

Early stages of barium sulphate precipitation

Barite is a problematic scale mineral in many industrial processes such as oil recovery. Commonly, different additives are used as inhibitors of scale formation and their performance depend on the type of additives that are used. A lack of mechanistic understanding of the early stages of barite formation limits the use of additives as crystallization inhibitors to prevent scale formation. To our knowledge there are not studies on early stages of barium sulfate precipitation thus it was decided to attempt to gain a better understanding of this process and to be able to understand in a near future how inhibitors act and modify barite precipitation.

With the aim of addressing all of these questions, HRTEM quenching experiments were carried out using Philips CM-20 and FEI-TITAN transmission electron microscopes.

1) Nanodomains of 5-10 nm: nanoparticles

The existence of crystalline nanodomains 5-10 nm in diameter was observed (Fig.1). These particles were randomly oriented but in the image we can see that many of them exhibit the same “d” spacing corresponding to 112 and 120 of barite. The size of these primary nanoparticles is in good agreement with bassanite nanoparticles found in gypsum formation by [Van Driessche and co-workers \(2012\)](#).

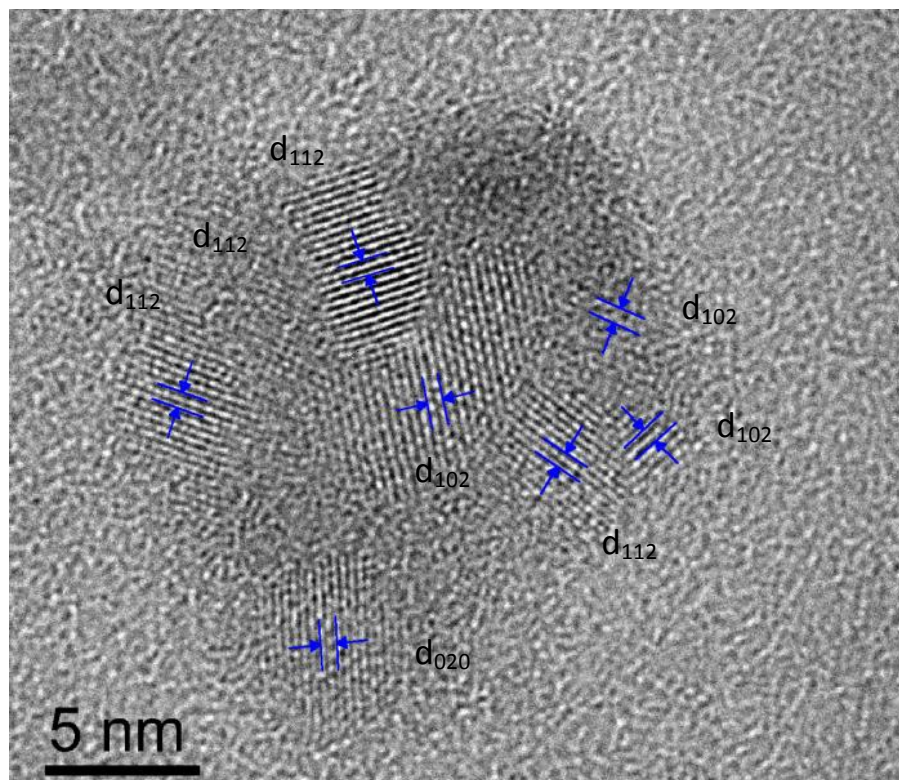


Figure 1. Set of primary nanoparticles with the characteristic 2.83 Å (d_{112}), 3.32 Å (d_{102}) and 2.72 Å (d_{020}) for barite. The attachment of several primary nanoparticles yields to larger, but still nanometer size particles.

2) Secondary structures of few to a hunder of primary units: nanorods

Secondary rice-shaped structures (nanorods) of 20-100 nm size were found as another stage of barium sulphate precipitation process. In HRTEM image (Fig. 2) we can distinguish different nanodomains corresponding with different primary nanoparticles that attached to each other to form a nanorod particle. This has been already reported by Li and co-workers (2012). They carried out high-resolution transmission electron microscopy using a fluid cell to directly observe the oriented attachment of iron oxyhydroxide nanoparticles. Nanoparticles rotate and interact until they reach a perfect lattice matching at time of attachment.

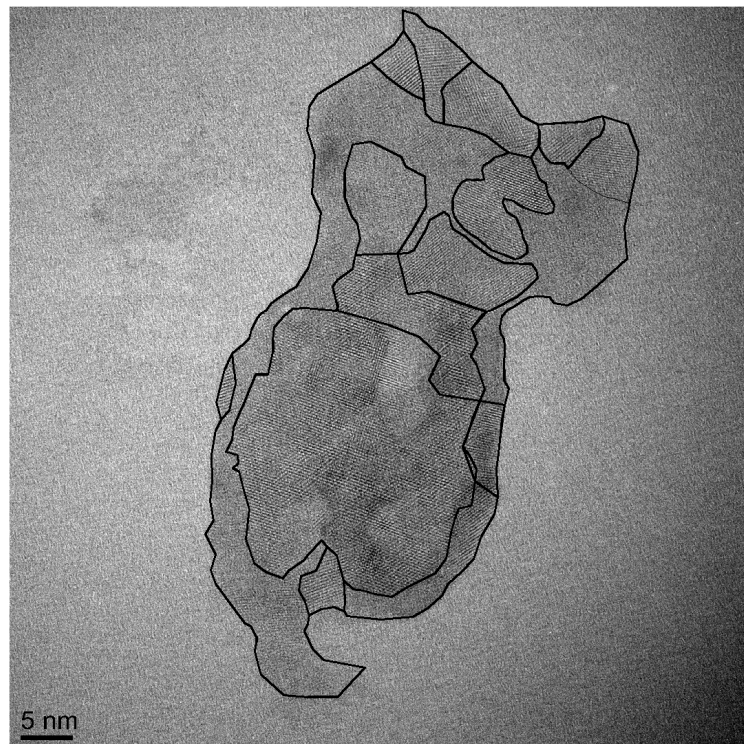


Figure 2. Nanorod particle formed from the assembly of primary nanoparticles. Different nanocrystalline domains have been delimited in the image

In figure 3 the contact between two different nanoparticles and the edge defect formed in the interface can be seen. A slight misalignment of the nanoparticles during the attachment process can result in defect formation in the interface. Both shared the same “d” spacing 2.83 Å corresponding to 112 of barite but the angle of the lattice fringe is slightly (40° and 46°) different at the moment of attachment which result in defect formation.

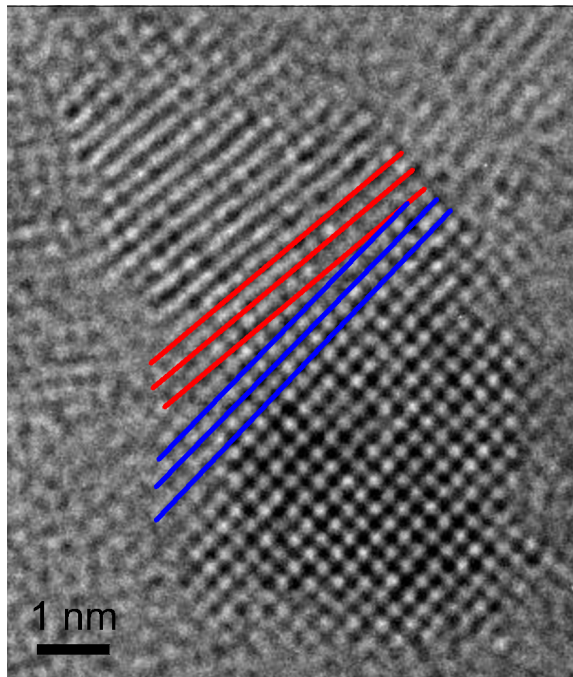


Figure 3. HRTEM image of two attached BaSO₄ nanoparticles. The edge dislocation at the interface is highlighted in red and blue for clarity.

3) Aggregation of these secondary structures:

As stage three of barite formation we found the aggregation of these nanorods particles to form a crystal (fig. 4). Different types of aggregates were observed: branched aggregates and nanorods aggregates with straighter edges and more crystal shape.

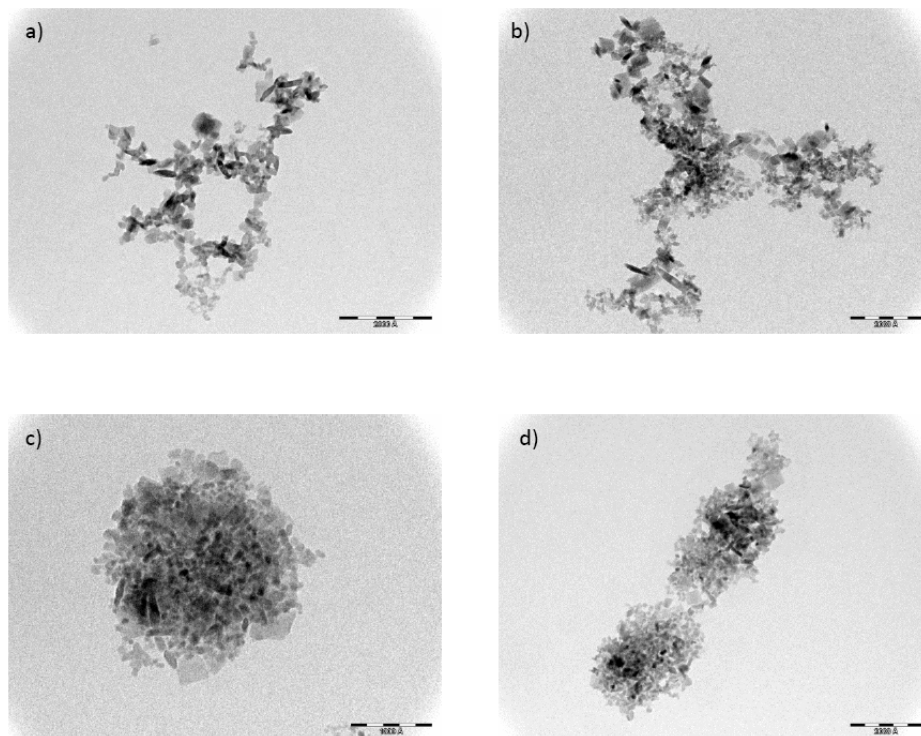


Figure 4. Different types of nanorods aggregates found. A) and b) fractal-like aggregates. C) and d) round aggregates becoming more crystal shape.

4) Ostwald ripening

It was observed that small particles when they are in the vicinity of larger ones they disappeared (fig. 5). The big particle grows at expense of the small particle. This is known as Ostwald ripening and it has been observed in the studies of other mineral systems in which oriented attachment was showed to be the dominant process ([Li et al. 2012](#)).

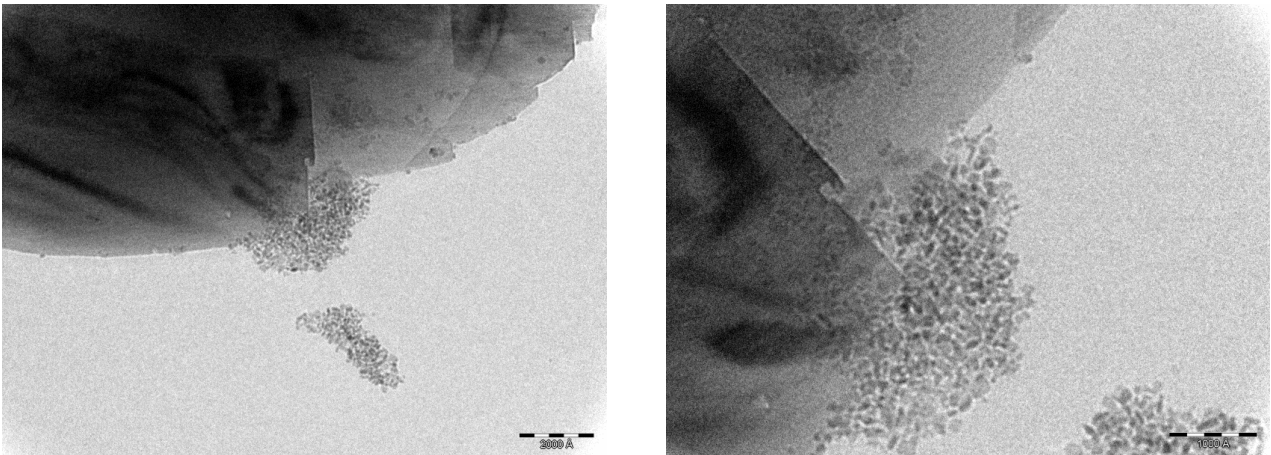


Figure 5. When nanorods are in the vicinity of a crystal the last one grows at expense of the small particle. This is known as Ostwald ripening.

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