Electronic Supplementary Information for:

Differences in the morphology and vibrational dynamics of crystalline, glassy and amorphous silica

Stewart F. Parker, STFC Rutherford Appleton Laboratory, ISIS Facility, Chilton, Didcot, Oxon OX11 0QX , *Corresponding Author: Email: stewart.parker@stfc.ac.uk

Ulrich Klehm, and Peter W. Albers, Evonik Technology & Infrastructure GmbH, Rodenbacher Chaussee 4, D-63457 Hanau/Wolfgang, Germany

Explanation of the differences between the TOSCA and MARI spectra of Silica I.

IINS spectra of Silica I were recorded on both TOSCA and MARI and are shown in Fig, 3(top panel) and Fig. 4 of the paper and are reproduced here as Figs. S1 and S2.

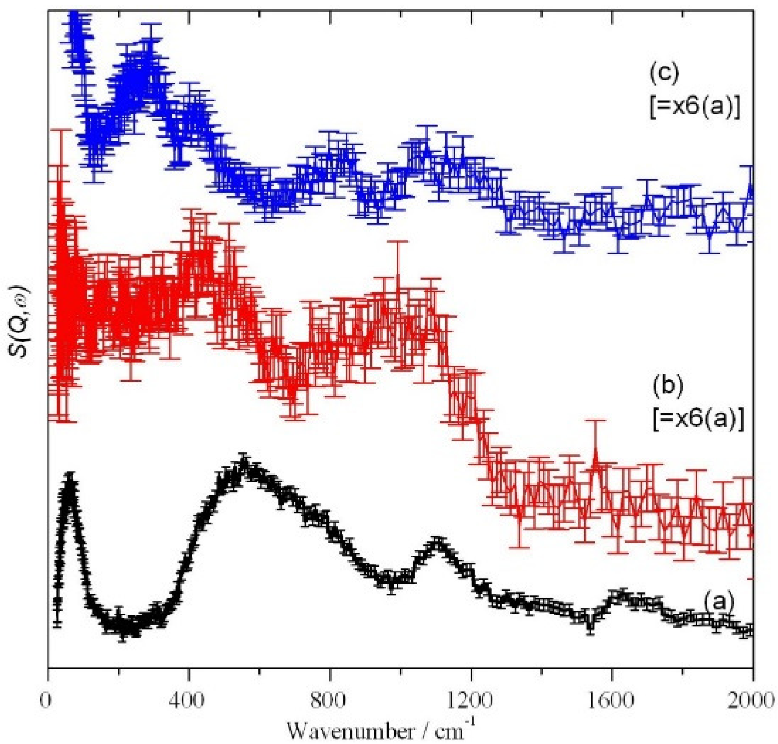

Fig. S1 TOSCA IINS spectra of Silica I: (a) original, (b) after drying at 120 °C and (c) after drying at 750 °C. Note the scale expansion factors. (This is the top panel of Fig. 3 in the paper).

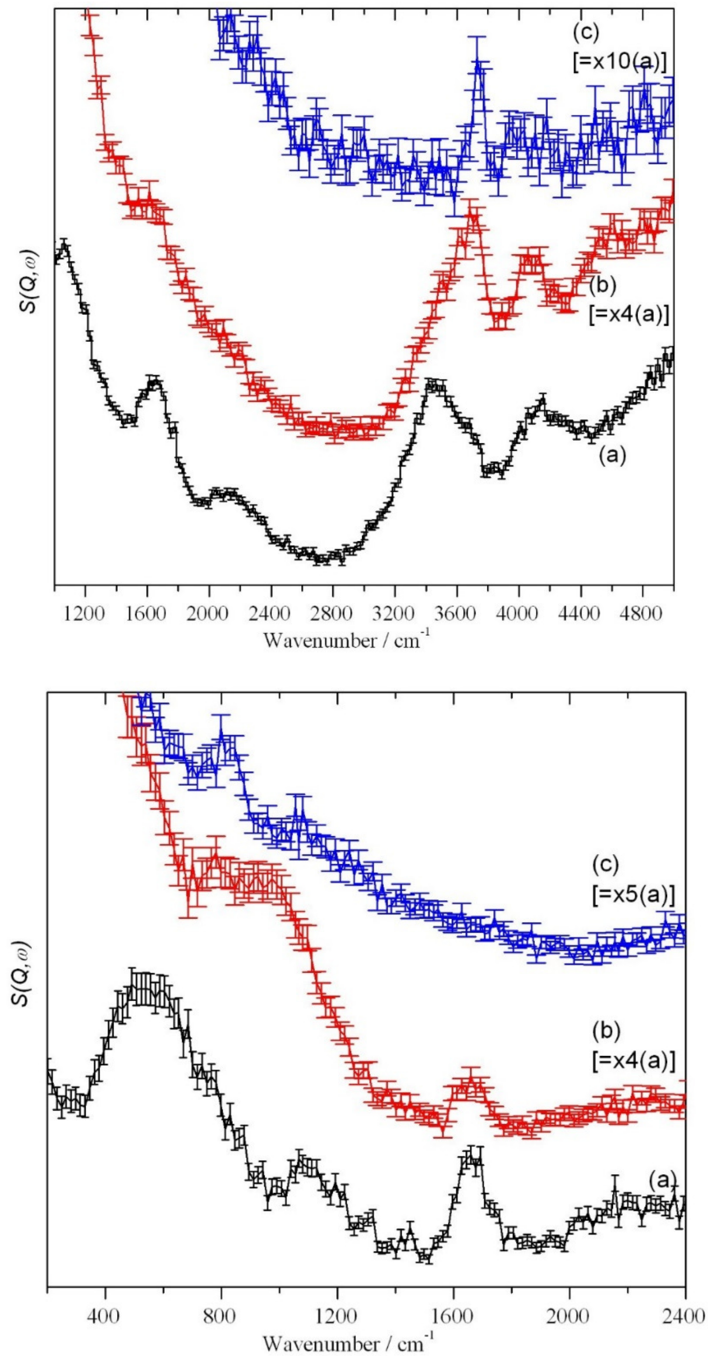

Fig. S2 MARI IINS spectra of Silica I recorded with an incident energy of 5240 cm^{-1} (top) and 2820 cm^{-1} (bottom). In each panel, (a) is the silica "as received", (b) after drying at 120 °C and (c) after drying at 750 °C. Note the scale expansion factors. (This is Fig. 4 in the paper).

It was noted that in Fig. S2, the water scissors mode at 1650 cm^{-1} is clearly seen with both incident energies for the "as received" and the 120 °C dried spectra. This mode is characteristic of water, so provides unambiguous evidence for the presence of residual water. This band is not apparent in Fig. S1b and the purpose of this section is to understand why, because the spectra are from the same sample.

The IINS spectra of Silica I dried at 750 °C look quite different when recorded on TOSCA [1] and MARI [2], compare Figs. S1c and S2c. To understand the reasons for this, and also why the water scissors mode is seen in Fig. S2b and not in Fig. S1b, it is necessary to consider how TOSCA and MARI differ. The operating principle of MARI is such that it can measure spectra as a function of both energy transfer, ω, and momentum transfer, Q, giving the "mitre plot" shown in Fig. S3. The design of TOSCA means that it follows a fixed trajectory in (Q,ω) space as shown by the solid black lines. This means that at all energy transfers MARI can access lower Q than TOSCA [3]. The significance of this is that the phonon wing intensity (combinations between the external density of states and the internal modes) depend on Q^{2n} (n = 2, 3, 4….), whereas the fundamentals depend on Q^2 [4]. Modes involving hydrogen maximise at low Q (they approximately follow the TOSCA trajectory) but on TOSCA at energies > 1500 cm^{-1} the Q is large and this reduces the sensitivity. This is why the scissors mode is not visible in Figure 3b and why the O–H stretch region does not yield useful information. The MARI data shown is just for the detectors at small Q so can observe the weak scissors mode and the O–H stretch, as seen in Fig. S4.

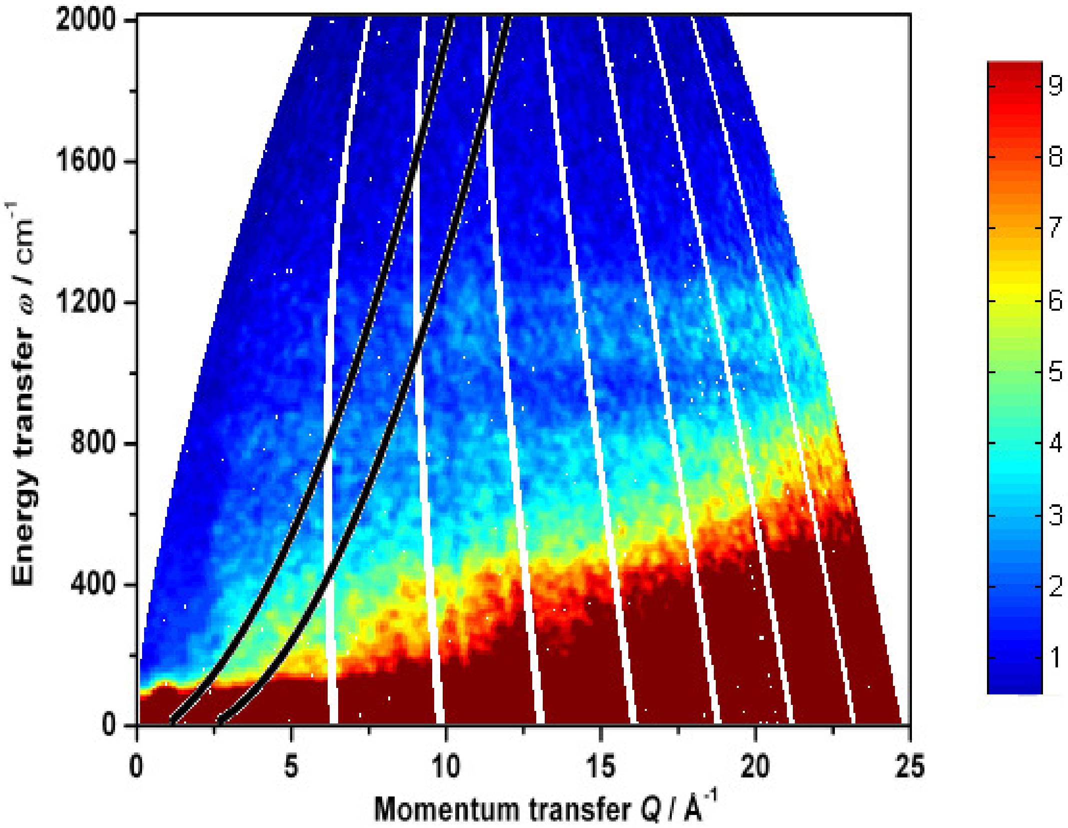

Fig. S3 (Q,ω) map of Silica I dried at 750 °C recorded with an incident energy of 2820 cm^{-1} on MARI. The (Q,ω) trajectories of TOSCA are shown by the thick black lines, (forward scattering bank: left, backscattering bank: right).

Modes involving heavy atom motion have their maximum intensity at high Q, so in the low Q plot Fig. S2c the silica modes do not appear. From Fig. S3, it can be seen that the TOSCA trajectory cuts across the silica modes at 800 and 1000 – 1200 cm^{-1} so these appear. The implication of this is that the low Q and high Q MARI spectra should look different and that the high Q spectrum should resemble the TOSCA spectrum. As can be seen from Fig. S4, this expectation is realised.

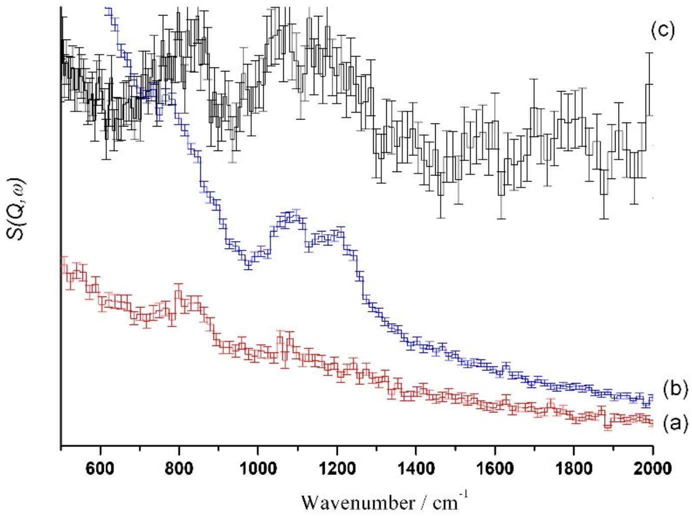

Fig. S4 Silica I dried at 750 °C recorded with an incident energy of 2820 cm^{-1}: on MARI: (a) low Q, data, (b) high Q data and (c) recorded on TOSCA. Note the similarity of (b) and (c).

References

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[3] S.F. Parker, D. Lennon, P.W. Albers, *Appl. Spec.* **2011**, 65, 1325.

[4] P. C. H. Mitchell, S. F. Parker, A. J. Ramirez-Cuesta, J. Tomkinson, *Vibrational Spectroscopy with Neutrons*, World Scientific, Singapore, **2005**, pp. 3; TFXA, pp. 100 - 193;