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Calcium carbonate precipitates are prepared from a solution of CaCl_2 and K_2CO_3 in the presence of polyacrylic acid. The effect of polyacrylic acid incorporation in the [20 – 80°C] temperature range on crystal morphologies and CaCO_3 precipitated polymorph concentrations are investigated using scanning electron microscopy and X-ray diffraction quantitative microstructural and phase analysis. Large changes in morphology and phase proportions are observed in the presence of polyacrylic acid, which strongly depend on the solution temperature. While crystallization of vaterite is favoured in presence of polyacrylic acid up to 50°C, it is largely destabilized at higher temperatures. Our process also enables the elaboration of particles in the range 10-20 nm.

Preparation and characterisation method

Doubly dionized water was used to prepare a 0.1M CaCl_2 and 0.1M K_2CO_3 aqueous solutions. The CaCl_2 solution is divided into two parts, one of them is mixed to PAA in the proportion 0.5mg of PAA in 5ml of CaCl_2 . The two solutions are mixed at different temperatures, 20°C, 50°C and 80°C. The solid precipitates, obtained immediately after mixing the two solutions, were collected using filtration through a cellulose membrane filter, and rinsed three times with doubly dionized water. CaCO_3 precipitates were dried under vacuum at 100°C for 1 hour, resulting in finely grained particles.

All the samples were examined using scanning electron microscopy (SEM) (Zeiss electron microscope). X-ray diffraction (XRD) patterns were collected on a Phillips X'PERT powder diffractometer using the Cu-K α radiation. The volumic ratio of calcite, vaterite and aragonite phases of the samples were calculated using the quantitative phase analysis based on the Rietveld method [1-2], implemented in the MAUD software [3,4].

Effect of PAA on CaCO_3 polymorphs at 25°C

Figures 1a and 1b show SEM micrographs of CaCO_3 particles obtained at 25°C without PAA. The average edge and diameter of rhombic calcite (fig 1a) and spherical vaterite (fig 1b) particles are 3 μm and 4 μm respectively. The volume fraction of calcite is 71(1) % and hence 29(1) % of vaterite with no aragonite (Table 1). The average size of the crystallites is 870(5) Å for Calcite and 161(3) Å for vaterite. The observed vaterite spherical particles, of typically several micrometers in diameter, exhibit a very porous substructure (Fig. 1a). This original substructure accommodates a quite perfect sphere with acicular crystallites disposed radially, and having typically a mean diameter of 50 to 100Å and a total length around 500Å. This explains a mean coherent size around 161Å determined from the x-ray diffraction patterns, and consequently points out that these acicular crystals are composed of only one coherent domain on an average. The calcite crystals exhibit step-like edges due to the interpenetration of the constituting rhombs (fig 1c).

In presence of PAA at 25°C (figs 1c and 1d), we observe modifications of the previous calcite and vaterite crystals. On one hand, the calcite rhombs, although exhibiting less interpenetration, show less regular faces with more steps and porosities. On the other hand, the vaterite particles agglomerate in overall raspberry shapes of about 15 μm in widths. The calcite particles have grown to around 10 μm edged rhombs (fig 1d). The difference in particle shape is clearly due to the presence of PAA in the solution. Under PAA addition at this temperature, calcite is destabilized in volume but results in averagely 10 times larger rhombs with less acute edges and faces, and correlatively vaterite growth is favoured up to 50% in volume, but with deformed spheres that glue together in raspberry-like conglomerates. The Rietveld refinement (fig 4b) provides with crystallite sizes of 2960(99) Å and 203(3) Å for calcite and vaterite respectively. This indicates clearly that the presence of PAA in soft enough conditions ($T=25^\circ\text{C}$) helps both calcite and vaterite growing, with an overall volumic balance in favour of vaterite. This change in crystal habits is accompanied by a reduction of cell parameters for calcite (with a 0.075% volume decrease, Table 1) as a result of the PAA-calcite interaction, while vaterite unit-cell increases in volume up to 0.23%.

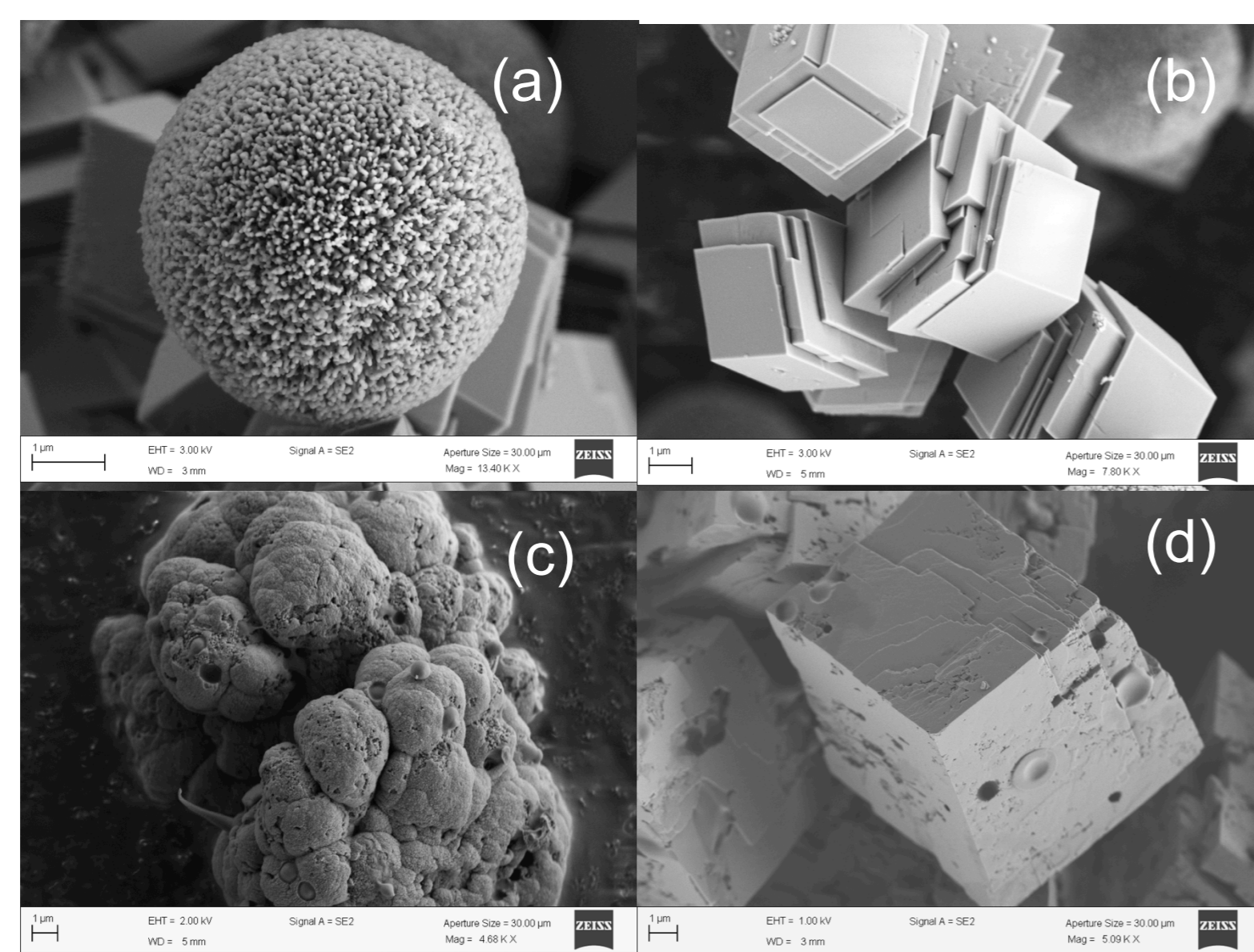


Figure 1: SEM backscattered images of CaCO_3 particles synthesized at 25°C without PAA incorporation (a) vaterite (b) calcite and with incorporation of PAA (c) vaterite (d) calcite.

Effect of PAA on CaCO_3 polymorphs at 50°C

Figure 3a shows the morphology of CaCO_3 particles produced at 50°C without PAA. At this temperature, a mixture of three types of particle shapes is observed: calcite rhombs exhibiting an average edge size of nearly 5 μm (fig 3c), raspberry agglomerates of vaterite with an average diameter of 10 μm (fig 3a) and cauliflower-like shaped particles of aragonite with an average diameter around 20 μm (fig 3b). The rhombic calcite particles exhibit more regular shapes than at 25°C without PAA, and in particular interpenetration of rhombs is no longer visible. This Face Centered Erosion (FCE) could come from a larger solubility due to temperature, eventually helped by the presence of specific crystalline defects in the centers of the rhomb faces. X-ray quantitative phase analysis (fig 4c) indicates 47(3)% of calcite, 46(3)% of vaterite and 7(3)% of aragonite, pointing out that calcite transformation is operated for 2/3 and 1/3 approximately into vaterite and aragonite at this temperature. The crystallite sizes are 999(18) Å for calcite, 216(5) Å for vaterite and 433(55) Å for aragonite. The increase in mean crystallite sizes of calcite and vaterite (around 15% and 34% respectively) is neatly in favour of vaterite formation compared to the sample elaborated at 25°C without PAA. This is linked to the progressive equilibrium shift towards vaterite formation at a larger temperature.

At this temperature of 50°C, PAA incorporation transforms the cauliflower shaped particles of aragonite into dendritic particles with an average length of 10 μm (fig 2e) and the raspberry-like vaterite opens into flowerslike conglomerates (fig 2d) with an average diameter of 5 μm . A small amount of rhombic calcite is observed (fig 2f), on which we see again the porosity observed at 25°C in presence of PAA, together with the FCE effect. This means that FCE is not influenced by PAA but temperature, the former influencing more the internal crystallization of the polymorphs. Quantitative phase analysis (fig 4d) shows a strong decrease of the volume fraction of calcite in favour of vaterite, and to a lesser extent of aragonite. We can also see a significant increase of the crystallites size of calcite (3900(350) Å) and vaterite (438(6) Å) which confirms the beneficial effect of PAA incorporation for crystal growing, as already observed at 25°C. A decrease in calcite unit-cell volume of 0.32%, while a 0.1% increase of the unit-cell volume of vaterite are observed, and aragonite unit-cell remains unaffected in our resolution limit.

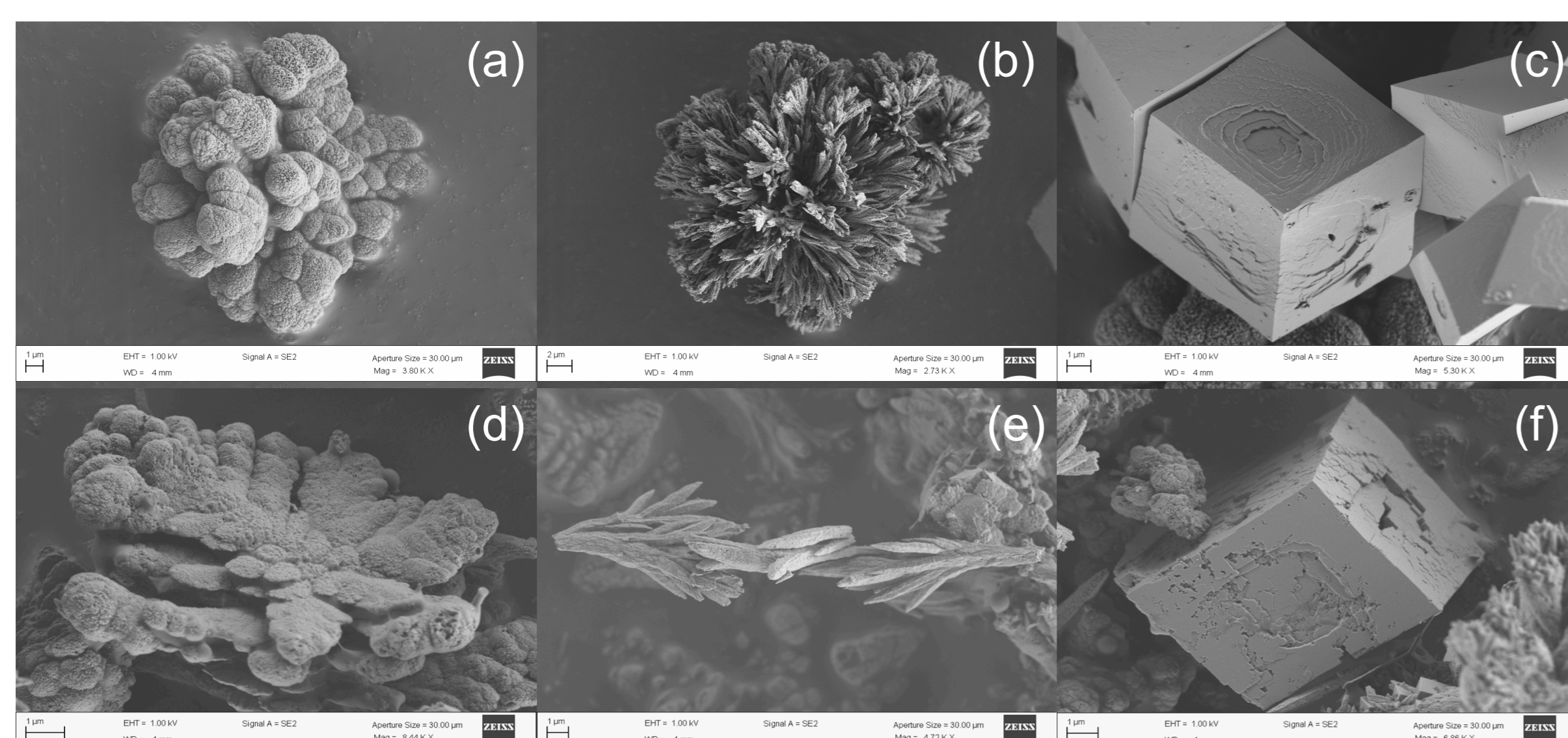


Figure 2: SEM backscattered images of CaCO_3 particles synthesized at 50°C without PAA incorporation (a) vaterite (b) aragonite (c) calcite and with incorporation of PAA (d) vaterite (e) aragonite (f) calcite

Effect of PAA on CaCO_3 polymorphs at 80°C

Fig. 3a shows the morphology of CaCO_3 particles at 80°C without PAA. Aragonite cauliflowers continued to grow into acicular crystals at this temperature, with an average length of typically 5 to 10 μm , and a smaller mean dimension less than 1 μm . A small amount of calcite particles with a perfect 2 to 4 μm -edge rhombohedral shape and a small amount of vaterite exhibiting a sponge-like shape (fig 3b) are also observed. The volume fractions are (fig 4e) 6.9(1) %, 12.7(6) %, and 80(7) % for calcite, vaterite and aragonite respectively. As usual at larger temperatures, aragonite formation is favoured at the expense of the two other phases, linked to the increase in calcium coordination at larger temperatures. The cell parameters of the aragonite are the closest to the bulk parameter values, as expected for its better crystallization at this temperature.

With PAA (fig 3c), aragonite needles are cut into smaller pieces of around 4 μm in length and a small amount of calcite and vaterite are observed, with a global further increase of aragonite content to 89(1) % in volume. The crystallite sizes are lowered with PAA incorporation for calcite and vaterite, correlatively with their destabilization at this temperature (this size decreasing is already observed without PAA compared to the 50°C sample). This destabilization is also underlined by the unit-cell decrease of calcite, whereas the unit cell volume of the remaining vaterite still increases in presence of PAA, anisotropically like at 50°C.

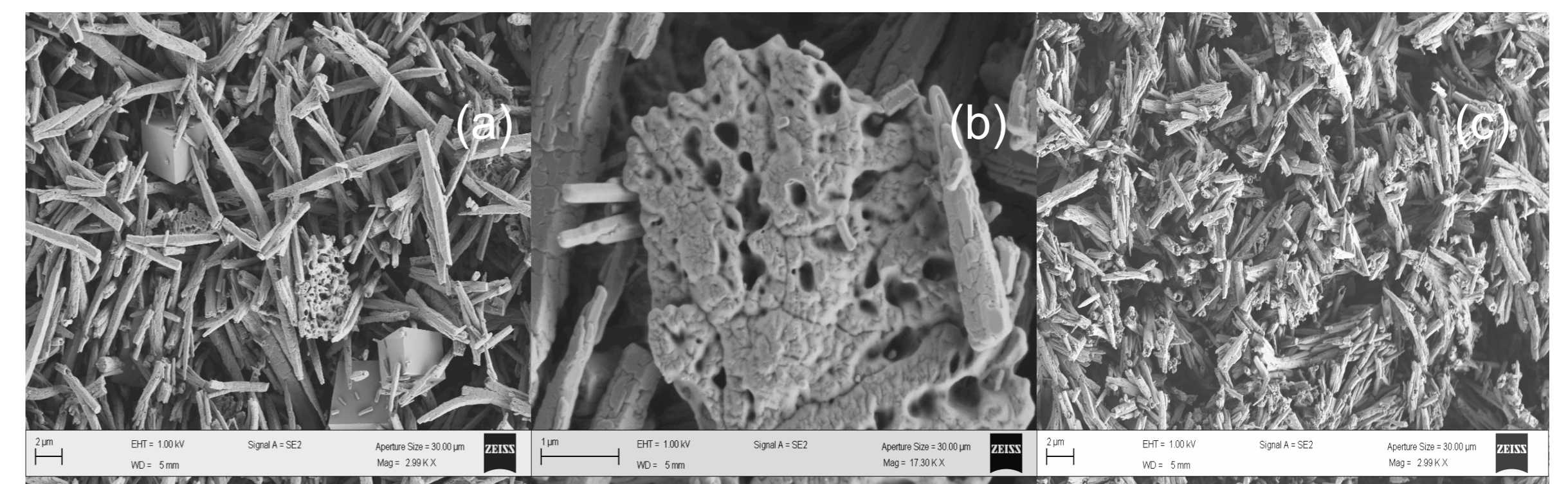


Figure 3: SEM backscattered images of CaCO_3 particles synthesized at 80°C without PAA incorporation (a) zoom in vaterite particle (c) with incorporation of PAA vaterite.

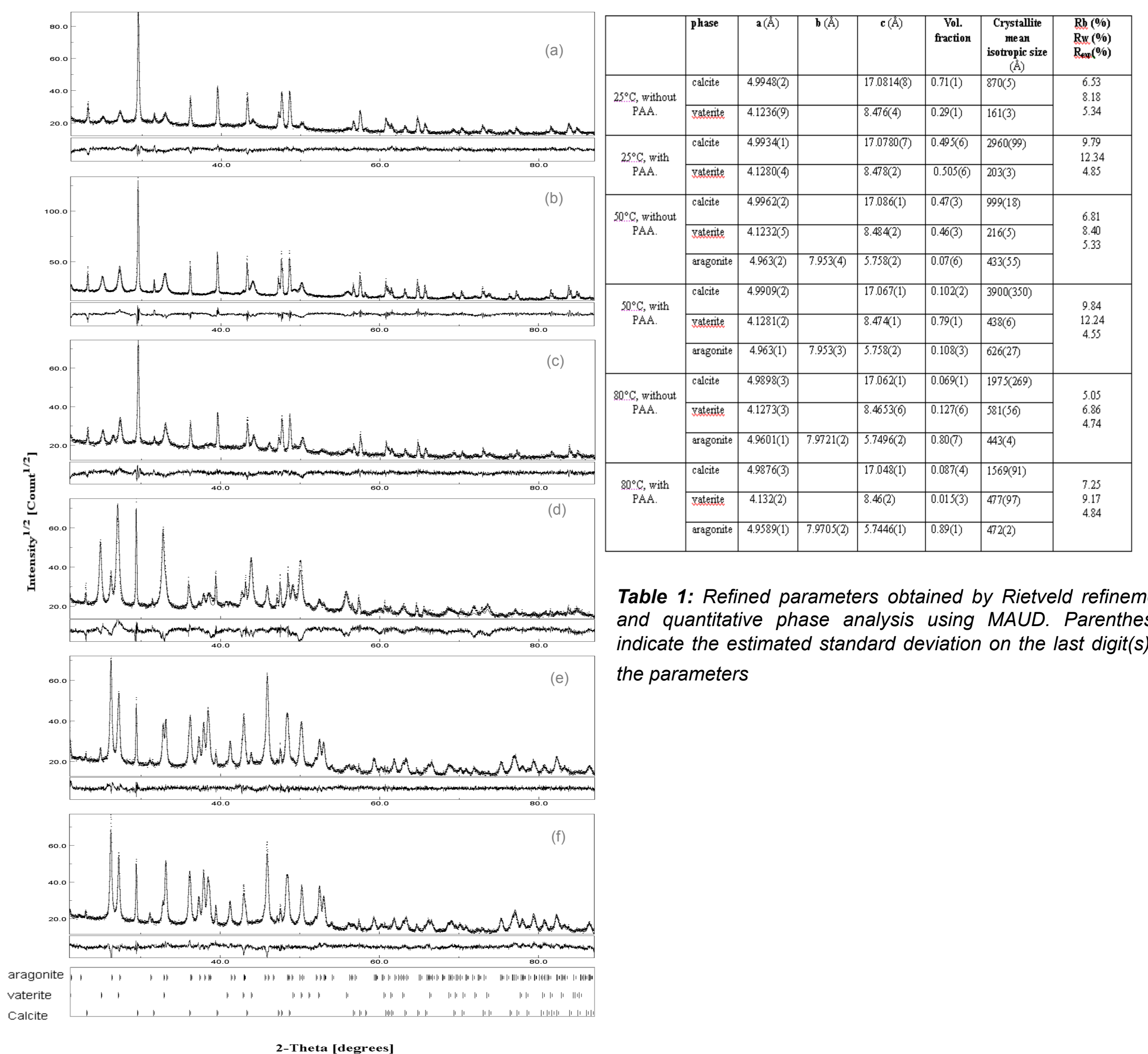


Table 1: Refined parameters obtained by Rietveld refinement and quantitative phase analysis using MAUD. Parentheses indicate the estimated standard deviation on the last digit(s) of the parameters

Figure 4: Calculated (lines), observed (dots) and difference curves after the last cycle of Rietveld refinement for quantitative phase analysis (a) 25°C without PAA (b) 25°C with PAA (c) 50°C without PAA (d) 50°C with PAA (e) 80°C without PAA and (f) 80°C with PAA.

Conclusions.

In this study Polyacrylic acid and temperature have been used as templates to induce CaCO_3 crystal growth. Various morphologies of CaCO_3 particles have been elaborated (rhombohedral, spherical, cauliflower, needles- and sponge like) in the 25-80°C temperature range by a simple method, which provides an easy route for the monitoring of CaCO_3 habits. Our results indicate that PAA can shift the chemical equilibrium between the allotropic forms of CaCO_3 , hereby increasing vaterite and aragonite fractions depending on the temperature used.

We showed also in this work that PAA can control crystal sizes, quality and shapes, via processes that also modify unit-cell parameters of the respective phases. There is then a strong interaction of PAA with CaCO_3 that could help understanding the growth of natural biominerals.

References

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