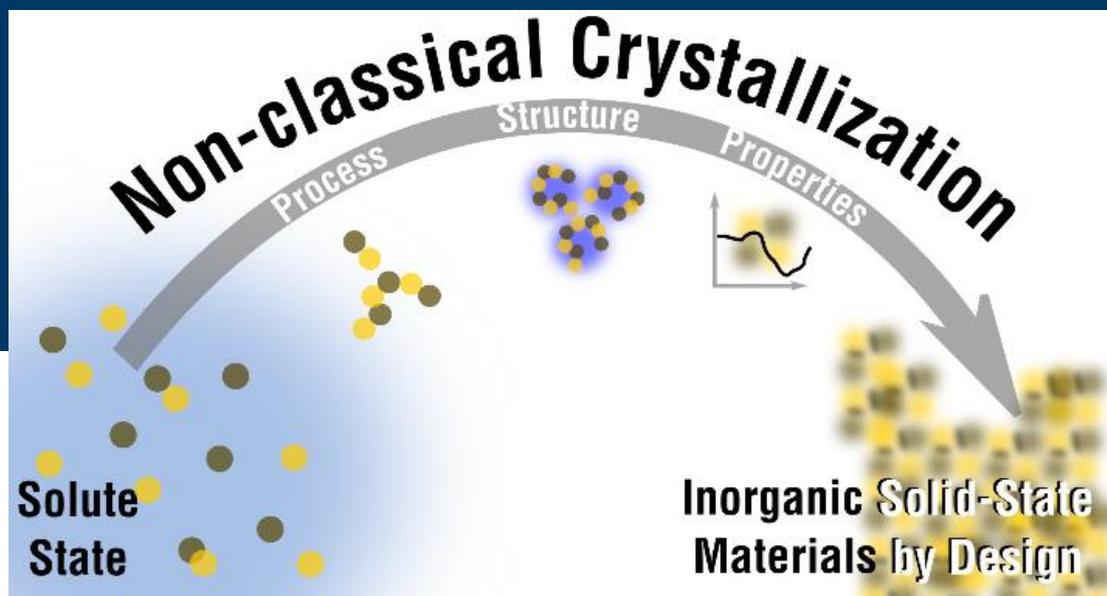


# From solutes to solids: towards a supramolecular view on mineralization processes



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SSP1.5: (Bio)mineral archives of past environmental conditions:  
from the Precambrian to the present  
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## “Nonclassical” crystallization

*Mineralization pathways fueled by the assembly of larger units than single ions*

In the last decades, various contributions have shown that mineralization pathways exist, in which larger units drive the formation of a crystalline phase. These findings conflict with the classical concept of nucleation and crystal growth and challenge our standard view on the genesis of a solid mineral phase.

**Nonclassical concepts bear major implications for materials chemistry but also biomineralization and geochemistry.**

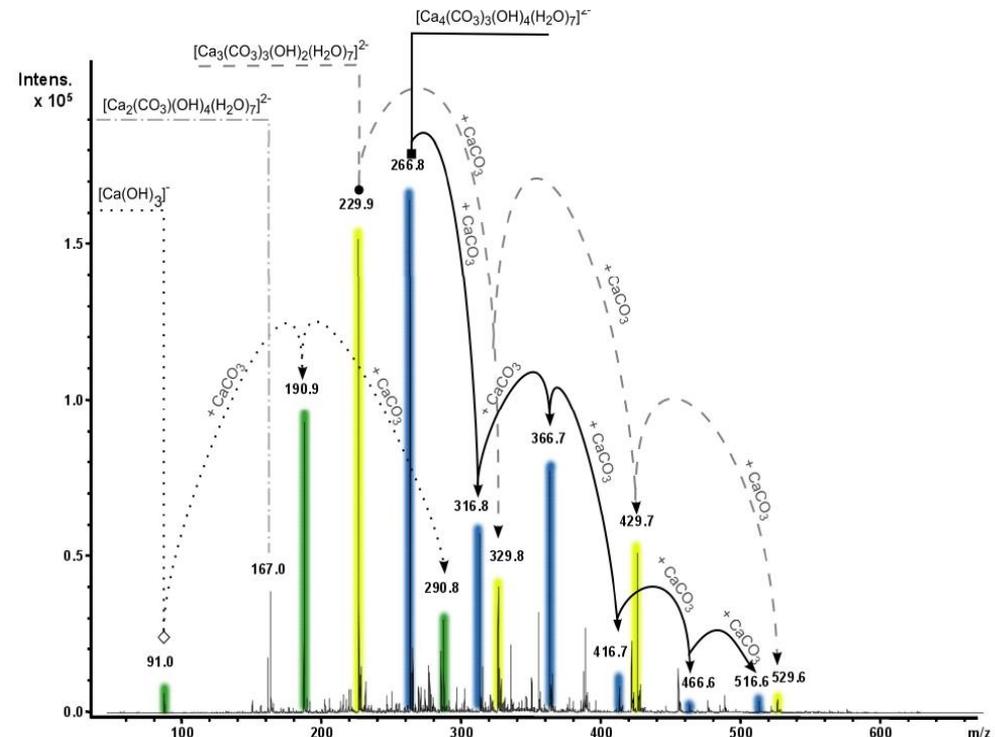
For the important case of calcium carbonate, Gebauer et al. (Science 2008) reported the formation of so-called prenucleation clusters even in undersaturated solutions. These stable prenucleation clusters represent an ergodic population and therefore conflict with classical concepts of nucleation. Their particle size is in the low-nm range, but they do not act as nuclei. Recently they have been described as “dynamically-ordered liquid-like oxypolyanions” (DOLLOP), i.e., unstable calcium carbonate chains bearing similarity to polymers with a characteristic 1:1 ratio of calcium to carbonate (Demichelis et al. Nature Commun 2011).

The prenucleation cluster theory is a matter of fierce debate (see, for instance, Hentzler et al. in Sci Adv 2018). The critical question is: are they involved in mineralization, or are they simple bystanders that are trapped in a thermodynamic sink? What is their chemical nature or are they an exceptional form of stable nuclei, calling for a “nonclassical nucleation” framework?

## The „prenucleation cluster“ theory

Are they involved in mineralization, or are they simple bystanders, trapped in a thermodynamic sink?  
What is their (physico-)chemical nature?

We demonstrated that the speciation in near-neutral calcium carbonate solution is more complex than typically predicted. Besides simple ion pairs, also large multi-centred coordination clusters with multiple calcium centres can be detected by ESI-MS. This observation is congruent with molecular simulations which provide the basis of the prenucleation cluster concept. Thus, a complex speciation is indeed present in calcium carbonate solutions.



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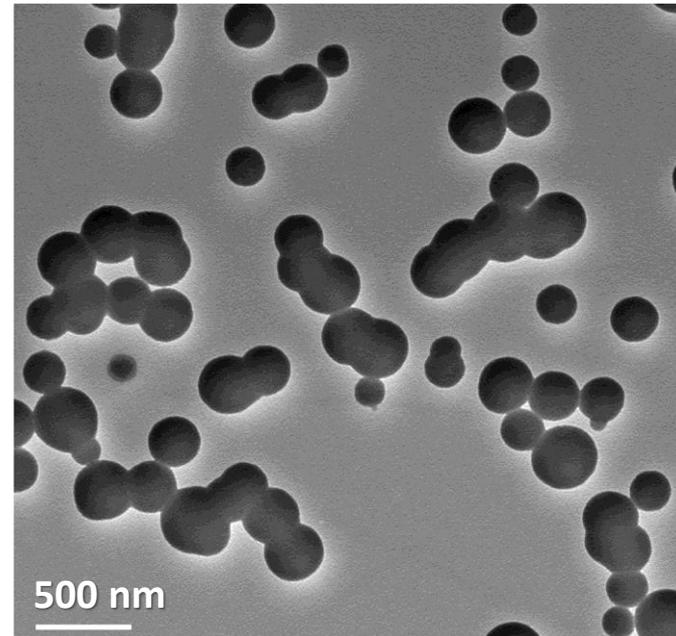
## Liquid-Condensed Mineral Precursors in the Calcium Carbonate System

Another peculiar mineralization pathway has been identified for the calcium carbonate system. Under specific conditions, a liquid-condensed mineral precursor can separate from calcium carbonate solutions; the droplets of this mineral precursor assemble and coalesce, eventually yielding a mineral body composed of calcium carbonate.

Already in the late 1990s, Gower et al. showed that the addition of traces of a polyelectrolyte (e.g. polyaspartic acid or polyacrylic acid) can cause the formation of this **liquid-amorphous precursor**.

However, the mechanisms which lead to this precursor and drive its ripening to the final crystalline state is still unsettled.

This peculiar mineral phase, which is called **polymer-induced liquid-precursor (PILP)**, seems to be a “quirk” of the calcium carbonate system but the **relevance for biomineralization processes have been suggested**.



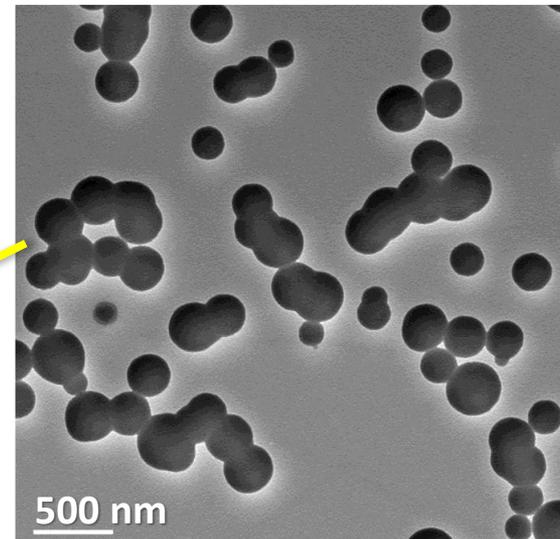
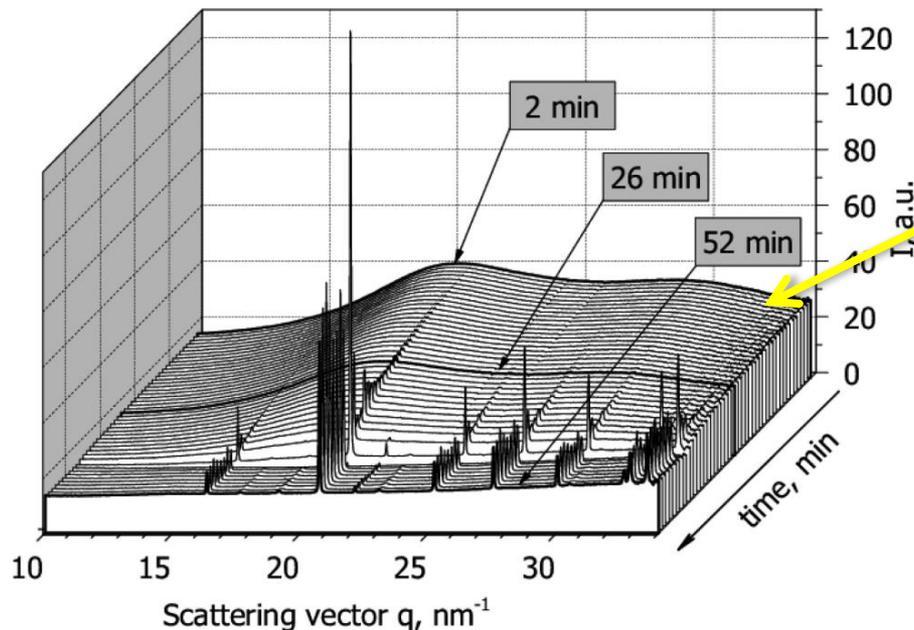
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The research of the Wolf Group focuses on the origin of this unexpected liquid-liquid phase separation in aqueous inorganic systems, their relevance for biomineralization and geochemical processes and their potential for materials chemistry.

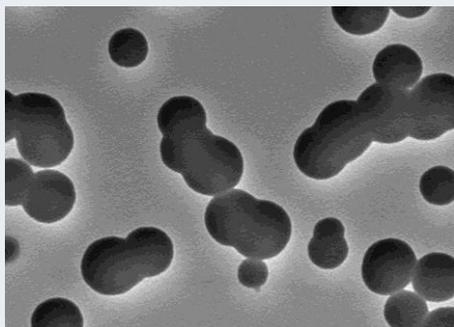
a liquid mineral precursor ?

## Liquid-condensed phases (LCP) of minerals

TEM micrographs of early stages of evaporation of a pure near-neutral solution of calcium bicarbonate (i.e., hard water) showed an emulsion-like and liquid intermediate composed of hydrated calcium carbonate.



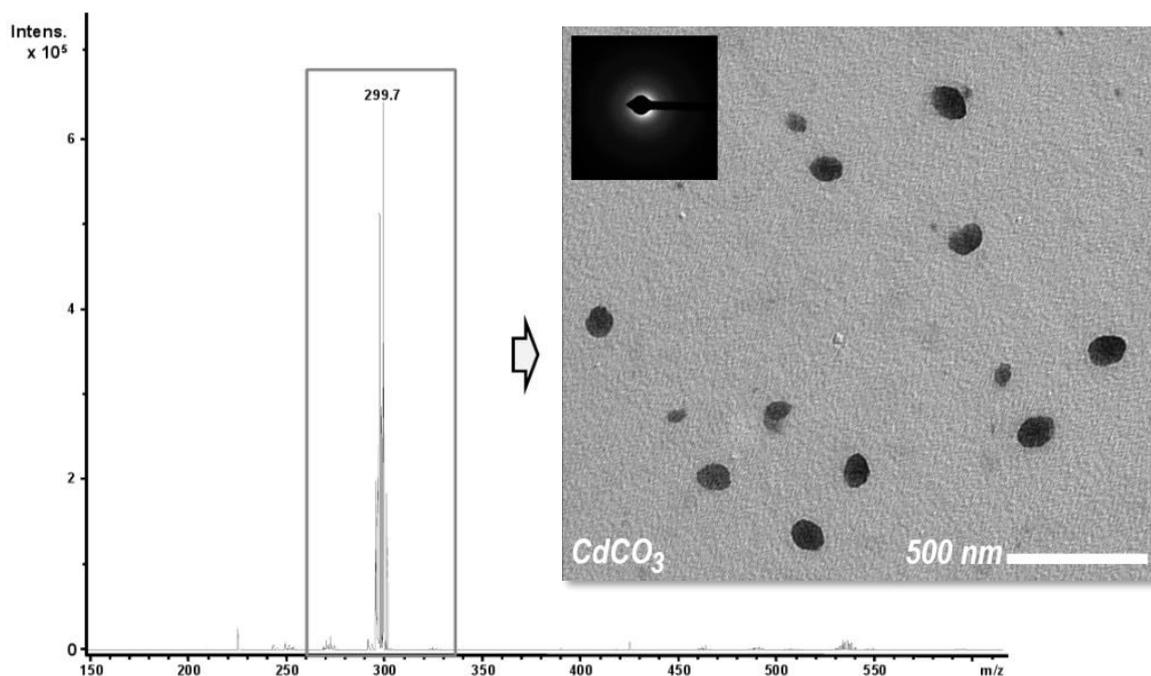
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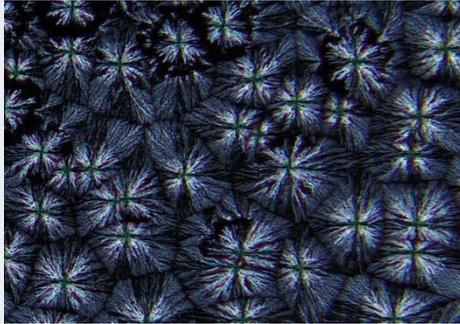
## Liquid-condensed phases (LCP) of minerals

It is commonly assumed that “DOLLOPs” are required for the formation of an LCP phase; thus that this should be restricted to some few mineral systems which generate similarly dynamical solute species. However, our studies showed that complex speciation is not necessary for liquid-liquid phase separation! In other carbonate systems, such as  $\text{BaCO}_3$  only very few and simpler carbonato-complexes were found.

In case of  $\text{CdCO}_3$ , only one and stable complex forms which bears only a single Cd-center, as evidenced by ESI-MS. Thus, **dynamic prenucleation clusters are not needed for LCP**. We assume that molecular coordination complexes, thus inorganic molecules, and their interaction are the key to liquid-liquid phase separation. **It is the solution speciation beyond ion pairs which allows for liquid precursors in aqueous mineral systems. They form at ambient conditions, and our data shows that they strongly affect distribution coefficients and incorporation rates.**



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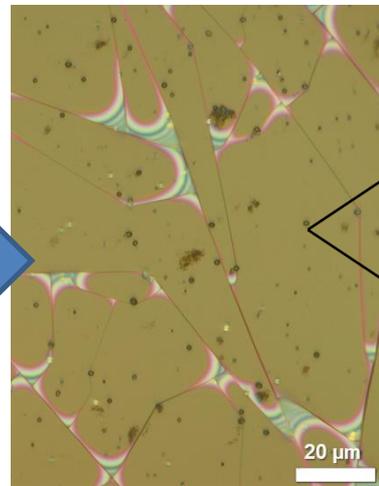


## PILP – polymer-induced liquid-precursor

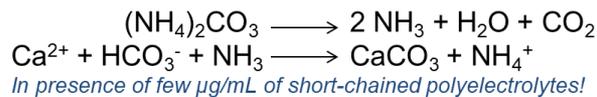
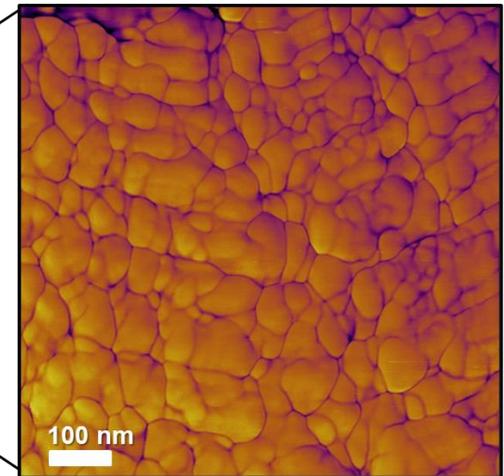
The induction of a PILP process appears to be non-trivial; however, already simple reaction conditions under slow diffusion (see below) allow its generation. It merely requires the presence of a classical nucleation inhibitor, e.g. PAA, and yields mineral films / non-equilibrium morphologies with a nanogranular ultrastructure which is indistinguishable from biominerals.



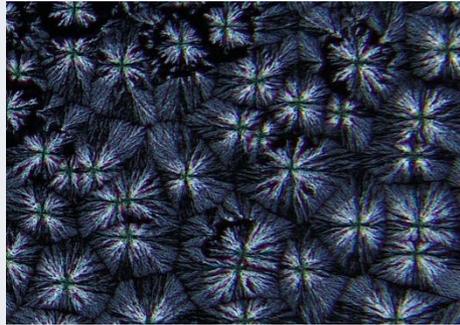
yields films



AFM micrograph

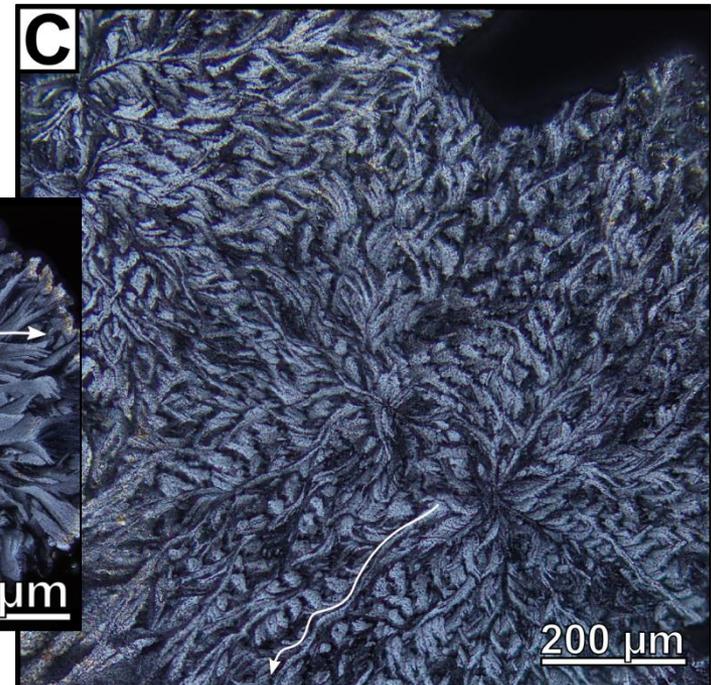
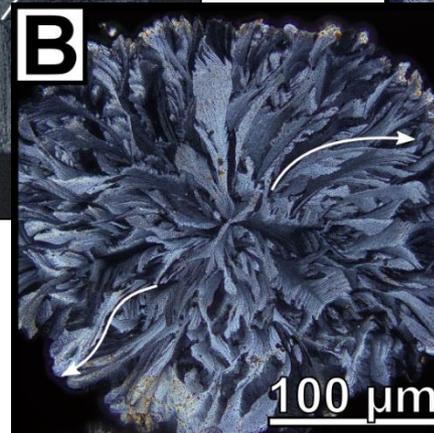
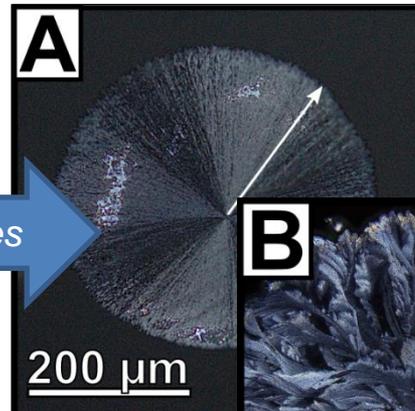
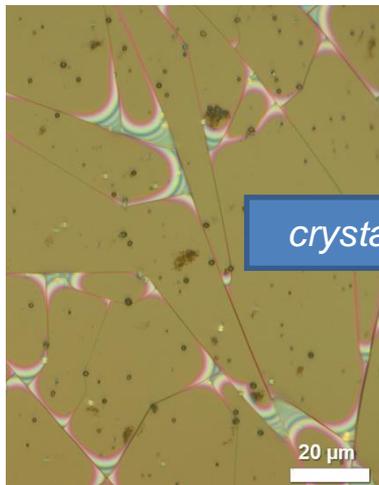


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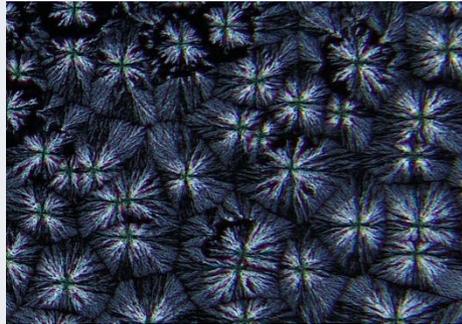
## PILP – polymer-induced liquid-precursor

This nanogranular structure is a hallmark of mineralization pathways via (liquid-)amorphous precursors. At the grain boundaries, foreign organic material is occluded, e.g., the PILP-triggering polymer. This intracrystalline organic matrix gives rise to pseudomorphic (thus shape-preserving) and diffusion-limited phase transformation. The crystallization of the amorphous precursor occurs by spherulitic growth processes.



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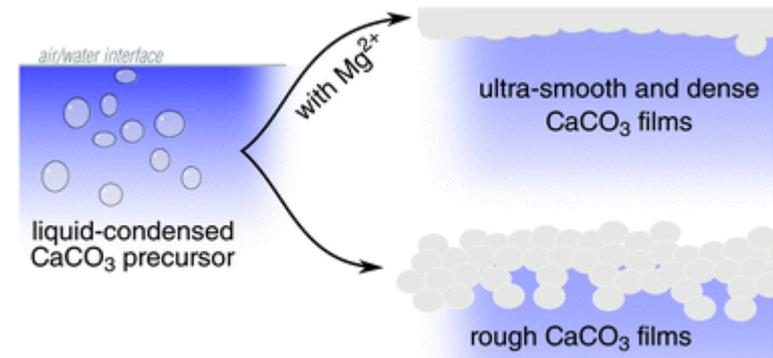
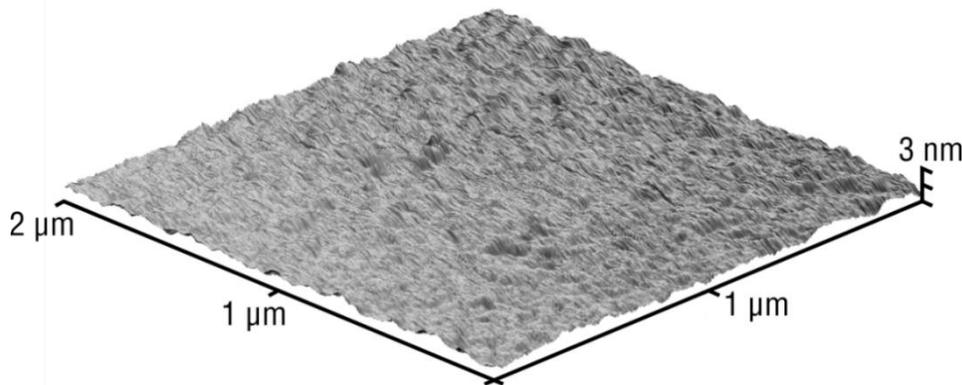
The spherulitic growth process can yield very uncommon mineral textures, which can even feature tilted features which point at autodeformation mechanisms for release of crystallization stress. The pseudomorphic and diffusion-limited conditions strongly affect trace element incorporation.



## PILP – polymer-induced liquid-precursor

Nonclassical crystallization is a particle-accretion process and should thus lead to porous materials. However, in the specific case of PILP, dense mineral films are formed since the assembling particles are liquid – they flow. We showed that under optimal conditions, e.g., in the presence of hydrating Mg, this can even lead to ultrasmooth films with unparalleled low roughness and dense mineral objects.

AFM micrograph of **ultrasmooth** thin film composed of Mg-doped calcium carbonate. 200  $\mu\text{L/ml}$  PAA, 15mM  $\text{MgCl}_2$  + 10 mM  $\text{CaCl}_2$ , 42h



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