

## Supporting Information for

# On the surface acid-base properties of amorphous and crystalline $\text{Mg}_2\text{SiO}_4$ as probed by adsorbed $\text{CO}$ , $\text{CO}_2$ and $\text{CD}_3\text{CN}$

*Matteo Signorile<sup>1\*</sup>, Lorenzo Zamirri<sup>1</sup>, Akira Tsuchiyama<sup>2,3</sup>, Piero Ugliengo<sup>1\*</sup>, Francesca*

*Bonino<sup>1</sup>, Gianmario Martra<sup>1</sup>*

<sup>1</sup> Department of Chemistry and Interdepartmental Centre “Nanostructured Surfaces and Interfaces – NIS of the University of Torino, and INSTM Reference Centre, Via P. Giuria 7, 10125, Torino, Italy

<sup>2</sup> Research Organization of Science and Technology, Ritsumeikan University 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

<sup>3</sup> Guangzhou Institute of Geochemistry Chinese Academy of Sciences, 511 Kehua Street, Wushan, Tianhe District, Guangzhou, 510640, China

\* Corresponding authors: Matteo Signorile, [matteo.signorile@unito.it](mailto:matteo.signorile@unito.it); Piero Ugliengo [piero.ugliengo@unito.it](mailto:piero.ugliengo@unito.it)

### S1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been performed with a TA Instruments Q600 instrument, increasing the temperature from RT to 1273 K at a rate of 5 K min<sup>-1</sup> under a flow of 1000 ml min<sup>-1</sup> of dry N<sub>2</sub>. The differential heat flow to the sample with respect to an empty reference sample holder has been measured together with the sample weight variation as a function of temperature. The measurement has been performed on AMS, in order to evaluate the better activation strategy able to preserve the sample in its amorphous form: results are presented in Figure S1.

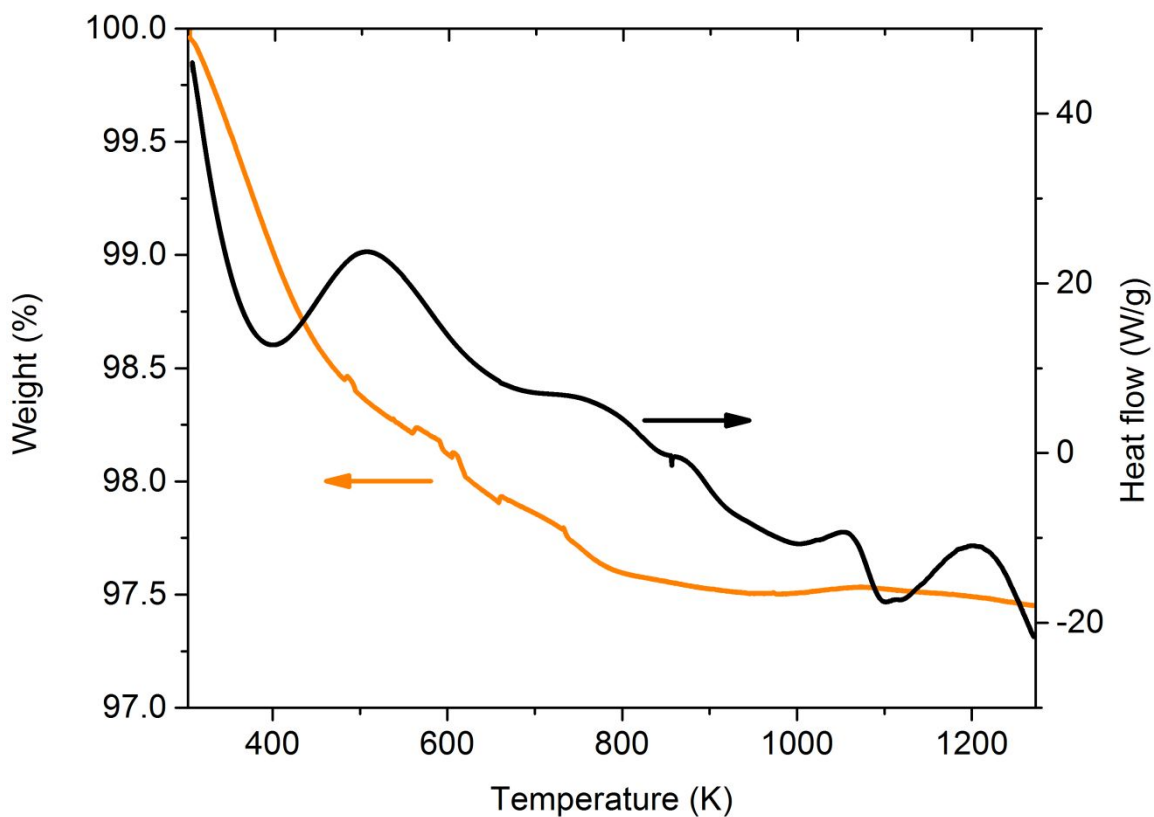


Figure S1. TGA of AMS (orange). The differential heat flow to the sample is reported as well (dot-dash black, exo down).

The result of TGA on AMS show a low overall weight loss (2.5% at 1273 K), mostly taking place in the RT-773 K range. The latter can be further divide in two subranges: i) from RT to ~473 K, where the steepest weigh decrease occurs, straightforwardly ascribable to the desorption of water; and ii) from 473 K to 773 K, whit a lower extent of weight loss, possibly associated to the desorption of strongly bonded species (e.g. carbonates, see IR data on CO<sub>2</sub> adsorption in Section 3.3). The heat flow to the sample, simultaneously monitored during the measurement, is positive (i.e. representative of an endothermic process) in the aforementioned RT-773 K range and turns negative (i.e. exothermic) above 873 K. The positive value of the heat flow at low temperatures is compatible with the postulated desorption processes, whereas the exothermic process above 873 K can be interpreted as the crystallization stage.

## S2. Attenuated total reflection (ATR) IR spectroscopy

The ATR-IR results are shown in Figure S2.

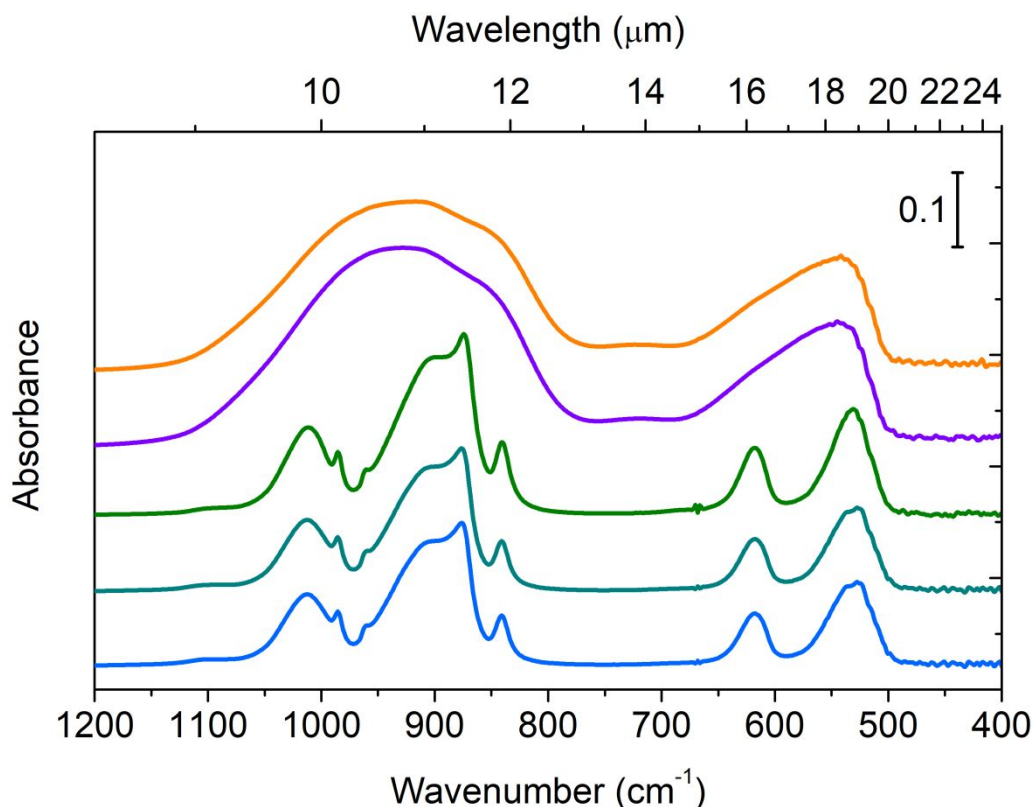


Figure S2. ATR-IR spectra of AMS (orange), CMS (cyan), AMS upon activation in vacuum at 673 K after transmission IR experiments (violet), CMS upon activation in vacuum at 673 K after transmission IR experiments (light blue) and AMS recovered after the TGA measurement (green).

These show as the spectra of AMS, collected prior and after the activation treatment in vacuum at 673 K, are identical, testifying such procedure does not induce the crystallization. The same treatment does not modify the structure of the crystalline CMS sample. Conversely, even after the short residence time (less than 5 min) at 1273 K occurring during the TGA analysis, the crystallization takes place for AMS.

### S3. Additional amorphous cluster models

Figure S3 shows the structure of additional amorphous model clusters.

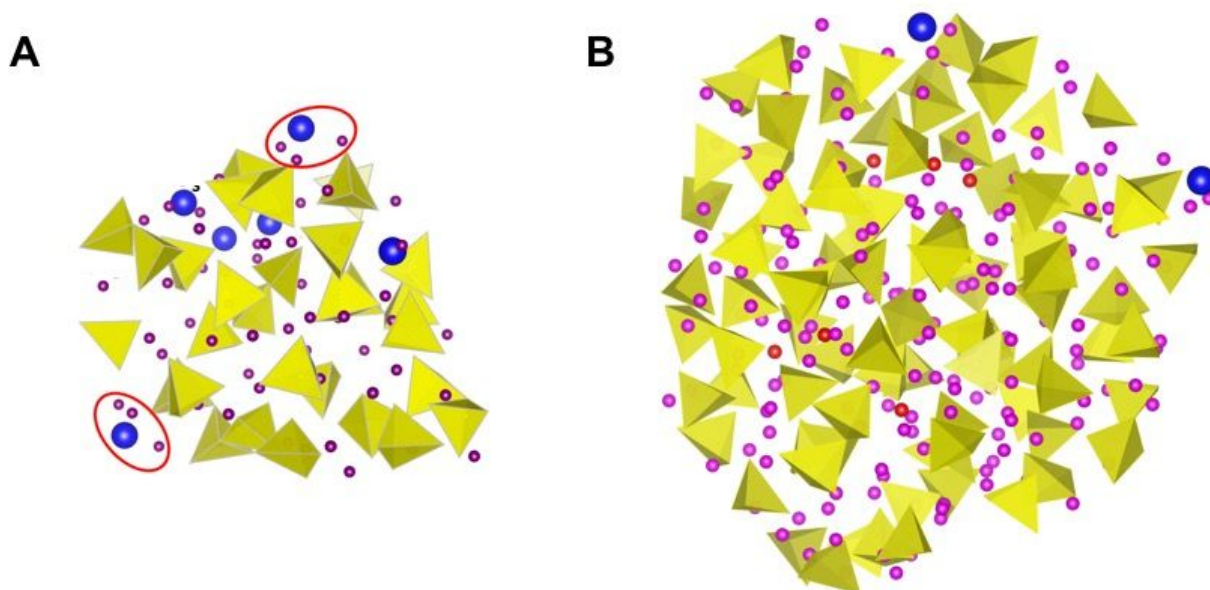


Figure S3. A: “30 A at 2400K” amorphous  $\text{Mg}_2\text{SiO}_4$  model (210 atoms, 30  $\text{Mg}_2\text{SiO}_4$  formula units); B: “92 A” amorphous  $\text{Mg}_2\text{SiO}_4$  model (644 atoms, 92  $\text{Mg}_2\text{SiO}_4$  formula units). Clusters are taken from Ref.1. Color code: Mg in purple;  $\text{SiO}_4$  tetrahedra in yellow; O not belonging to  $\text{SiO}_4$  units in blue.

As in the case of the “80 A” cluster (see Figure 7A), both the models in Figure S3 exhibits O atoms not belonging to  $\text{SiO}_4$  units, thus possible basic centers. Also in this case, Mulliken charges have been computed for the different atoms and are reported in Table S1.

Table S1. Average B3LYP Mulliken net charges and their standard deviations for the different kind of ions in the considered amorphous  $\text{Mg}_2\text{SiO}_4$  models.

Ion kind	Mulliken net charges		
	A 80	A 30 at 2400K	A 92
O (belonging to $\text{SiO}_4$ )	$-1.22 \pm 0.07$	$-1.21 \pm 0.09$	$-1.22 \pm 0.07$
O (not belonging to $\text{SiO}_4$ )	$-1.41 \pm 0.02$	$-1.40 \pm 0.02$	$-1.40 \pm 0.02$
Si	$1.85 \pm 0.07$	$1.84 \pm 0.05$	$1.85 \pm 0.02$
Mg	$1.52 \pm 0.02$	$1.51 \pm 0.02$	$1.52 \pm 0.02$

Interestingly, the Mulliken net charges are almost insensitive to the cluster size.

## References

- (1) Zamirri, L.; Macià Escatllar, A.; Marinõso Guiu, J.; Ugliengo, P.; Bromley, S. T. What Can Infrared Spectra Tell Us about the Crystallinity of Nanosized Interstellar Silicate Dust Grains? *ACS Earth Sp. Chem.* **2019**, 3 (10), 2323–2338. <https://doi.org/10.1021/acsearthspacechem.9b00157>.