

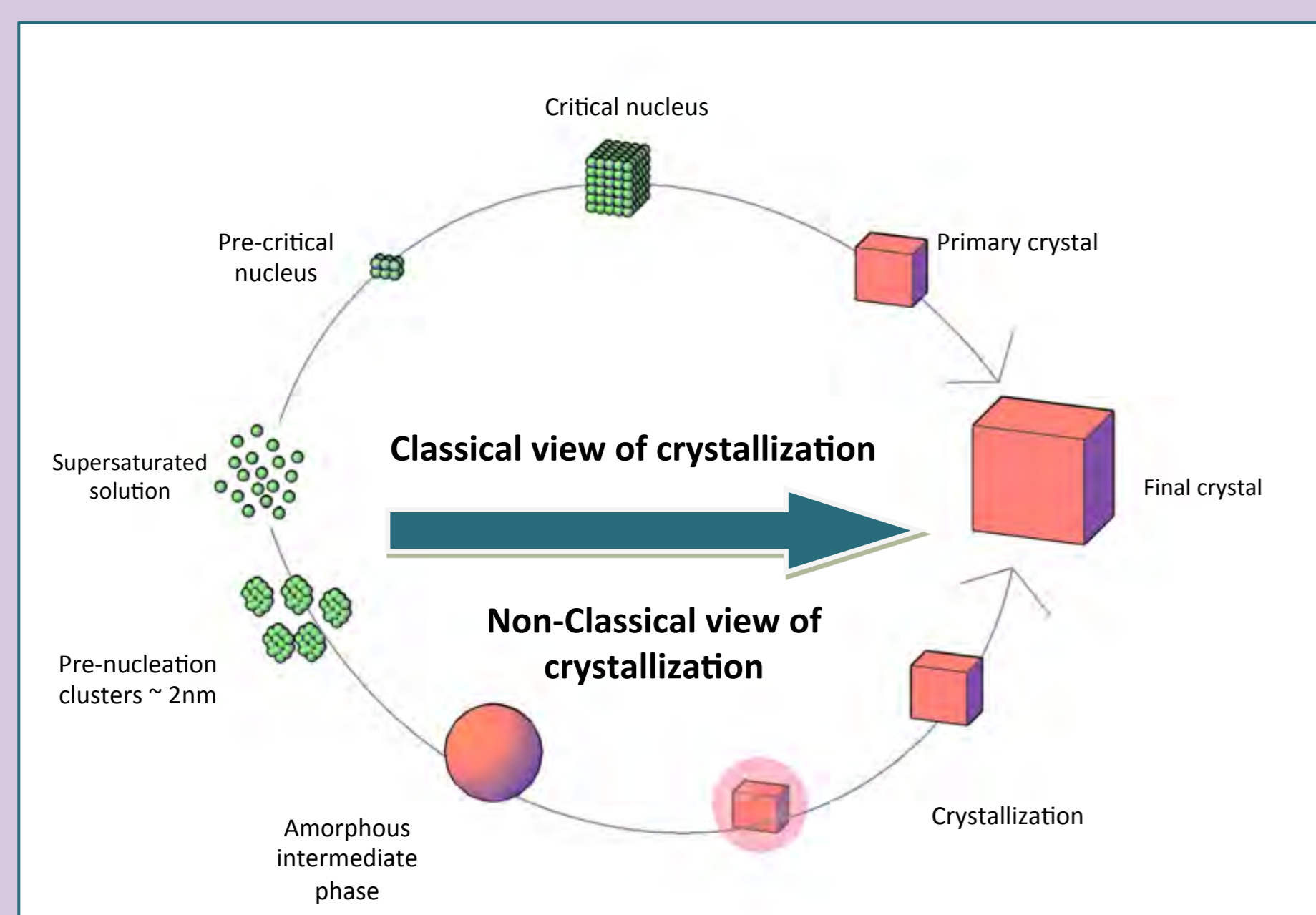
Introduction

Barite (BaSO₄) scale formation is a problem in many industrial processes, especially in oilfields where mixing sea water with reservoir water can result in solid layers of barite scale that can completely block pipes.

Additives that act as inhibitors of barite precipitation are widely used. Different additives can affect different stages involved in crystal nucleation and growth, including the formation of prenucleation clusters, the aggregation of nanoparticles and the precipitation of precursor phases. Thus, the lack of knowledge of the early stages of barite formation limits the selection and use of additives to prevent scale formation.

The aim of this work is to gain a better understanding of BaSO₄ precipitation process before the performance of additives can be assessed.

Classical VS non-classical nucleation theory



Experimental procedure

Transmission electron microscopy (TEM) analysis of barite nanoparticles were carried out using a Philips CM20, operated at 200 kV and a FEI Titan, operated at 300 kV. Prior to TEM observations, 1 ml droplet of 1 mM BaCl₂ solution and 1 ml droplet of 1 mM Na₂SO₄ solution were mixed in a 10 ml beaker. At different times (0 min, 5 min, 15 min, 60 min) barite precipitation was quenched by addition of 8 ml ethanol to replace water molecules absorbed to barium sulfate surfaces and to prevent the solid from dissolving (Ihli *et al.*, 2013). BaSO₄ particles in the water/ethanol dispersions were collected in carbon/Formvar grids for TEM observations and analysis.

Observations

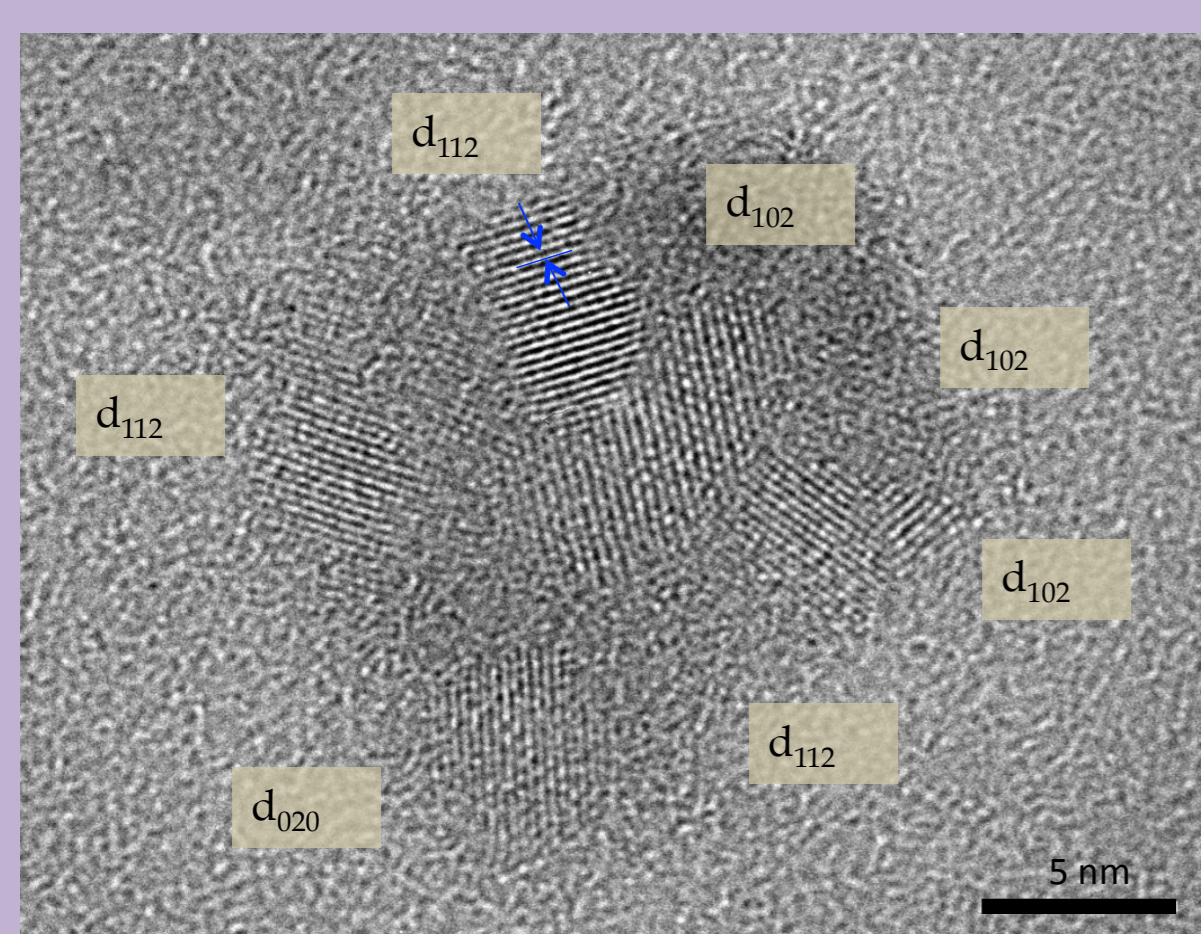


Fig. 1. Set of primary nanoparticles with the characteristic 2.83 Å (d₁₁₂), 3.32 Å (d₁₀₂) and 2.72 Å (d₁₀₀) for barite.

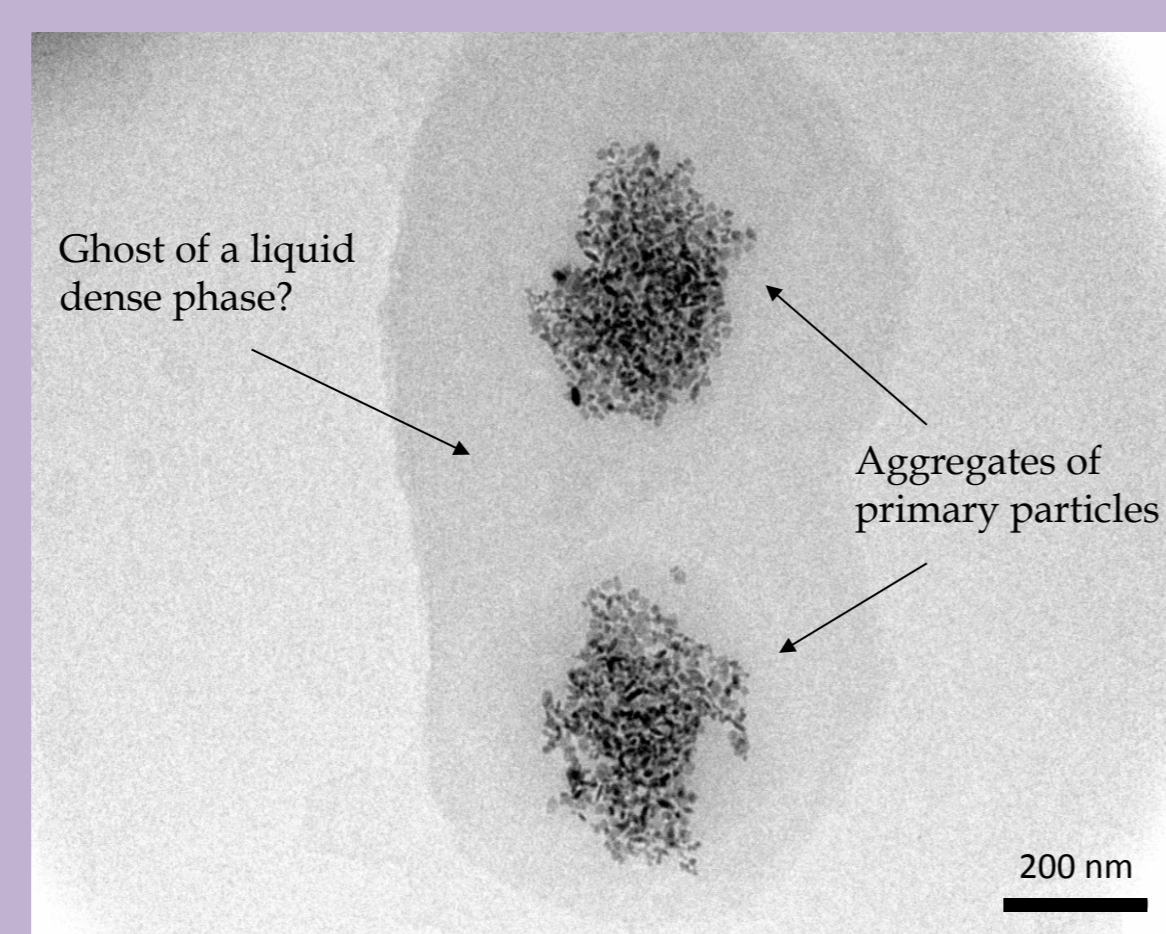


Fig. 2. TEM photomicrograph of nanoparticles of barite formed after a liquid precursor. Nanoparticles within "ghosts" of droplets of a liquid dense phase made up of the solids remnants of the liquid precursor.



Fig. 3. The first image is high angle annular dark field image (HAADF) taken in STEM mode using FEI-TITAN. The line in blue delimited the aggregates of barium sulphate nanorod particles and the yellow line is around the "ghost" area. EDX mapping carried out in this area. Ba and S are mainly concentrated in the "ghost" area.

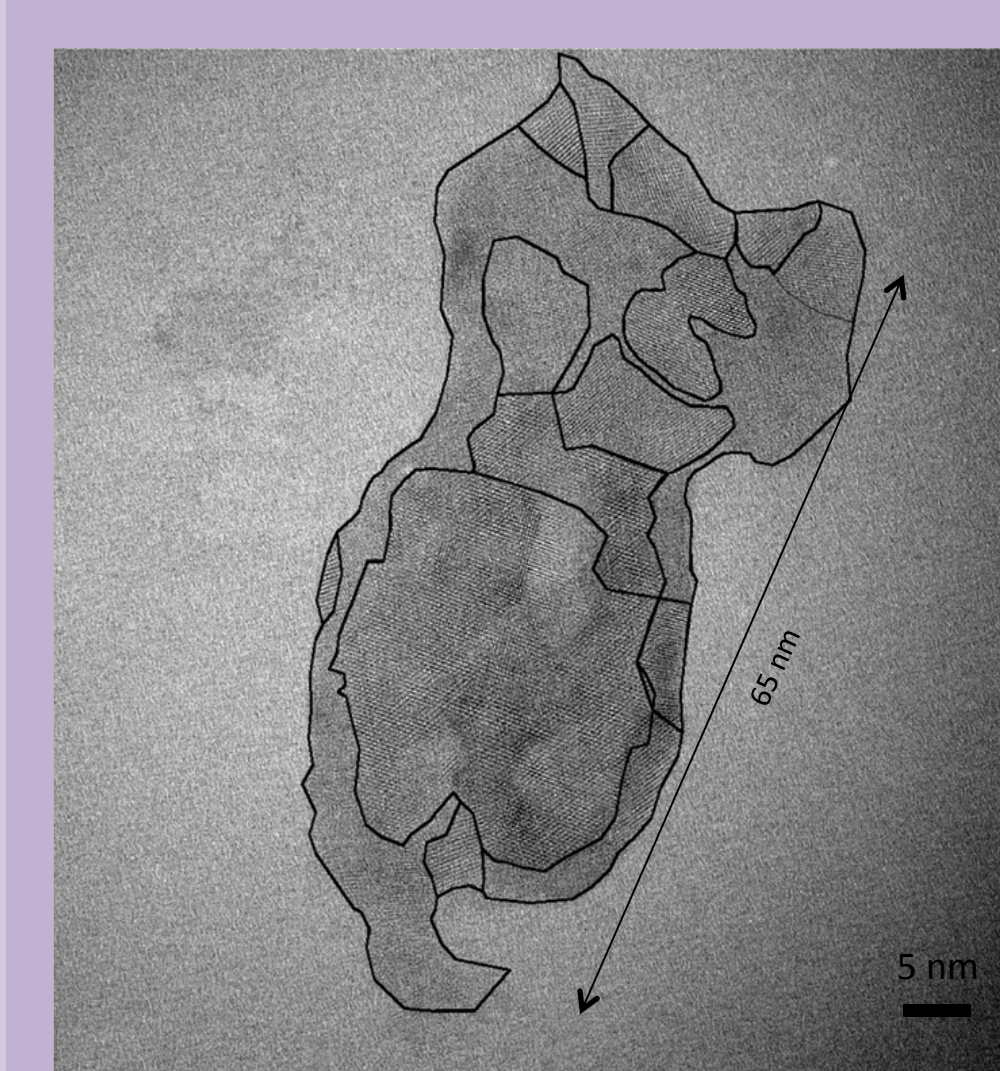


Fig. 4. TEM photomicrograph of a BaSO₄ nanoparticle. The contour of domains with lattice continuity is delimited by the black lines.

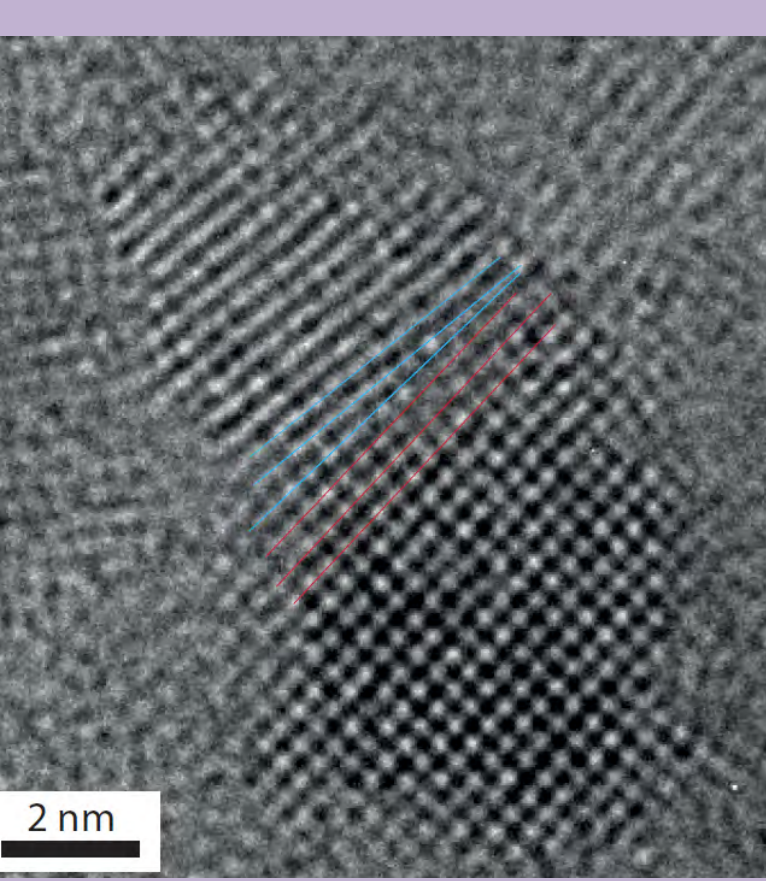


Fig. 5. Defect formation during oriented aggregation of primary BaSO₄ particles. Edge dislocation formed as a consequence of the slight misalignment of the primary particles during the oriented aggregation process.

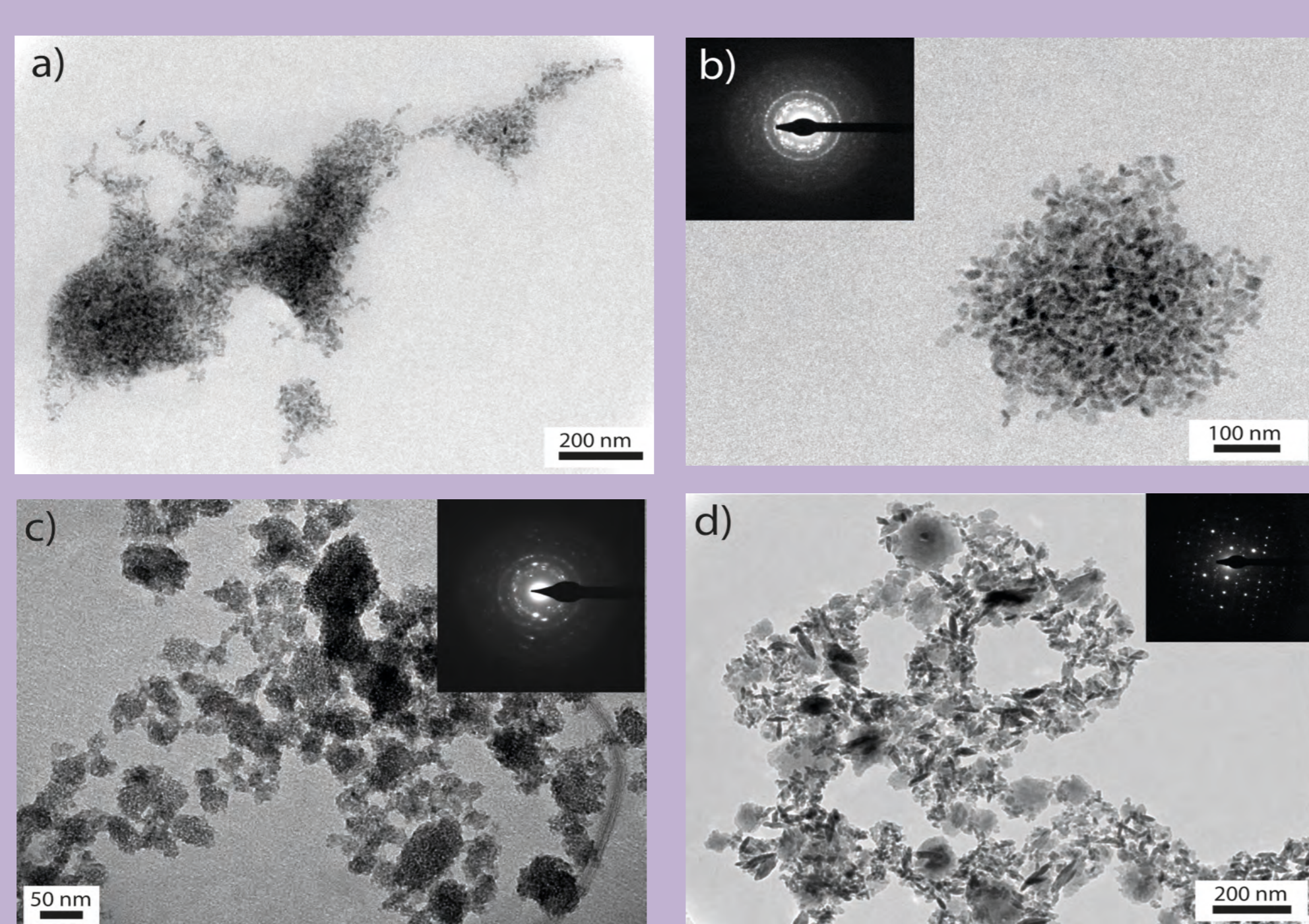


Fig. 6. Aggregates of nanoparticles of different shapes, sizes and degree of orientation. SAED patterns are shown in the insets

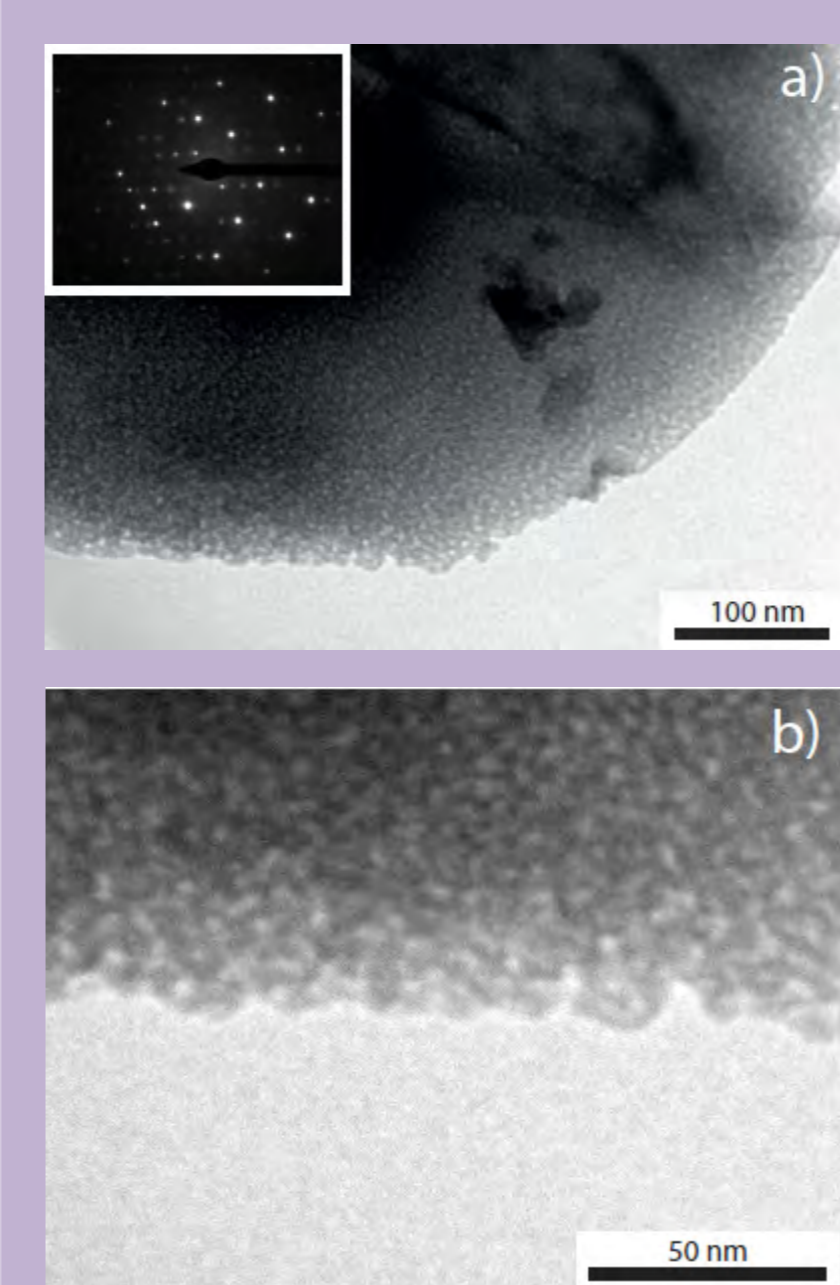


Fig. 7. Second step of oriented aggregation. a) Single crystal of barite (see SAED pattern in the inset), formed by oriented aggregation and showing nanoporosity. b) Detail from a).

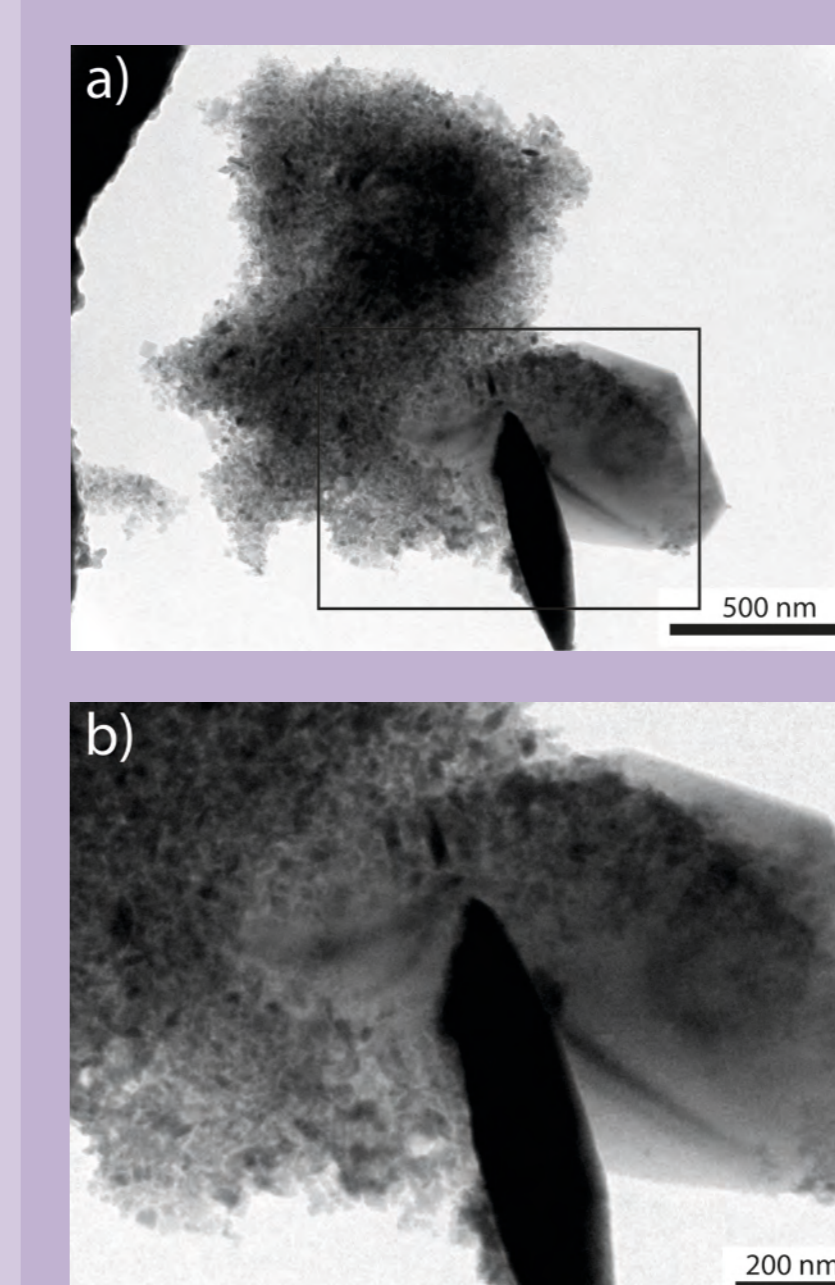


Fig. 8. Compact, micron-size aggregate of randomly oriented nanoparticles in contact with a monocrystalline particle. a) Detail from a) showing an area of the monocrystalline particle in which the aggregation process has not finished.

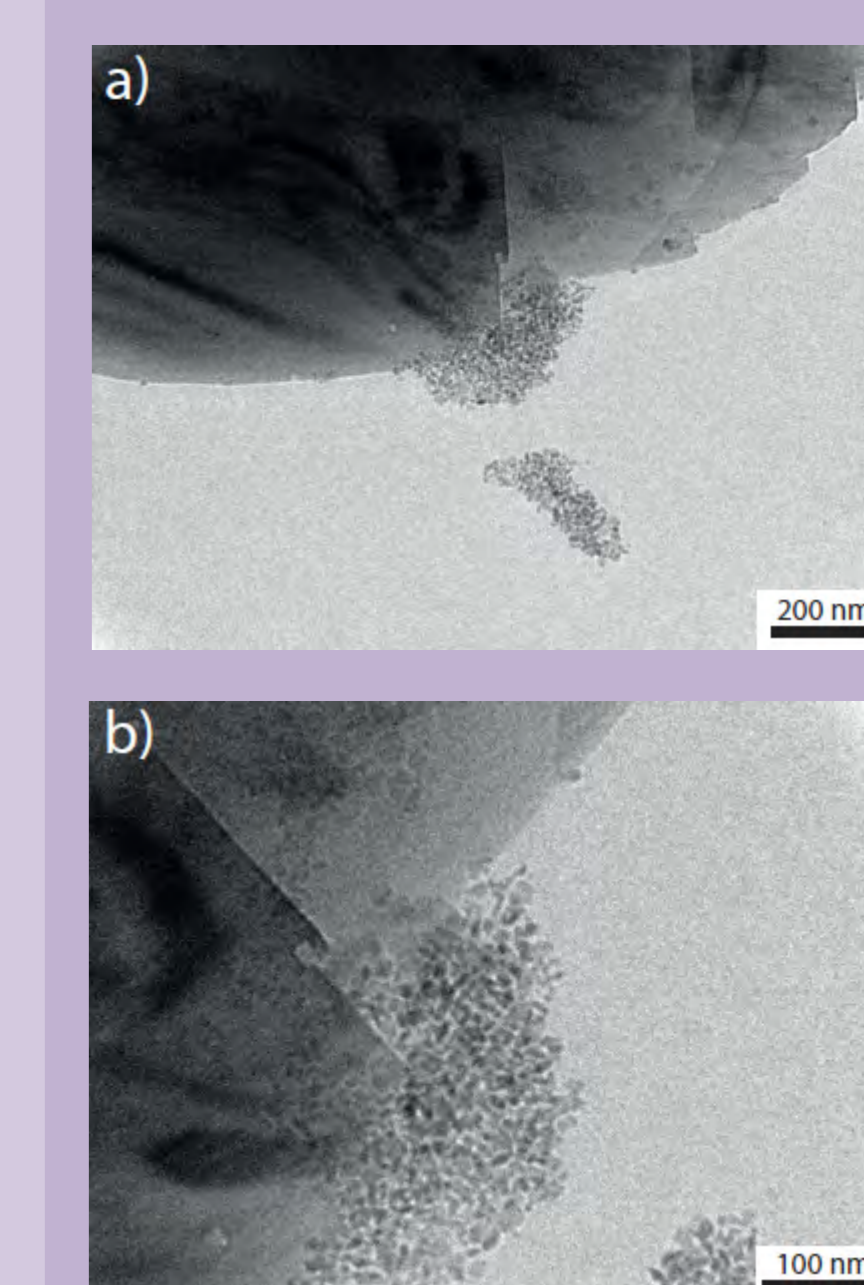


Fig. 9. Single crystal and polycrystalline aggregates of barite. b) Detail from a) showing the attachment of the aggregate to the monocrystal.

Conclusions

- Barite precipitation at high supersaturation follows a **non-classical** crystallization route.
- Evidence of **liquid-liquid spinodal decomposition** previous to barite nucleation is observed (fig. 2 and fig. 3).
- **Two hierarchical** levels of **aggregation** are detected:
 1. Aggregation of 5-10 nm particles to form larger, but still nanometer-sized (20-60 nm) particles (fig. 4).
 2. Aggregation of these particles to produce bigger crystals (200-500 nm) that can be observed in fig. 6.
- **Ripening processes** in which large crystals seem to grow at the expense of aggregates of nanoparticles are observed (fig. 9).
- There is **no** evidence of an amorphous or crystalline **precursor phase** previous to crystalline barite. The 5-10 nm primary particles were already crystalline (fig. 1).