

Spherulitic CaCO₃ from lacustrine sediments (Bathgate, Scotland) and its formation mechanism

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Spherulitic CaCO₃ is widely found in nature, especially in lacustrine and marine environments, and their formation mechanisms remain debatable. In this work, we revealed the microstructures of the spherulites and their surroundings collected from East Kirkton Quarry, Bathgate. We also synthesised spherulitic CaCO₃ in various environments, in order to propose a formation mechanism of these crystals. The microstructures and local compositions of the spherulites were studied using SEM, EDX, XRD and HRTEM. The naturally occurring spherulites are made up of radially arranged calcitic micro-rods (~ 150 μm in length and 10-20 μm in width). Silicates were detected in the centre and in the gaps of the micro-rods. Mg-containing silicates are also the main component in the surroundings.

In the syntheses, nanocrystallites of calcite formed in gel mixture of alginate and stevensite. The soft substrate allowed the nanocrystallites to move and rotate to achieve self-orientation and aggregation.

A multistep formation mechanism of spherulitic CaCO₃ was proposed. (1) Formation of a gel of organic/inorganic composite. (2) Nucleation and growth of nanocrystallites of calcite inside the gel. (3) Aggregation of the crystallites into spherulites inside the gel. To achieve this phase separation, migration of the crystallites in the gel must be allowed. Therefore, the property (or softness) of the gel is critically important. We also believe the dipole field of calcite crystallites is the driving force of their aggregation into the radially located microrods, similar to the formation of spherulites in other environments.[1]

[1] (a) S.T. Wu, C.-Y. Chiang, W.Z. Zhou, *Crystals* 7(10), 319 (2017); (b) H.F. Greer, M.-H. Liu, C.-Y. Mou, W.Z. Zhou, *CrystEngComm* 18, 1585 (2016).