| ESRF | **Experiment title:** Valence state and redox properties of Fe in quartz | **Experiment number**: 08-01-848 |
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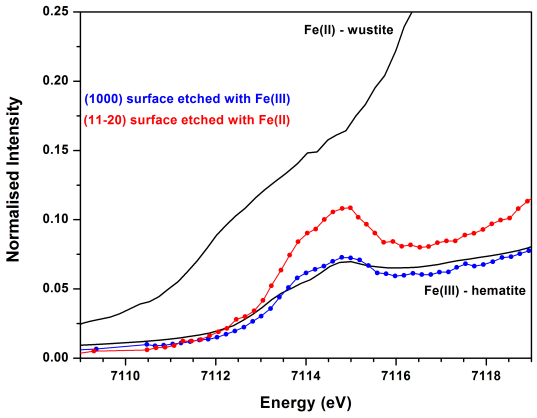
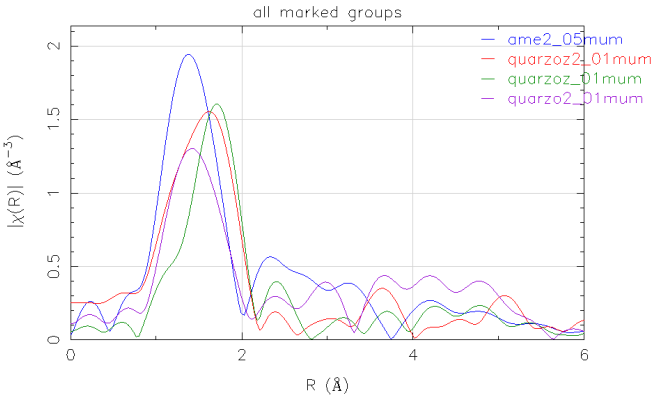
**Report:**

In order to understand how quartz dusts are modified/interact during thermo-mechanical processing, three different quartz surfaces (1000, 11-20, 0001) were etched by acidic solutions of Fe(II) and Fe(III). The raw and etched surfaces were investigated through grazing incidence XAS spectroscopy. This particular experimental set up, in fact, allowed us to obtain information relative to the first atomic layers. This investigation was paralleled by the sample characterisation performed using AFM, able to discriminate changes in surface roughness and cluster deposition.
Preliminary spectral interpretation allowed us to point out that:

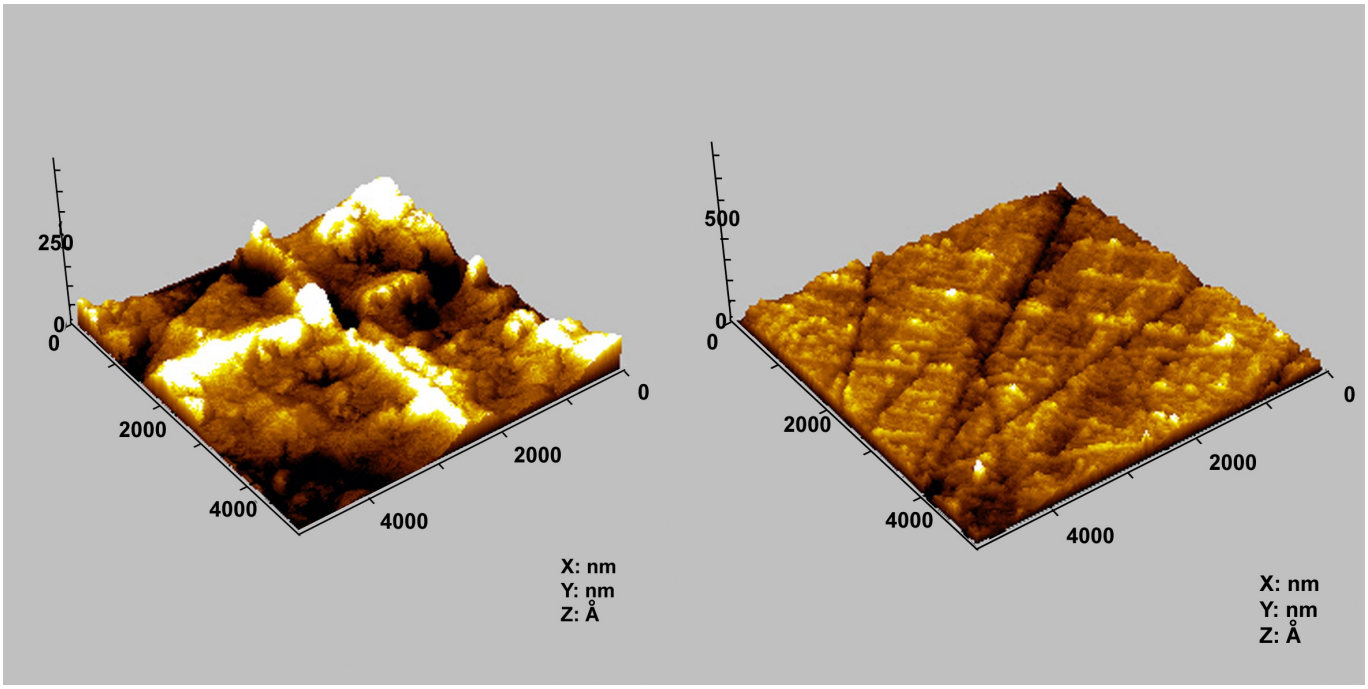
1) unetched surfaces do not exhibit Fe content (in agreement with the poor content expected for intrinsic Fe in natural quartz crystals
2) after Fe(III) etching, Fe is deposited onto surfaces in form of cluster. Fe occurs in largely predominant trivalent state and octahedral coordination; changes are observed among different etched surfaces. Fe-O distances are found to range from 1.98(3) - 2.06(3) Å
3) after Fe(II) etching, Fe is again deposited onto surfaces in form of clusters, but not in the reduced state. Fe(III) occurs partly in octahedral and partly in tetrahedral sites. Mean coordination numbers are smaller than the previous case, as well as the Fe-O distances (1.89(3) - 2.02(3) Å)




AFM investigations on the same samples, highlight that:

1) Surface roughness increases from from 1.5 to 1.7 nm after Fe(III) etching, due to the occurred clusters deposition. Although detectable, the change of the surface properties is limited
2) Surface roughness increases from from 1.5 to 6.0 nm after Fe(II) etching, also in this case due to the clusters deposition: however, the deposition of Fe(III) clusters results largely more efficient with the Fe(II) etching, although the physical conditions (pH, T, duration of etching) were the same. The observed change of surface properties is dramatic, and a fully different surface reactivity is expected.




**Quartz surface after Fe(III) etching** **Quartz surface after Fe(II) etching**

In conclusion, exposure of qz surfaces to etching solutions induces apparently different surface roughness, as a combined effect of cluster deposition and partial surface dissolution. Wet processing of quartz in mixtures containing “reactive” Fe can significantly alter the old and new quartz surfaces. Potentially, increase of reactive surface can be produced also in

biological environment, where Fe under weak acidic conditions is provided by the biologic tissues.
In order to verify the differences between surface Fe adducts and the bulk Fe in quartz (e.g. in amethyst variety) we also analysed a Fe(IV) standard, namely SrFeO4: the position of the pre-edge feature occurs at higher energy values than that of Fe(III), and Fe(IV) pre-edge intensity is definitely larger.