeSnS ₄ (STANNITE)	T
Fe(OH) ₃ (FERRIDRITE)	T	CoFe ₂ O ₄ (Co-FERRITE)	T
FeOOH (GOETHITE)	T	Na ₂ Fe ₅ Si ₈ O ₂₃ (NASIL)	T
		Li ₂ Fe ₅ Si ₈ O ₂₃ (LISIL)	T

Table 1 – analysed standard samples (T = transmission)

A selection of pure quartz samples (commercial powders and breathable flours), and of quartz/cristobalite-bearing materials, coming from relevant industrial activities of Tuscany, were thus investigated. To reproduce the industrial crushing process, the reagent-grade quartz powders and flours (mean size: < 5 μm) were also analysed after grinding in agate ball mill (15' at 400 rounds-per-minute) alone and added by α-Fe or Fe₂O₃. The list of the analysed samples are shown in **Tables 2** and **3**

sample	raw	ground
Jewellery sands	F	F
Terracotta	T	T
Concrete	F	X
<i>Serena</i> stone	F	X
Inert building materials	F	F

Table 2 – analysed unknown samples (T = transmission; F = fluorescence)

Finally, total reflection spectra were registered on selected (1, 0, 0) and (1, 0, 1) surfaces of Fe-doped quartz crystals. A chemical doping of the selected surfaces was performed, as the raw surface did not show a Fe amount able to allow the registration of reflection XAS spectra. The doping was performed, in agreement with **Waychunas et al. (1999)**, exposing the selected surface to an acidic solution ($2 \cdot 10^{-4}$ M in HCl) of FeCl_3 for three hours. Excellent spectra were thus stored. A list of the single crystal spectra is also reported in **Table 3**.

Quartz standards	raw	Ground	g.+Fe	g.+Fe₂O₃	chem. etched
Commercial pwds.	F	F	X	F	X
Breathable pwds.	F	F	F	X	X
Pale quartz crystal	X	NO	NO	NO	R
Amethyst crystal	F	NO	NO	NO	R

Table 3 – analysed quartz standards samples (F = fluorescence; R = reflection)

A preliminary data analysis is in progress on both the edge (XANES) and extended (EXAFS) regions. The XANES analysis includes comparison with reference compounds and simulation using state-of-the-art software package (FEFF). Quantitative EXAFS data analysis will be performed using XAFS data analysis software (e.g. FEFF and/or GnXAS) and including the analysis of nearest neighbour as well as next nearest neighbour shells taking into account for multiple scattering effects.

Results

The expected results of the present study concern the structural characterisation of Fe chemi- and/or physisorbed at the quartz surface. They can be formally divided into two categories:

- 1) assessment of the local coordination of Fe in the chemical topology of quartz surface, with specific reference to the valence state, coordination number and geometry; assessment of the eventual relationships between Fe and Si in its second coordination shell;
- 2) possible differences of the surface topology as a function of the grinding process, i.e. of the formation of fresh surfaces.

A first overview of the obtained results allowed us to ascertain that different ferrous, ferric and also elemental Fe coordinations are present in the unknown samples, and also differences occurring between raw and ground samples. A systematic re-consideration of the large dataset is still in progress. In addition, single crystal measurements pointed out different Fe speciation for different quartz surfaces. This point, based on the analysis of two spectra only, is particularly relevant to the purposes of the research, and needs to be confirmed and implemented by further investigation by both ReflEXAFS and EPR.

Future Perspectives

The performed experiment allowed us to evidence some peculiarities of the relationships between Fe and quartz in both the pure and “real” industrial samples. These peculiarities sometimes change after a mechanical treatment (without buffering the temperature or adding fluids). These results parallel some recent evidences obtained with EPR spectroscopy in our laboratory. The interpretation of these evidences will constitute in our opinion a good basis for classifying, according to a reactivity

criterion, the risks associated to specific industrial activities that involve silica bearing materials. In order to better understand the differences observed in the obtained data, we plan to submit a new application for beamtime at BM08/ESRF. This new experiment should be dedicated to an exhaustive ReflEXAFS study of Fe interacting with not only the (1, 0, 0) and (1, 0, 1) quartz surfaces, but also the (1, 1, 1) surface.

References

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Publications

Conferences

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Health effects of crystalline silica: a crystal chemical study of quartz surfaces.
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