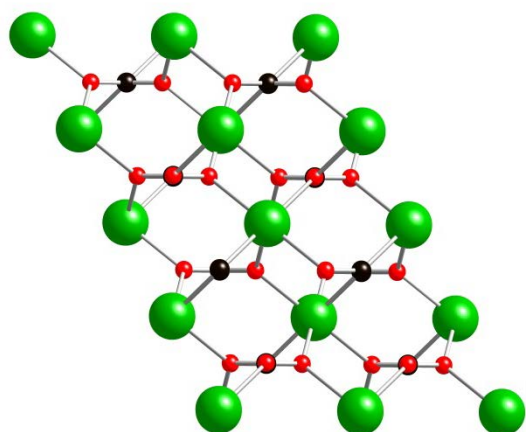


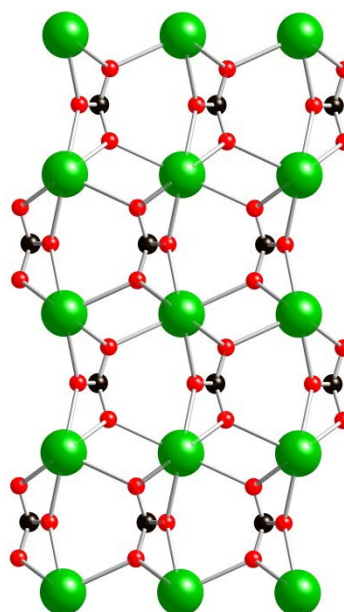
### What can a diffraction pattern tell you about your sample?

A diffraction pattern is like a 'fingerprint' and can be used to identify what crystals are present in your sample. Although calcite and vaterite both consist of calcium carbonate (they have the same chemical formula,  $\text{CaCO}_3$ ) the atoms are arranged differently in each structure – we call these polymorphs.

The crystal structures of calcite and vaterite are shown below. In the carbonate group ( $\text{CO}_3^{2-}$ ) the oxygens are arranged in the 3 corners of a triangle, each bonded to the carbon in the centre. Both structures are made up of alternating layers of calcium and carbonate. Have a good look at the arrangements of the layers and see if you can describe the differences between the calcite and vaterite structures, before reading the summary in the table below! Don't worry if you find the differences hard to see – it is very difficult to try and represent 3D crystal structures as 2D drawings!



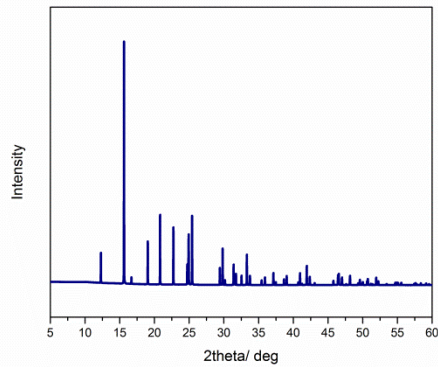
A view of the crystal structure of calcite  
Ca = green, C = black and O = red.



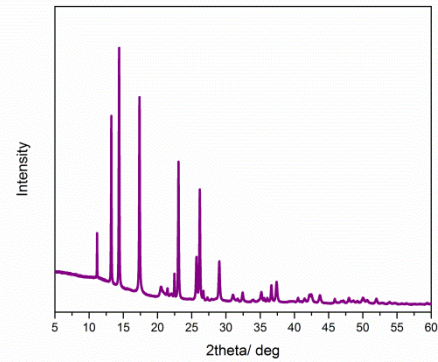
A view of the crystal structure of vaterite  
Ca = green, C = black and O = red.

	<i>Calcite</i>	<i>Vaterite</i>
Orientation of carbonate groups in the layers	Lie flat in the layer	Stand perpendicular to the layers
Calcium layer stacking	The Ca in a layer is offset from those in the layers above and below. There is an ABCABC Ca layer stacking	The Ca in a layer sits in the same position as those in the layers above and below.
Carbonate layer stacking	Alternate carbonate layers have the carbonate triangle pointing into the page then out of the page, ABAB layer stacking	Alternate carbonate layers have the carbonate triangle pointing into the page then out of the page, ABAB layer stacking

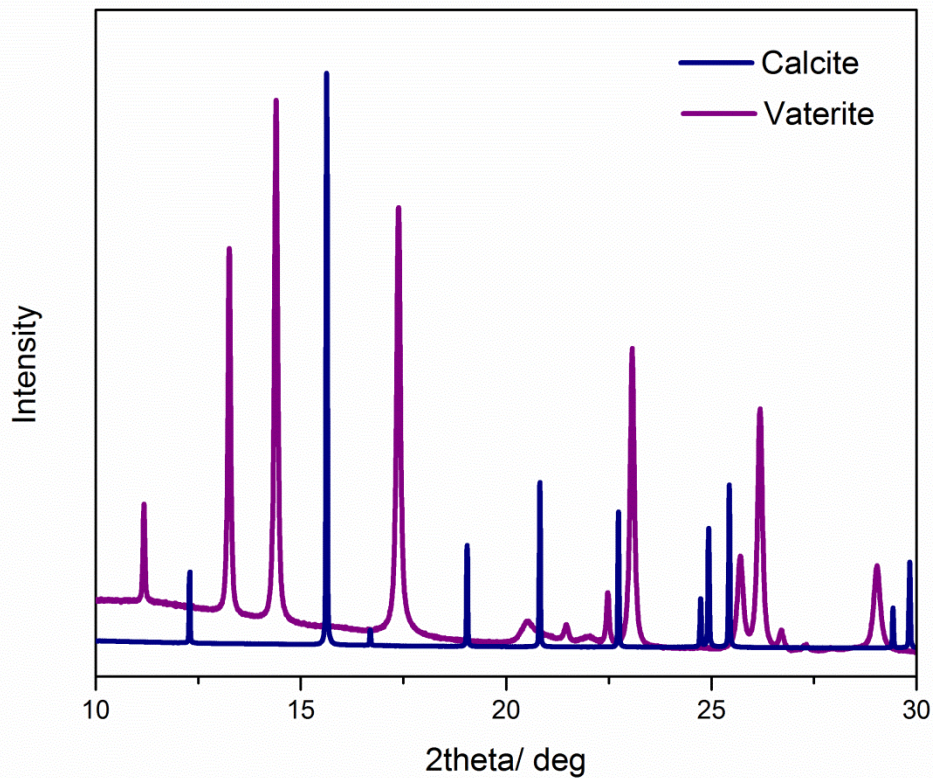
Because the crystal structures are **different** the diffraction patterns of calcite and vaterite are **different** to each other and act as a fingerprint, or signature, of the presence of calcite or vaterite in your sample



*Calcite diffraction pattern*



*Vaterite diffraction pattern*

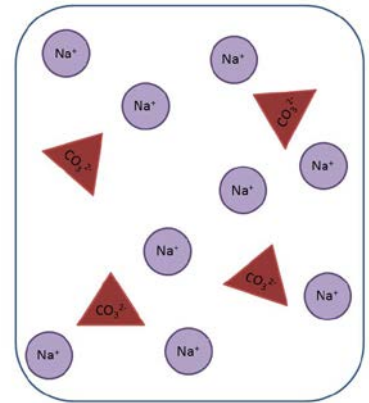
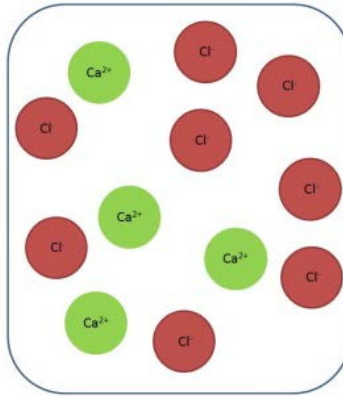


*Both patterns plotted together*

**Why do we see different amounts of calcite and vaterite in the different samples, and what might this tell us about the effect of the additive?**

To explain this it is useful to take a step back and think about what happened when we made our samples.

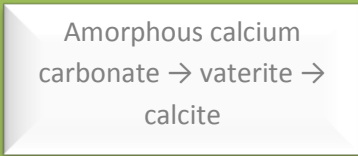
Solutions of calcium chloride and sodium carbonate



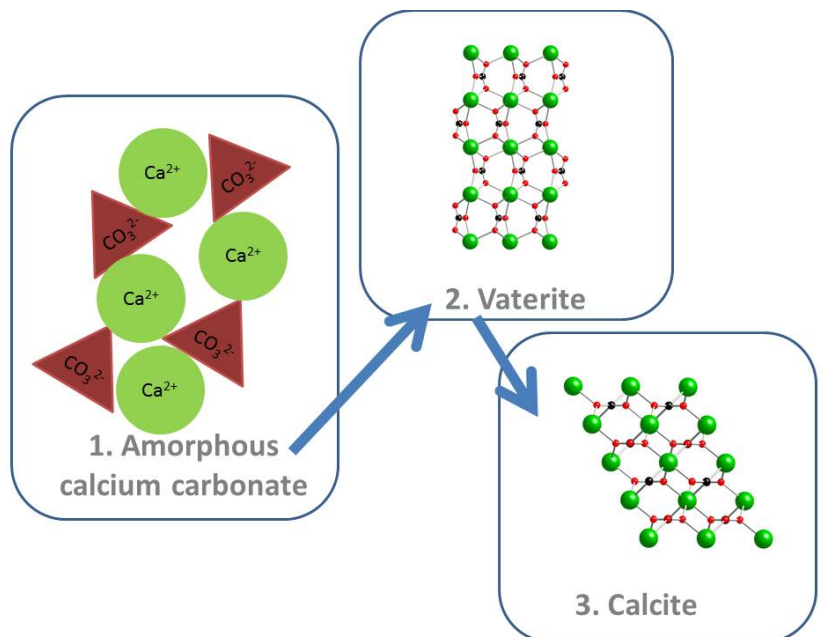
Mix together - solution turns milky or cloudy as a precipitate is formed

During the precipitation of calcium carbonate an **amorphous** phase forms first. This then **crystallises** to form vaterite and then calcite

We call this the reaction pathway:

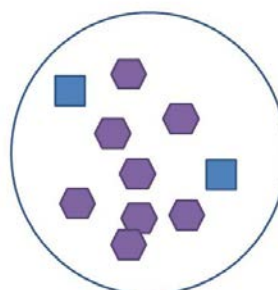


The atoms in crystals have a long range, regular repeating order whereas an amorphous solid does not - the atoms are more randomly arranged like a glass

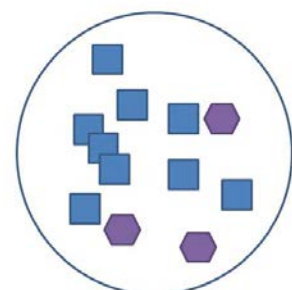


Filter to isolate the calcium carbonate crystals from the solution

This stops the reaction, giving a mixture of vaterite and calcite. How much of each will depend on whether the additive **promoted** the transformation of vaterite to calcite (made it faster) or **inhibited** it (slowed it down)



Calcite ■ formation inhibited = more vaterite ⬡ in sample

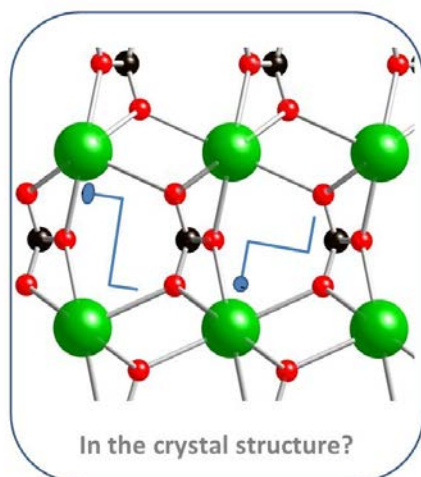
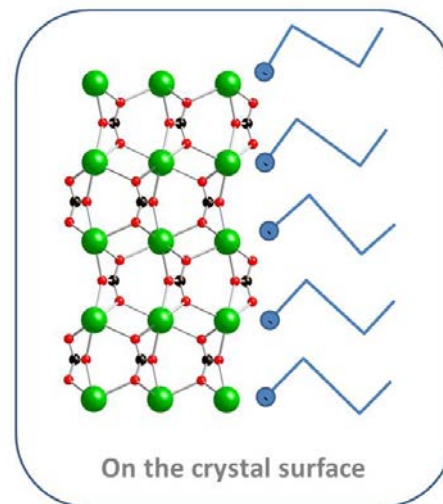
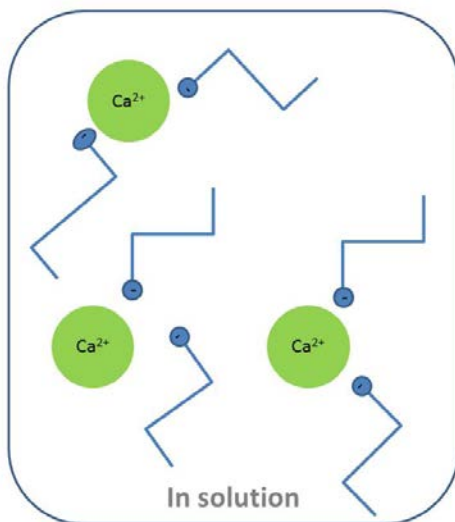


Calcite ■ formation promoted = less vaterite ⬡ in sample

Inhibiting the formation of crystals is important for many processes, e.g.:  
Preventing limescale build up  
Prevention of kidney stones

***How might the additive promote or inhibit the transformation of vaterite to calcite?***

The additives used were amino acids, or other similar molecules. These are essentially wiggly chain molecules containing certain groups (called functional groups) which can be charged. In solution the negatively charged groups on the amino acids are attracted to the positively charged calcium ions. As the vaterite, and then calcite, crystallises the amino acid may be adsorbed on the surface of the crystals or even incorporated into the crystal structure. Depending on the size and the charge of the amino acid there may be certain layers or positions where it fits best in the vaterite or calcite.



We don't know exactly how the additive is incorporated in to the structures, or where it goes – this is something the diffraction patterns from your samples can help us to figure out!

The presence of the additive on the surface or within the crystal changes how stable the structures are and determines whether calcium carbonate would rather exist as vaterite or calcite. For example if the additive makes the vaterite crystal structure much less stable then the calcium carbonate will form calcite much faster and you will see relatively more calcite in your sample.

**Other additive effects** include changing the size of the crystals formed, by adsorbing on the surface and stopping the crystals growing bigger.

Using additives to control crystal size is useful when making calcium carbonate for use in building materials such as cement, concrete and synthetic marble, as the particle size will affect the appearance and the strength of the material

### What do the peak positions in the diffraction pattern mean?

The peaks in the diffraction pattern occur due to X-rays diffraction from the different planes (or layers) of atoms in the crystal structure. The angle at which the X-rays are diffracted is related to the spacing between the layers by a relationship called Bragg's law

$$\lambda = 2d\sin\theta$$

where,  $\lambda$  = the wavelength of the X-rays (in Angstroms)

$d$  = the layer spacing (in Angstroms),

$\theta$  = the diffraction angle ( $2\theta$ ) / 2 in degrees

An Angstrom is a unit used for measuring distance in crystal structures, it is  $10^{-10}$  m, so 1 m contains **10 billion** Angstroms.

The peak positions of the vaterite and calcite diffraction peaks will therefore move if the layer spacings become bigger (if the additive is incorporated into the layers expanding them) or smaller (if the additive restricts the layers)

The X-rays used for the Project M data collection had a wavelength of 0.826 Angstroms. Peak positions for a reference sample of calcite and vaterite are given below. Try using Bragg's law to calculate the spacings in the crystal structure for these peaks and in the reference samples and in your sample. Is the spacing the same, larger or smaller? What do you think that means?

Calcite peak position  $2\theta = 15.632$  degrees

Vaterite peak position  $2\theta = 14.396$  degrees

**!?!Error message!?!**

Error, or variability, is an unavoidable factor in all experiments!!! It is highly unlikely that the samples that are the same as yours (made with the same amount of the same additive) have an identical diffraction pattern to yours! It is therefore important to be able to estimate what the size of the errors in an experiment might be, this is why we have repeat runs for each sample in Project M. We will use these to estimate our error and determine if differences we see between samples are 'real' (and due to the additive) or just down to experimental variability.

- Can you list some possible sources for error in this experiment? E.g.
  - Weighing out the chemicals, how accurate was this? Might some have been spilt or left on the weigh boat?
  - Mixing for different times.