

# Forsterite and Porous Silica – A Preliminary Investigation

Langston Tillman, Albert Voskanyan, Alexandra Navrotsky, Rick Hervig

School of Molecular Sciences, ASU  
Center for the Materials of the Universe, ASU

## Introduction

The goal of this project is to find out whether structure direction by simple organic molecules occurred to form mesoporous or other structured silica during silicate mineral dissolution on the prebiotic earth. When silicate minerals are subject to acidic aqueous environments, a dissolution-precipitation reaction can take place where the mineral is dissolved and (because of its low solubility), aqueous silica is precipitated on the surface of the mineral as an amorphous phase.

In this preliminary investigation, we are testing the dissolution-precipitation mechanism and investigating the morphology of the amorphous silica formed on a mineral surface.

We found that after subjecting a silicate mineral such as forsterite ( $Mg_2SiO_4$ ), to acidic conditions, amorphous silica forms, confirming the dissolution of the mineral phase forsterite. Further investigations will be required to demonstrate that this does proceed by a dissolution-precipitation mechanism.

## Bigger Picture

It is hypothesized that, in the prebiotic earth, simple organics acted as surfactants to induce mesoporous silica formation[1]. These mesoporous silica structures could then oligomerize or polymerize simpler organics like amino acids into more complex organics like peptides or polypeptides, which, in turn, can act as templates that produce more silica[1]. We already know that similar mechanisms are being used in industry today to catalyze important complex reactions. The processes we use today on an industrial scale could have been utilized by nature in the prebiotic earth to synthesize early complex organics, which would have been essential to the formation of life.

## Surfactants

Generally, surfactants have a hydrophilic head and a hydrophobic tail. At a critical concentration, surfactants form micelles and micelle aggregates with different shapes and sizes, as shown in water-surfactant phase diagram of Figure 1[2].

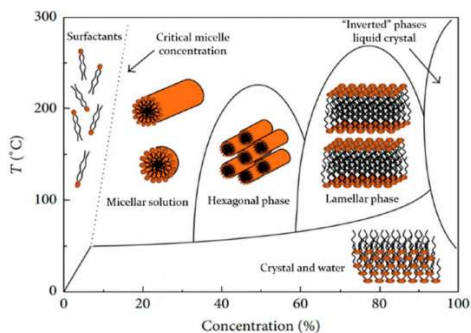


Figure 1. The formation of micellar structures in a binary surfactant water system. Taken from D. Lombardo, Adv. Cond. Matter Phys, 1–22 (2015).

## Mesoporous Silica

Mesoporous silicas (pore size 2-50 nm) are widely used as catalysts[3]. We investigate mesoporous silica because they are preferred over microporous silica due to their high surface area-to-volume ratio, while being preferred over microporous silica since mesoporous silica provides enough volume in its pores to promote organic catalysis. Mesoporous silicas can be formed via the pathway outlined in Figure 2. This method, known as soft templating, uses the micelle aggregates to template silica formation.

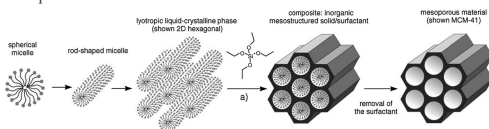


Figure 2. Schematic representation of MCM-41 silica formation via soft templating. The pore walls of mesoporous silica can chemisorb organic molecules forming covalent bonds between peptides and the inner surface walls of mesoporous silica[4]. These amino acid-functionalized mesoporous silica can then bind with other organics to form oligomers and polymers under the right conditions[5].

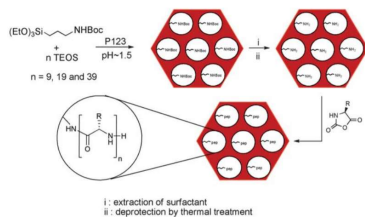


Figure 3. Depiction of amino-acid functionalized mesoporous silica synthesis which can further catalyze organic oligomerization. G. Subra et al, J. Mater. Chem. 6321–6326 (2011).

## Silica dissolution

There were many silicate minerals in the prebiotic earth, many of which were in acidic environments. We know that a dissolution-precipitation reaction happens at the interface of the mineral and the liquid environment, coating the silicate in an amorphous silica layer[6]. Presumably, then, silica spends some time in an aqueous state, where it would have a chance to interact with the surfactants as mentioned above. We know that there were many simple organics in the prebiotic earth that could function as surfactants.

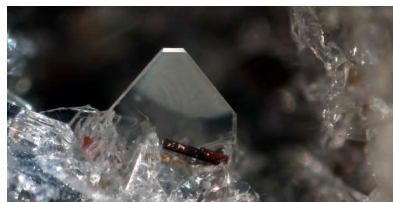


Figure 4. An image of forsterite crystal. Taken from Wikipedia.

## Materials and Methods

Forsterite ( $Mg_2SiO_4$ ) was synthesized by grinding together stoichiometric amounts of silica ( $SiO_2$ ) and magnesium oxide ( $MgO$ ) in a mortar and pestle. After thorough mixing, this mixed powder was pressed into pellets using a hand press. These pellets were then heated up to  $1000^\circ C$  in a muffle furnace for 24 hours, after which they were allowed to cool completely in air.

Two experiments were then performed:

### Experiment I:

A forsterite pellet and an equal amount of ground-up forsterite were placed in two Teflon containers containing an acidic (HCl) solution at pH 1. After 5 days, the Teflon container containing the pellet was decanted and the pellet was allowed to dry in air. The container containing the powder was centrifuged and washed three times with deionized water, then left in a  $100^\circ C$  oven to dry completely.

### Experiment II:

The same process was repeated as in experiment 1 but with more forsterite (2 pellets) and lower acidity (pH 2 solution).

## Results and Conclusions

We used X-ray diffraction (XRD) to characterize the sample after the acid treatment. The absence of diffraction peaks (Fig. 5) demonstrates the loss of crystallinity in the sample. This suggests amorphous silica material.

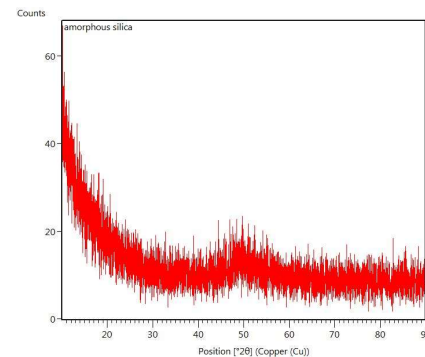


Figure 5. XRD characterization of forsterite powder that had been subject to pH 1 conditions



Figure 6. A photo of the synthesized forsterite pellets.

## Future Directions

The next steps will be to investigate the dissolution of silicates in the presence of surfactants that may possibly be present in the prebiotic earth. We think that the surfactants will be able to direct the formation of mesoporous silica, these structures can then be examined, and their catalytic properties will be explored. This will likely happen first by a literature review to see what surfactants might have been present in the prebiotic earth. Inspiration will be drawn from modern industrial mesoporous silica synthesis, as we believe that the pathways used in modern technologies may have already been utilized by nature eons ago.

## References

- [1] A. Navrotsky et al., Cooperative formation of porous silica and peptides on the prebiotic Earth. Proc Natl Acad Sci USA. 118(2), 1-7 (2021).
- [2] D. Lombardo, M.A. Kiselev, S. Magazu, P. Calandra, Amphiphiles self-assembly: Basic concepts and future perspectives of supramolecular approaches. Adv. Cond. Matter Phys. 2015, 1–22 (2015).
- [3] J. M. Newsam, “Zeolites” in Solid State Chemistry: Compounds, A. K. Cheetham, P. Day, Eds. (Clarendon Press, 1992), vol. 2, pp. 234–280
- [4] M. Brodrecht et al., Structural insights into peptides bound to the surface of silica nanopores. Chemistry 25, 5214–5221 (2019).
- [5] G. Subra et al., Functionalized mesoporous silica: A good opportunity for controlled peptide oligomerization. J. Mater. Chem. 21, 6321–6326 (2011)
- [6] R. Hellmann et al., Unifying natural and laboratory chemical weathering with interfacial dissolution-precipitation: A study based on the nanometer-scale chemistry of fluid-silicate interfaces. Chem. Geol. 294-295, 203–216 (2012).

## Acknowledgements

A special thanks to Albert Voskanyan, Alexandra Navrotsky, and Rick Hervig for helping with the project. I look forward to working with them on the future directions of this project.

This research was supported by the NSF PIRE grant and the Fulton Undergraduate Research Initiative (FURI).