

Interactive comment on “Artifacts from manganese reduction in rock samples prepared by focused ion beam (FIB) slicing for X-ray microspectroscopic analysis” by Dorothea S. Macholdt et al.

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This manuscript presents an analysis of the Mn oxidation states in a rock varnish, for one sample prepared by room temperature focused ion beam (FIB) milling. This is said to be representative of a larger set of samples which exhibit similar properties.

The data quality is good, and the analytical methods are appropriate. The authors interpret the results as evidence that the FIB drastically alters the Mn oxidation state, which is quite plausible since metal ion reduction by FIB is known from other work.

C1

However the conclusion is not really supported by the data. The evidence, as presented, suggests the thicker regions in the sample have lower amounts of Mn(2+), but there really is not very strong evidence for the presence of Mn(4+) (green in Fig 3), except in some very localized spots. Similarly, the areas identified as Mn(2+) (blue in Fig 3) are localized in a line across the sample, whereas, if the reduction was due to FIB beam damage, then I would expect a more broad distribution of Mn(2+) signal, more like the Mn(3+) distribution (red in fig. 3) reported by the authors.

One way to make a more convincing argument would be to use the authors' favourite method to estimate the fraction of Mn(2+), Mn(3+) and Mn(4+) at each pixel in the thinner area they say is not affected by absorption saturation, and also to estimate the thickness of each pixel (for example, from the average STXM image below the onset of the Mn2p edge). A plot of the fraction of each Mn oxidation state as a function of thickness (with suitable binning to improve statistics) should then directly reveal any (anti)-correlation of Mn(2+) amount with thickness.

A second way would be to do that type of thickness-oxidation state correlation on several other samples the authors say they have made by FIB and analysed by STXM.

Perhaps the best way might be to compare results from this sample, with the results from one where the final FIB polish was deliberately done at high keV and high current – i.e. deliberately emphasize the damage.

As is, I think the manuscript is a good contribution to the discussion on optimizing sample preparation for these types of samples. It should stimulate discussion.

In the future (NOT SUGGESTED FOR THIS PAPER), the authors might want to explore using STXM with total electron yield (TEY) detection on a cleaved or other, non-FIB prepared sample.

Detailed comments

* (p2 27) 'phosphor screen;' – change to 'phosphor coating – screen implies imaging

C2

but only a single number is read from the detector at each pixel in a STXM image.

* (p2, 27) 'generated visible' → 'generated burst of visible' – it is not individual visible photons, but bursts since there is ~1 visible photon per ~3 eV of photon energy

* (p3, 16) to a few hundred degrees - is this proven or speculation ? reference ? would it be worth to compare FIB of RT and heated varnish samples ? – if the heat during FIB is important, a change in degree of radiation damage might occur. (cryo-FIB is known to reduce damage).

* (p 4 ,14) the metal coating is done, in part to reduce damage from heating or charging. Was there any study of the dependence on the amount of damage on the thickness of the Pt coating ?

* (p 6, 23) 'main absorption edges at different energies' → it would be useful to define what you mean by 'edges'. I suspect the XPS peak energies for Mn(2+/3+/4+). As you note, the spectra of each ox state (in fact each 'compound' or local environment) are characterized by multiple peaks, and a single 'energy', 'edge (in XAS sense)' or 'peak' is not enough to uniquely identify oxidation state. It is the overall pattern that is needed. This should be brought out.

* (p 6, 25) connecting multiplets to oxidation state is actually a gross simplification. Multiplet refers specifically to the [core electron – valence electron] exchange interaction. Oxidation state (interpreted as a net valence electron count) is only indirectly connected.

* (p 6, 27) “ for each oxidation state the absorption at a certain energy (Mn 2+ ~ 639.7 eV, Mn 3+ ~ 641.35 eV, Mn 4+ ~ 643.05 eV) is predominant, so that the oxidation states can be distinguished from each other ” again, I would stress that it is the PATTERN of peaks that is connected to oxidation, not a single peak.

* (p 7, caption to Fig 2) The caption calls (c) and (e) “images”, but they are not – they are color coded cluster signal distributions.

C3

* (p 8, 37) ‘ While STXM-NEXAFS measurements are conducted with energies in the eV range, FIB preparation and SEM imaging utilize energies in the keV range.’ The correlation of damage-potential and particle energy is an oversimplification. The X-rays transfer ALL their energy to the sample on absorption, whereas the ion and electron beams transfer only a portion. For ions it is momentum rather than energy transfer that is important I suspect. The reduction is probably done by liberated electrons.

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C4