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|                          | <b>Experiment title:</b><br><i>Pore sintering during vaterite to calcite solid-state transition observed by CXDI</i> | <b>Experiment number:</b><br><b>CH-5277</b> |
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**Report:**

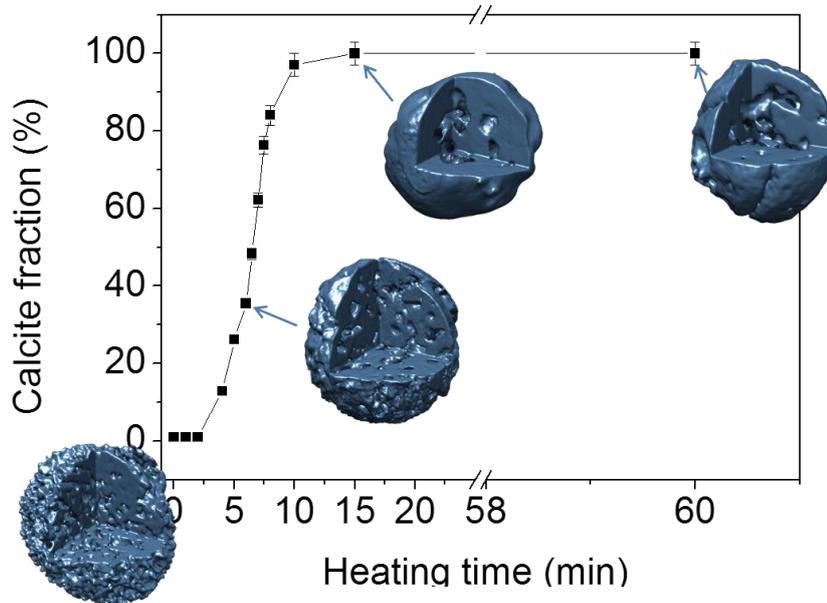
**Abstract:** Calcium carbonate exists in three allotropic forms: calcite, aragonite and vaterite. Particles of vaterite, the least stable allotropic form, have a spheroidal morphology with a high porosity. This last property can be utilized in different fields of applications (plastics, papers, paints). Yet such particles suffer from a major drawback when they stay in contact with water.<sup>1</sup> They transform into rhombohedral and non-porous calcite particles by a *dissolution-recrystallization* process.<sup>2-3</sup> To circumvent this problem, dry vaterite particles can be stabilized by a thermal annealing at 420°C during which calcite is formed *via a solid-state transformation*.<sup>4-5</sup> The aim of this study is to follow step by step the evolution of this solid-state transition by carrying out CXDI of vaterite particles at different stages of annealing in order to unveil the mechanism of rearrangement during the vaterite-calcite solid-state transition.

**Sample Preparation:** The initial vaterite particles were prepared by quickly mixing 500mL of an aqueous solution containing 0.5M of Ca<sup>2+</sup> and 500mL of an aqueous solution containing 0.5M of Na<sub>2</sub>CO<sub>3</sub>. The solution was stirred during 2 min. Then the suspension is filtered and dried at 60°C. The phase transformation is initially monitored ex-situ by heating the powder at 420°C during different duration. Then, the particles are deposited on Si<sub>3</sub>N<sub>4</sub> membranes for analysis. For the in-situ analysis, the initial vaterite particles are deposited on a fast scanning chip nanocalorimeter device heated at 400°C within a few seconds with 100°C/s heating rate.

**Methods:** To analyze the phase transition, CXDI measurements were performed. The measurements were carried out at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a monochromatic X-ray beam of energy 8.1 keV.

**Results:** The heated particles were analyzed by X-ray diffraction to determine the kinetics of transformation of the vaterite into calcite (Fig.1). It is shown that at 420°C, the vaterite transforms to calcite after 10 min of

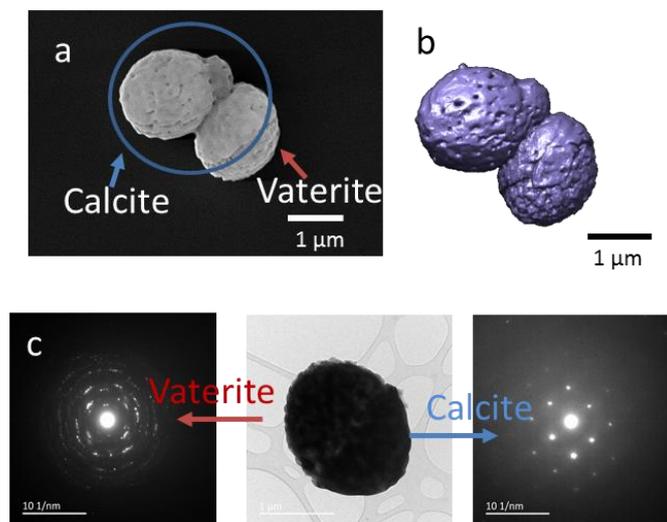
heating. To determine the evolution of porosity inside the particles during the transformation, 10 samples were analyzed by CXDI: initial particle and particles after 5, 6.30, 8, 10, 20, 40, 60, 300 and 1440 min of heating. Some results are summarized in Fig. 1.



**Figure 1:** Kinetics of the vaterite to calcite transformation. CXDI images of  $\text{CaCO}_3$  microspheres obtained after different heating times.

The results obtained by CXDI allow determining in a quantitative way the porosity and surface area of the studied particles. It is shown that the porosity is quite similar for all particles (between  $18 \pm 5$  and  $25 \pm 8\%$ ). However, the specific surface of particles decreases with increasing of heating time. The particles heated during 24h had a specific surface of  $2.8 \text{ m}^2/\text{g}$  instead  $9.2 \text{ m}^2/\text{g}$  for the initial particles.

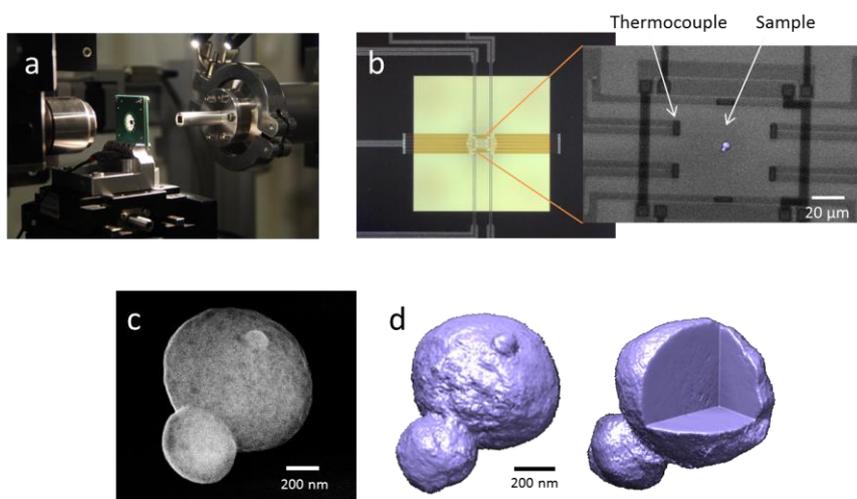
We show that the transformation of vaterite to calcite is progressive and not homogeneous inside the particle. Indeed after 6.30 min, we can clearly observe the existence of two structures (vaterite and calcite) in one particle (Fig 2a,b). This double structure is noted in SEM and CXDI images. The existence of particles having polycrystalline vaterite and monocrystalline calcite structures after 6.30 min of heating was also confirmed by TEM and electron diffraction (Fig.2c).



**Figure 2:** Existence of particles with two structures imaged by: (a) SEM, (b) CXDI, (c) TEM images and electron diffraction.

During ex-situ measurements, it was only possible to study the transformation on different particles. Yet it was interesting to analyze in a quantitative way how the porosity and specific surface of one particle could change during the heating. For this, in-situ experiments were performed by using a fast scanning chip nanocalorimeter<sup>6</sup> working at 400°C with the heating rate of 100°C/s (Figure 3a). In this case, the particles were also deposited on the Si<sub>3</sub>N<sub>4</sub> membrane of the microrcalorimeter (Figure 3b). To resist the thermal shock, the membrane of the chip was thicker and reinforced with SiO<sub>2</sub> so that the thickness of membrane was 1 μm instead of the usual 100nm used for ex-situ experiments. Additionally, as one can see on Figure 3b, a metallic thermocouple is located near to the sample, which gives noise during the background measurements. Therefore, the background was measured separately from the measurements of the sample.

During the heating, the particles were not displaced due to the thermal shock facilitating the data recovering. Despite that the reconstruction of particles was not easy. It was possible to reconstruct the shape of particles like we can see by comparing the SEM and CXDI images, but it was not possible to recognize the porosity inside (Figure 3d). The invisibility of the inner structure is probably due to the thickness of membrane or/and to the impossibility of measuring the background simultaneously with the sample.



**Figure 3.** (a) Setup of in-situ experiment, (b) scanning chip nanocalorimeter, (c) SEM and (d) CXDI images of in-situ studied particles.

At the end of measurements, WAXS analyses on particles were tested in order to determine their structure during the transformation. We have succeeded to get some diffraction pattern of particles, but they were not good enough, because we did not have the time to optimize the measurements due to a long shut down.

**Conclusion:** CXDI is particularly relevant to study such particles and to understand the transformation of vaterite to calcite. We highlight that inner porosity of vaterite is mostly changing after the vaterite to calcite transition. In addition, we show that the transformation of vaterite occurs progressively and not homogeneously in the particles. This is confirmed by the coexistence of two structures in one single particle. It was shown that the vaterite particles resist to thermal shock even at high heating speed because no crack was found on surface of particles due to the thermal contrast. After the in-situ experiments, it was possible to reconstruct only the outer part of particles but not the inner one, probably because of the thickness of membrane or/and to the impossibility of measuring the background simultaneously with the sample. A new chip is presently under discussion to circumvent these encountered problems.

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