Natural vs. Man-Made Materials: An Investigation of the Aragonite - Calcite Transformation

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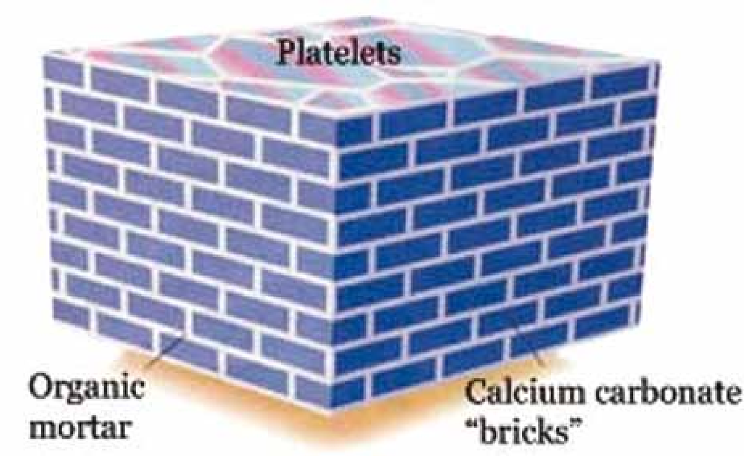
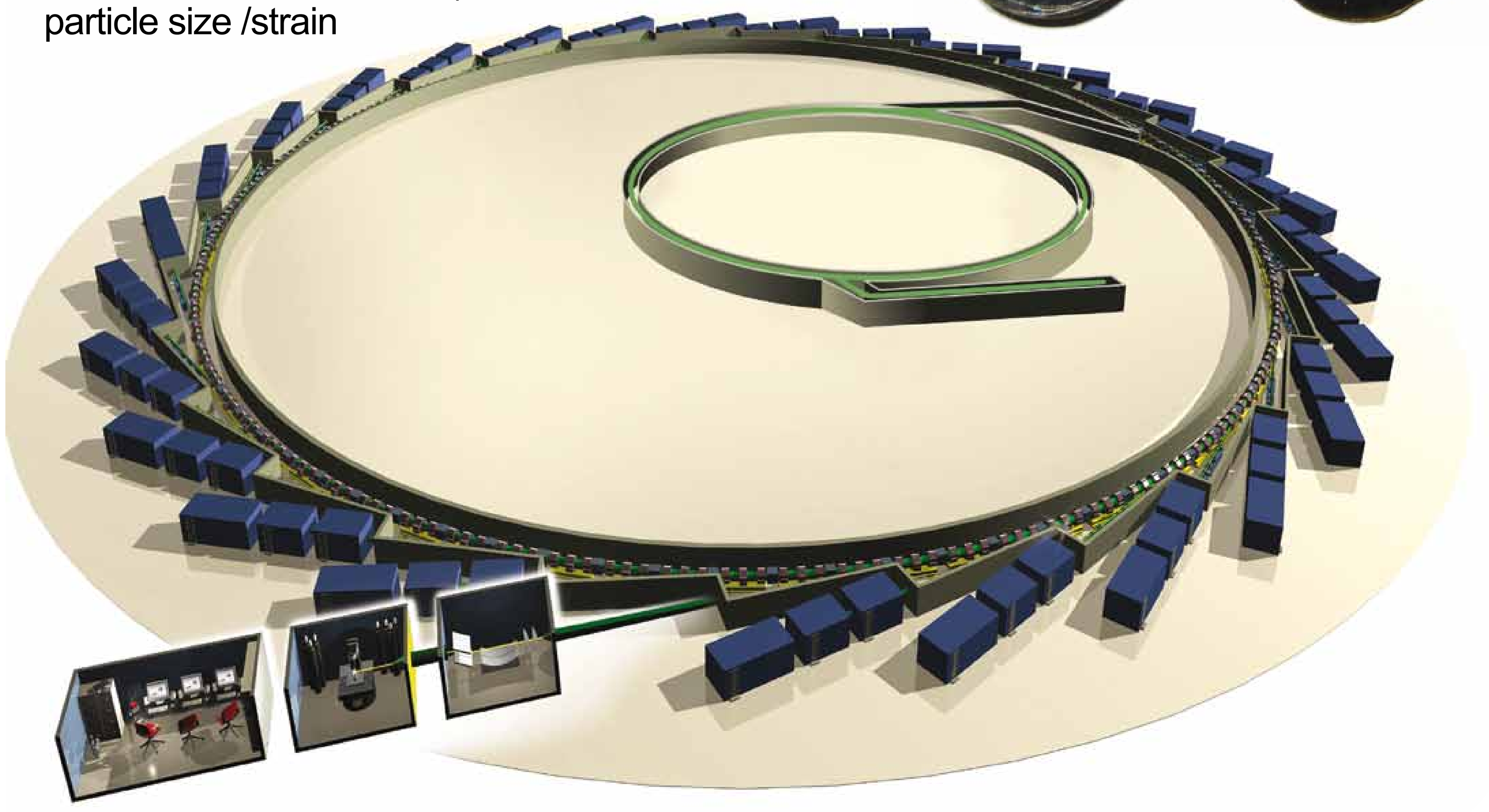
- Calcium carbonate exists in several different polymorphic forms, the most common of which are the minerals calcite and aragonite. Aragonite is only meta-stable under ambient conditions, transforming to calcite on heating.
- Aragonite is a component of many rocks and also forms the shell or skeletons of many marine organisms including molluscs, corals and sea snails.
- Mussel shells are an extremely strong natural material (outer calcite shell and inner aragonite layer) - composite architecture, with the mineral crystal and a protein matrix forming a ‘brick-bridge-mortar’ structure
- Important component in the development of new bio-medical framework materials as well as stronger structural composites for other engineering and domestic applications.



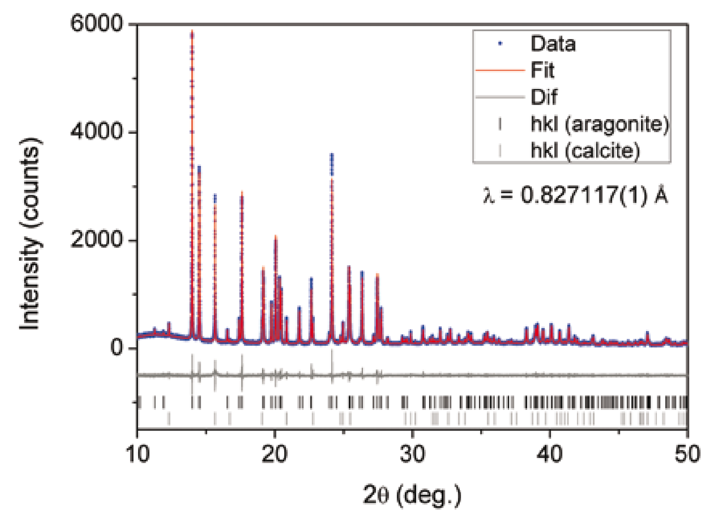
Experimental

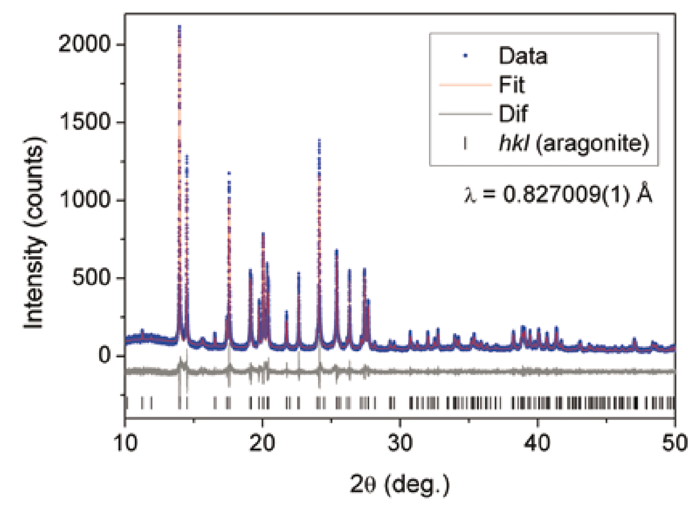
- **Synthetic:**
  $CaCl_2$ + urea in solution _ aged overnight @ 90°C
  Needle shaped aragonite crystals precipitated
- **Biogenic:** Sample extracted from inner aragonite layer
- **Beamline I11 at Diamond Light Source:**
  High resolution X-ray powder diffraction experiment with in-situ heating of sample.
- **Powder diffraction:**
  information about crystal structure (arrangement of atoms and size of unit cell)
  particle size /strain



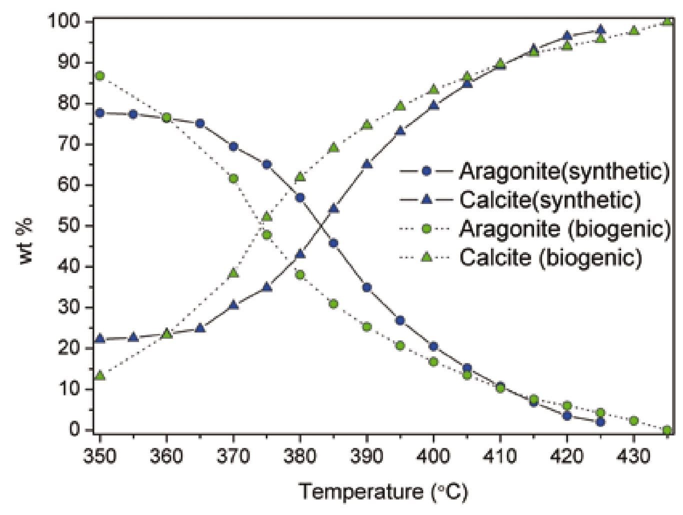
Results I

- The X-ray diffraction patterns show that synthetic sample consists of aragonite with a small amount of calcite (~5%), *below left*, mussel shell sample is mostly aragonite, *below right*.

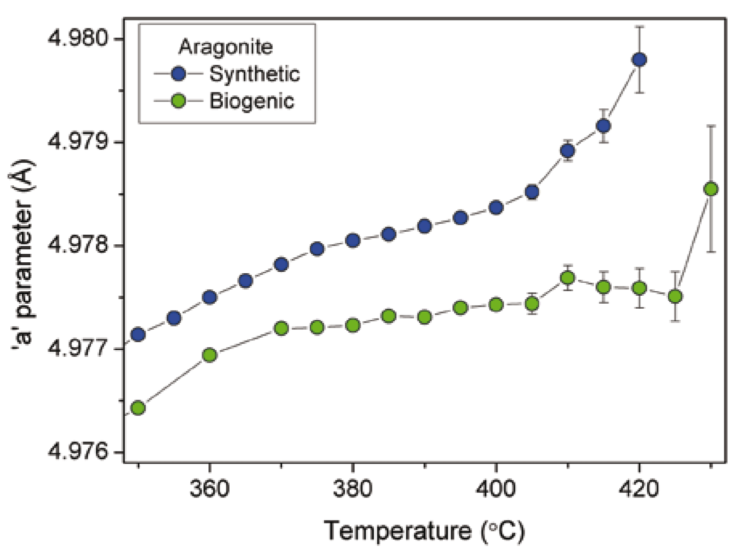




- On heating meta-stable aragonite transforms to more stable calcite phase.
- Mussel shell aragonite transforms at a lower temperature than synthetic sample, *right*.



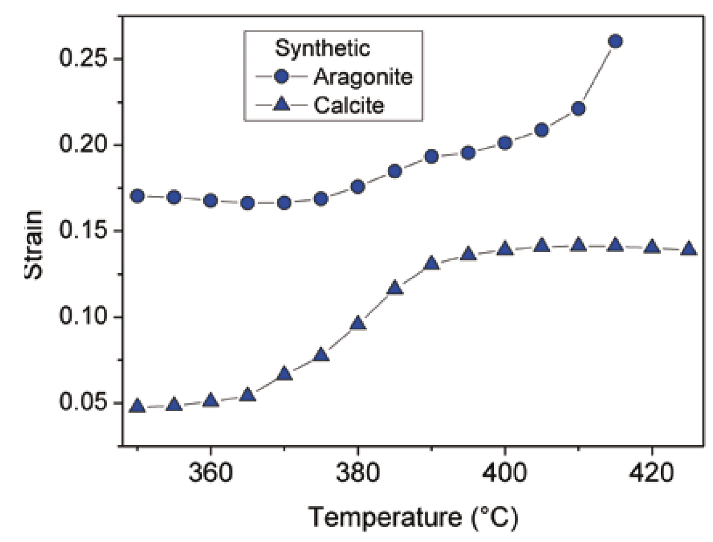
- Interesting thermal behaviour of both the aragonite and calcite phases is observed a plateau region in the lattice parameter expansion, *see right.*
- A near linear increase in unit cell size with temperature would be expected however both the mussel shell and the synthetic aragonite show a halt in their expansion. This is believed to be caused by trapped gas within the structure.

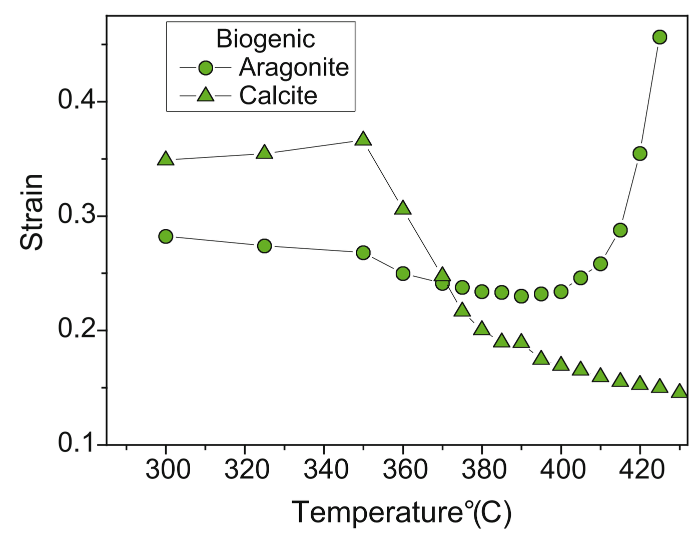


- On heating evaporating gas inclusions are trapped within the structure, increasing the internal pressure and lowering the rate of thermal expansion.
- Inclusions likely to be the macromolecules (proteins) for the mussel shell, but not for the synthetic sample.

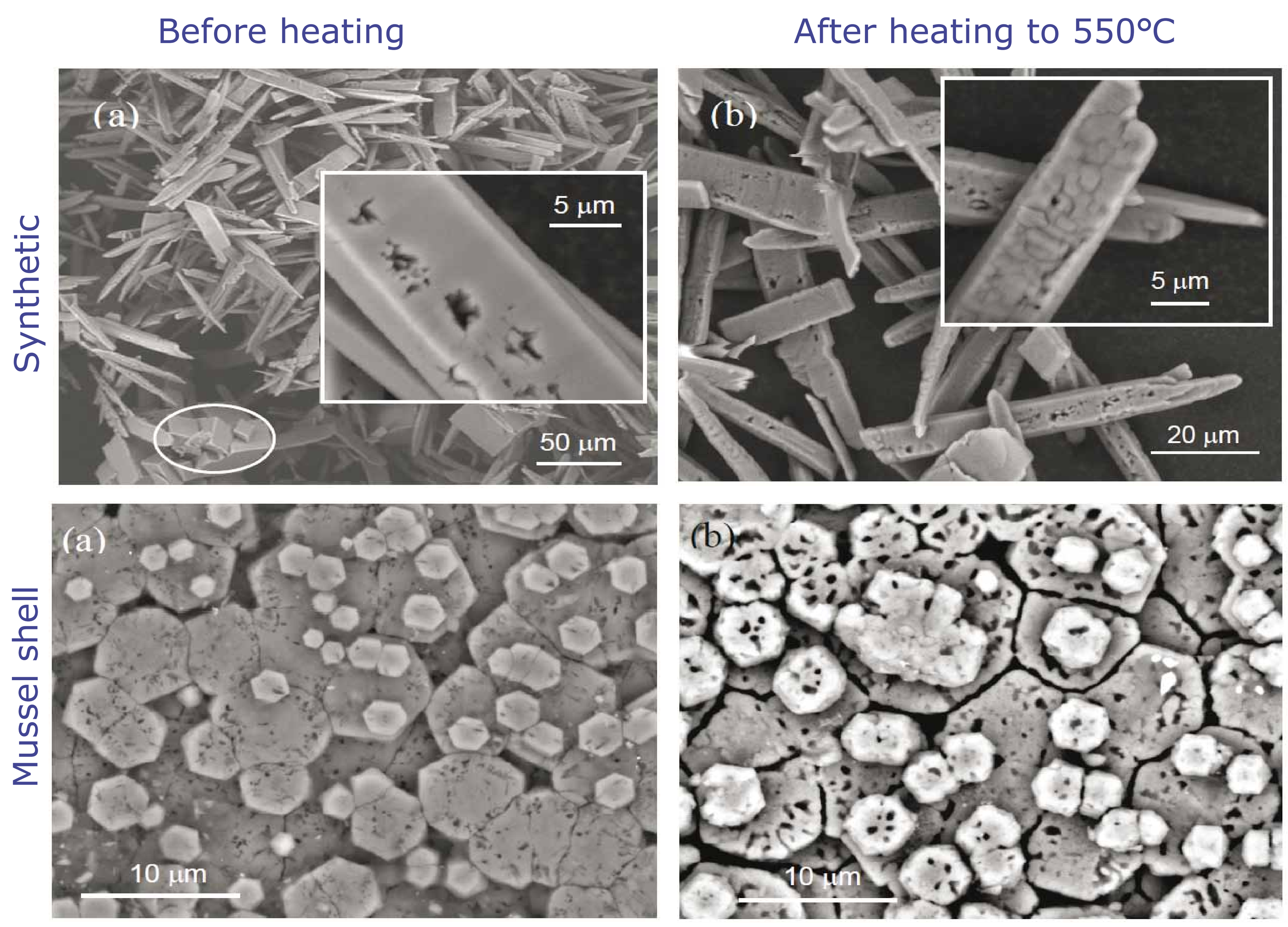
Results II

- The diffraction results also reveal the effect of temperature on the micro-strain within the structure as the transformation proceeds
- **Synthetic,** *below left:*
  Initially low micro-strain, strain increases during the transformation
- **Biogenic,** *below right:*
  Initially high micro-strain, strain decreases during the transformation





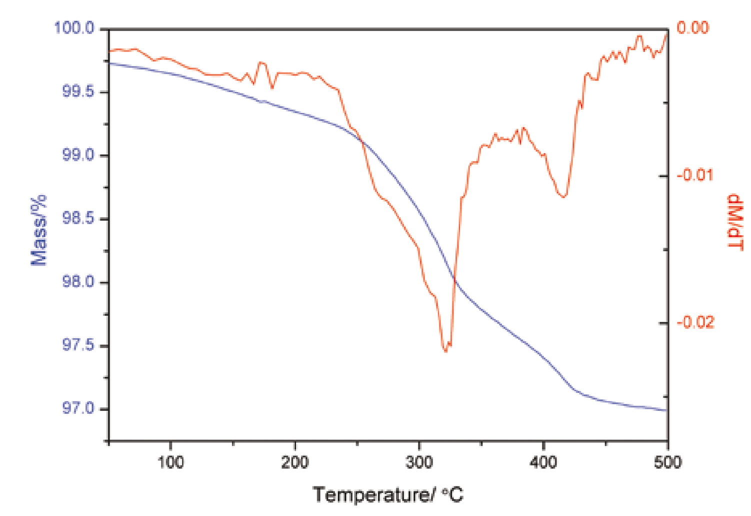
- Differences can be related to the underlying sample microstructure as observed in scanning electron microscopy (SEM) images, *below.*



- Synthetic, top: smaller calcite crystals forming are constrained within the original aragonite particles, increasing strain.
- Biogenic, bottom: protein matrix holding the crystals in the mussel shell together is degraded by the thermal treatment, decreasing strain.

Further work

- Mussel shell ~3% mass loss on heating, right.
- Analysis of the nature of the gas produced to determine its origin and role in the thermal expansion behaviour observed.
- Further experiments are being carried out to investigate the gas produced by the samples.



Conclusions

- Anomalous thermal expansion (plateau in lattice parameters) occurs in synthetic and biogenic samples
- Attributed to increase in internal pressure caused by organic molecules/gases trapped in the structure during crystallisation
- Synthetic and biogenic samples show opposite microstrain behaviour during the transformation, due to the underlying differences in sample microstructure.

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