The effect of a protein (lysozyme) on the mechanism of amorphous silica precipitation

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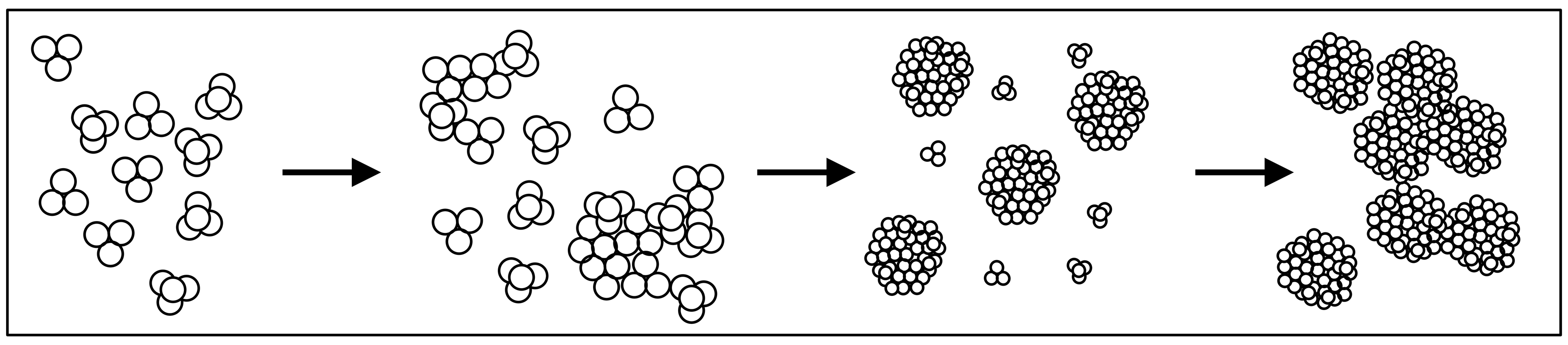
Motivation

Biological activity can lead to the **precipitation of amorphous silica**. It can be directly precipitated by organisms (e.g. diatoms) or formed by abiogenic processes on "sticky" microbial surfaces [1,2]. In both cases, the **interaction between amorphous silica and macromolecules**, like proteins, are crucial for the formation of amorphous silica. However, how and if proteins affect the structure, composition and morphology of the amorphous silica formed at the molecular level is only poorly understood. Here, we quantified the effect a characteristic protein (lysozyme) has on the structure and composition of amorphous silica.

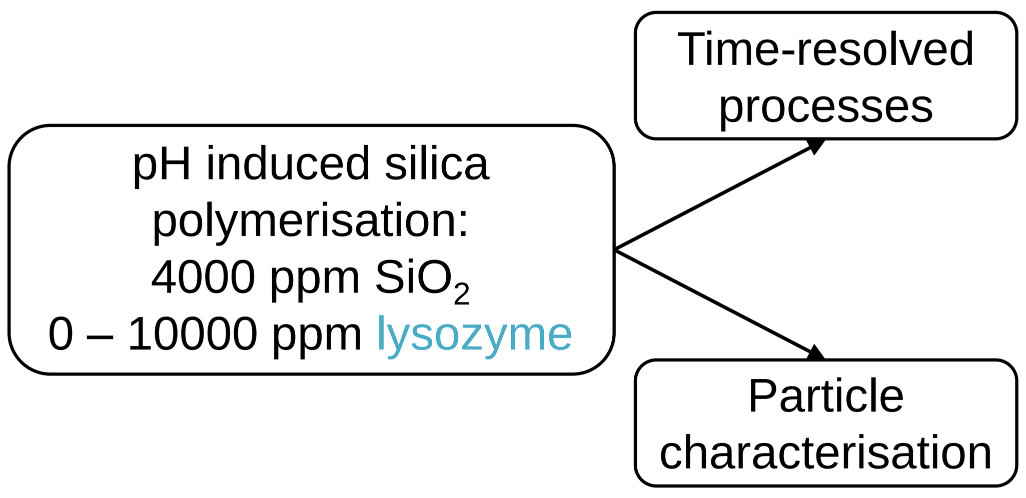
Proposed mechanism of amorphous silica formation [3],[4]

In the absence of lysozyme (pure silica system)



monomeric silica | polymerisation | particle growth | aggregation

Methods

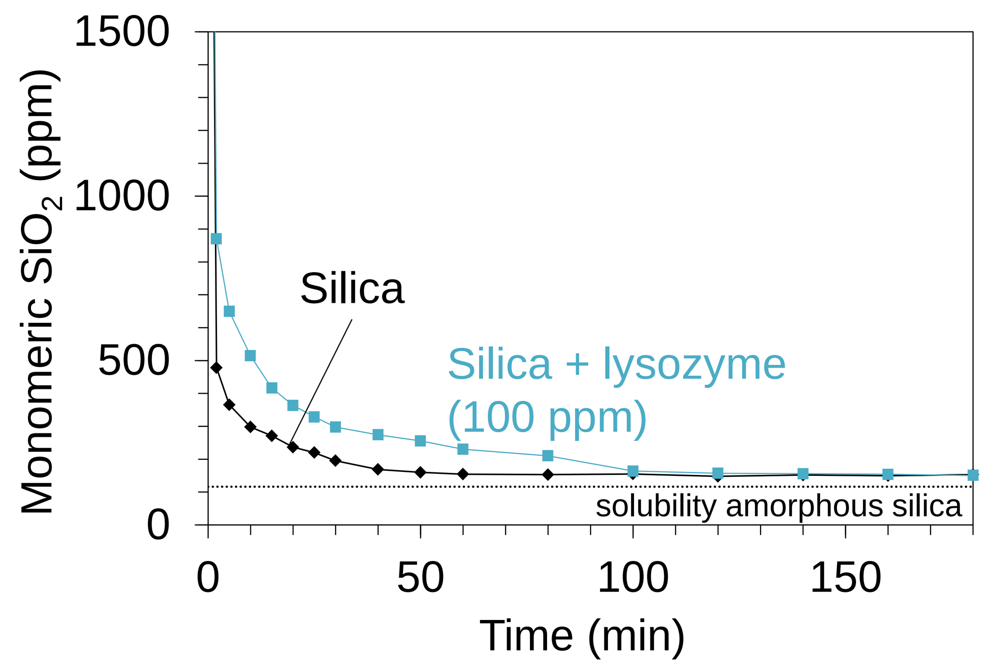


- Spectrophotometric molybdate yellow method
- Synchrotron-based small angle X-ray scattering (SAXS)

- Pair distribution function (PDF) analyses
- High resolution imaging (TEM)
- Quantitative Fourier-transform infrared spectroscopy (FTIR)
- Carbon elemental analyser

Time-resolved processes

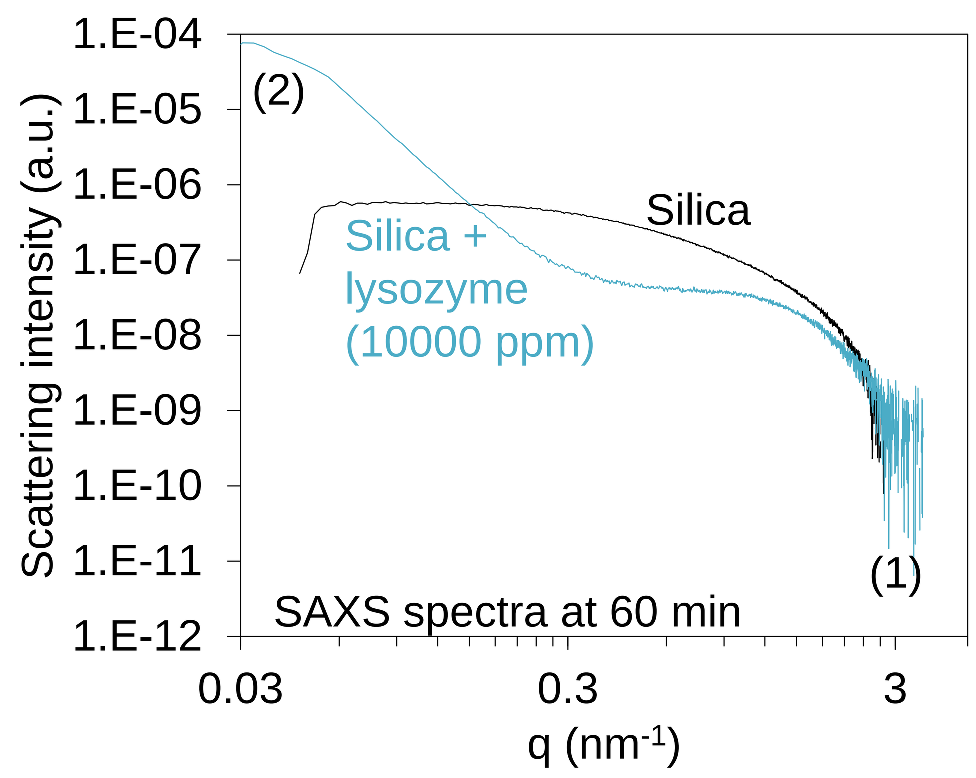
Polymerisation of monomeric silica



Presence of lysozyme slows down decrease of monomeric SiO_2

→ slower polymerisation rate

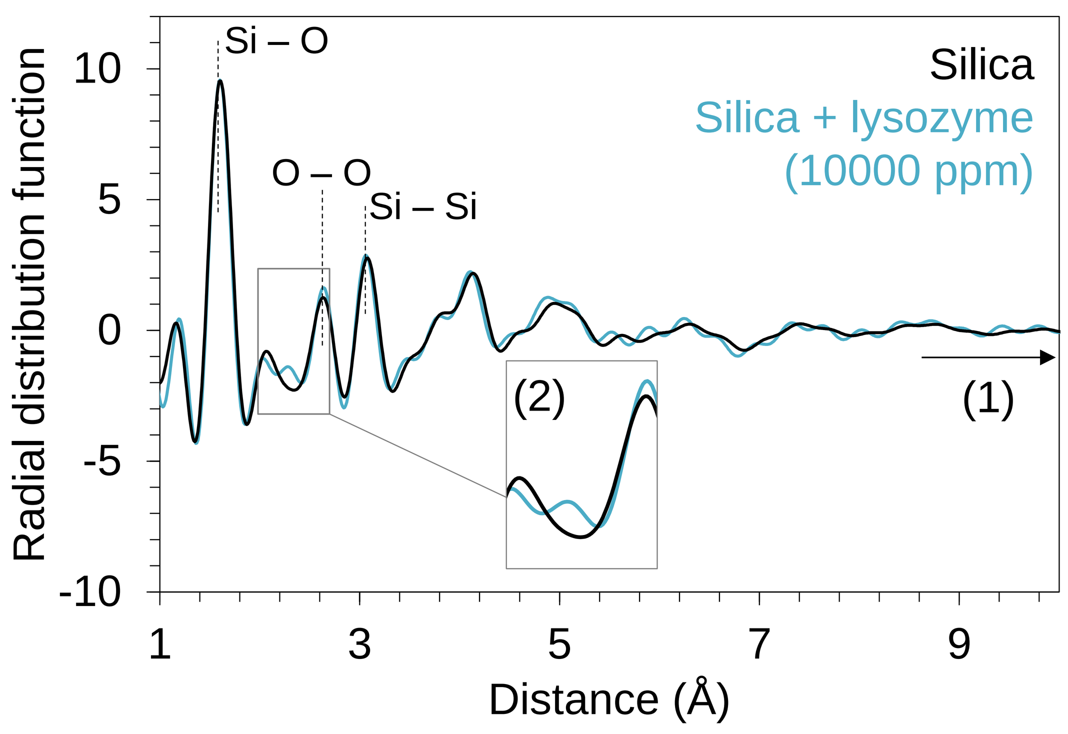
In-situ real time particle growth



(1) Similar maximum q-values
→ particle size (~2.5 nm) similar in both systems

(2) High intensities at low q values in the presence of lysozyme
→ formation of aggregates

Characterisation of silica precipitates



Structural information

(1) No long-range ordering (> 10 Å) indicates that particles are amorphous

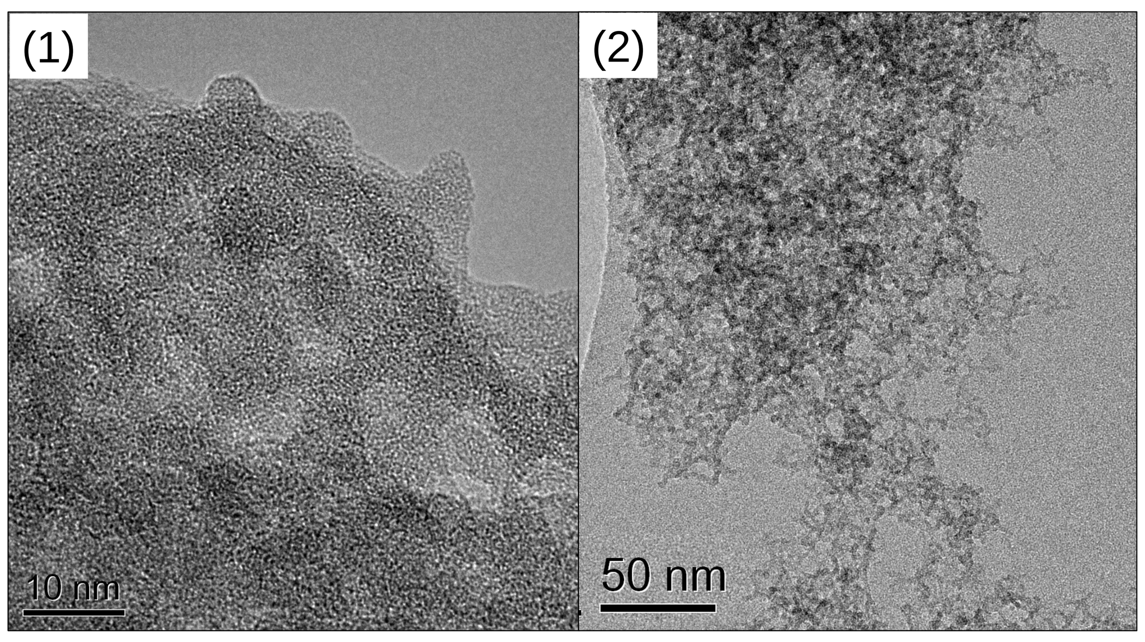
(2) Minor changes in the short-range ordering in presence of lysozyme
→ limited incorporation of lysozyme into silica particles

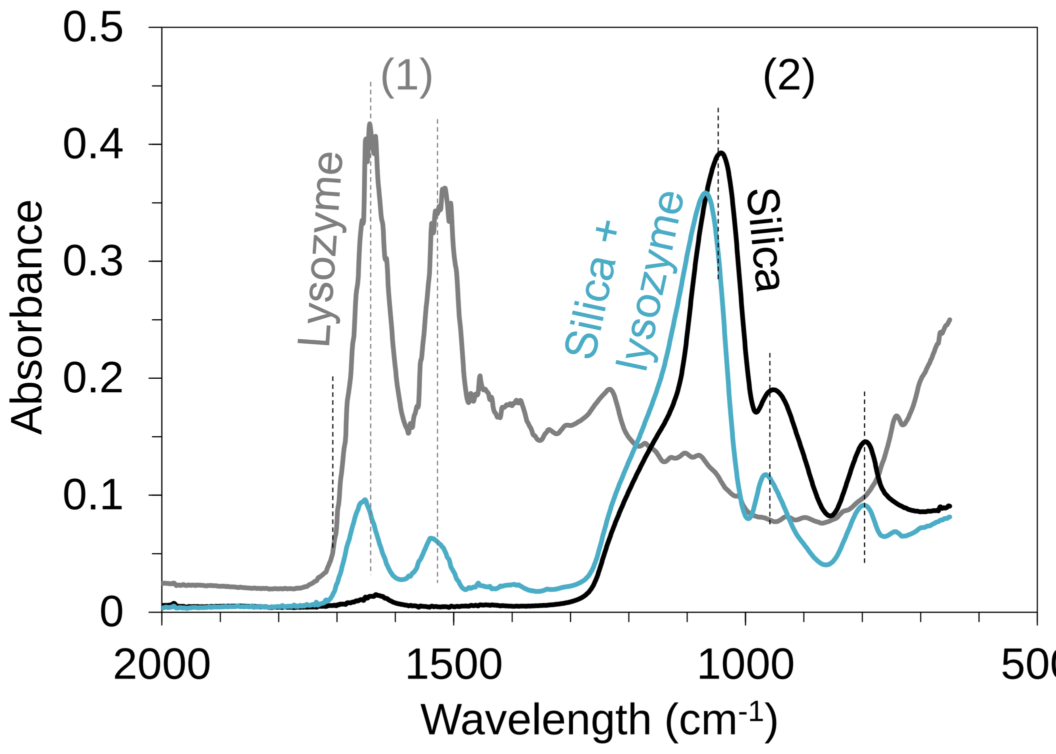
Particle size & morphology

(1) Spherical particles around 3 nm in size

(2) Loosely packed aggregates (up to several 100 µm) of individual particles

→ no effect of lysozyme on particle size and shape





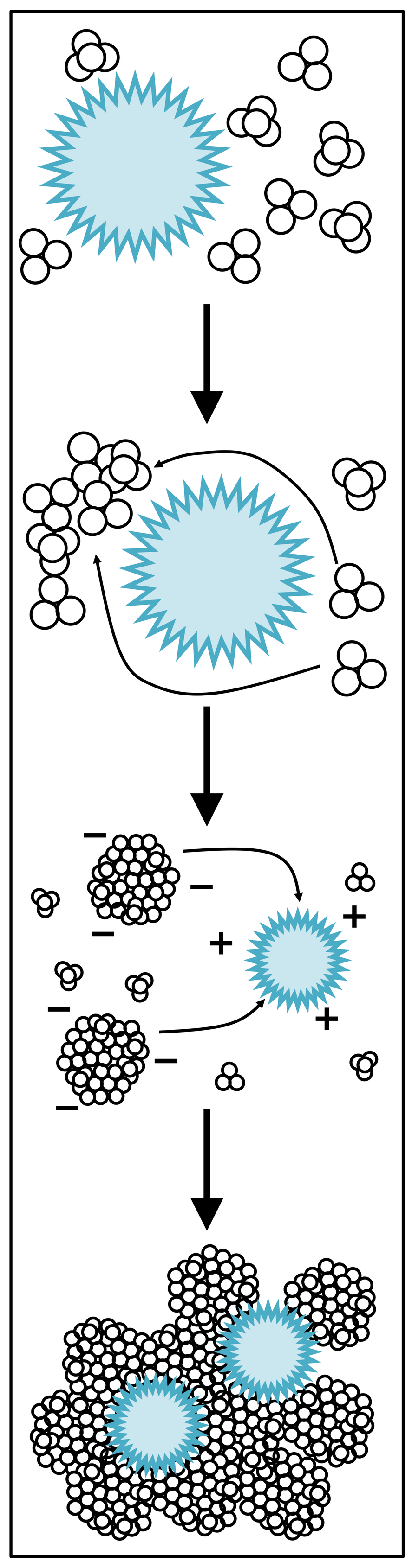
Composition of sillica precipitates (bulk analysis)

FTIR spectra of samples shows protein (1) and silica (2) peaks
→ lysozyme is incorporated into the silica precipitates

Precipitates contain between 2.3 and 10.3 wt.% of lysozyme

Effect of lysozyme on the mechanism of amorphous silica formation

- Slower polymerisation rate: diffusion and collision of monomeric silica molecules hindered by large lysozyme molecules
- Final size and shape of silica particles not significantly affected by lysozyme
- Incorporation of lysozyme into silica particles limited due to large size of the lysozyme molecule[5]
- Strong aggregation caused by opposite surface charge of silica particles and lysozyme molecules[6]
  → lysozyme acts as flocculating agent
  → lysozyme is incorporated into the silica precipitates



References

[1] Perry. *Reviews in Mineralogy and Geochemistry*. **2003**, 54, 537. [2] Benning et al. *Geochimica and Cosmochemica Acta*. **2004**, 68/4, 729. [3] Iler. John Wiley and Sons. 1979 [4] Tobler et al. *Geochimica and Cosmochemica Acta*. **2009**, 73/18, 5377. [5] Blake et al. *Nature*. **1965**, 206/4986, 757. [6] Forciniti et al. *Biotechnology & Bioengineering*. **1991**, 38/9, 986.

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