

Understanding the Crunch: A Deep Dive into Cheese Crystals



Paul Kindstedt, PhD
Pat Polowsky
November 15th 2017



The University of Vermont



The research team



**Prof. John Hughes, Dr. Gil Tansman
and Prof. Paul Kindstedt**



Pat Polowsky

**Dr. Pallavi Rajbhandari
Jignesh Patel
Ellie Valentine**



For More Information

- Rajbhandari, P., J. Patel, E. Valentine and P.S. Kindstedt. 2009. Chemical changes that predispose smoked cheddar cheese to calcium lactate crystallization. *J. Dairy Sci.* 92:3616-3622
- Rajbhandari, P., J. Patel, E. Valentine and P.S. Kindstedt. 2013. Effect of storage temperature on crystal formation rate and growth rate of calcium lactate crystals on smoked cheddar cheese. *J. Dairy Sci.* 96:3442-3448
- Rajbhandari, P. and P.S. Kindstedt. 2014. Surface roughness and packaging tightness affect calcium lactate crystallization on Cheddar cheese. *J. Dairy Sci.* 97:1885-1892.
- Tansman, G., P.S. Kindstedt and J.M. Hughes. 2014. Powder X-ray diffraction can differentiate between enantiomeric variants of calcium lactate pentahydrate. *J. Dairy Sci.* 97:7354-7362.
- Tansman, G., P.S. Kindstedt and J.M. Hughes. 2015. Crystal fingerprinting: Elucidating the crystals of Cheddar, Parmigiano-Reggiano, Gouda and soft washed-rind cheeses using powder X-ray diffractometry. *Dairy Sci. Technol.* 95(5):651-664. DOI 10.1007/s13594-015-0225-6
- Tansman, G., P.S. Kindstedt and J.M. Hughes. 2017. Minerals in food: Crystal structures of ikaite and struvite from bacterial smears on washed-rind cheese. *The Canadian Mineralogist* 55:89-100.
- Tansman, G., P.S. Kindstedt and J.M. Hughes. 2017. Crystallization and demineralization phenomena in stabilized paste white mold cheese. *J. Dairy Sci.* 100:6074-6083.10
- Tansman, G., P.S. Kindstedt and J.M. Hughes. 2017. Crystallization and demineralization phenomena in washed rind cheese. *J. Dairy Sci.*



Crystal Overview

Calcium Lactate

- Cheddar (et al.)

Tyrosine & Leucine

- Aged Italian, Dutch, and Swiss

Calcium Phosphate

- Camembert-type/Blue (et al.)

Ikaite & Struvite

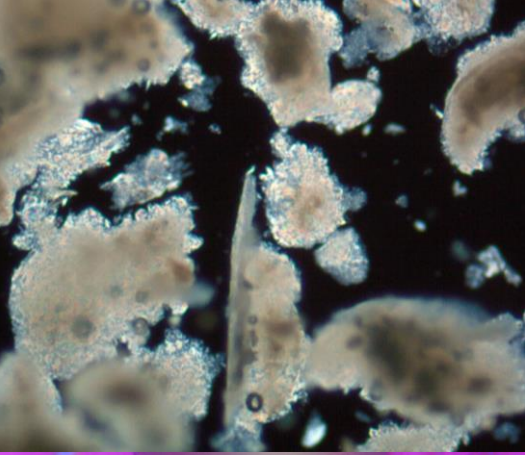
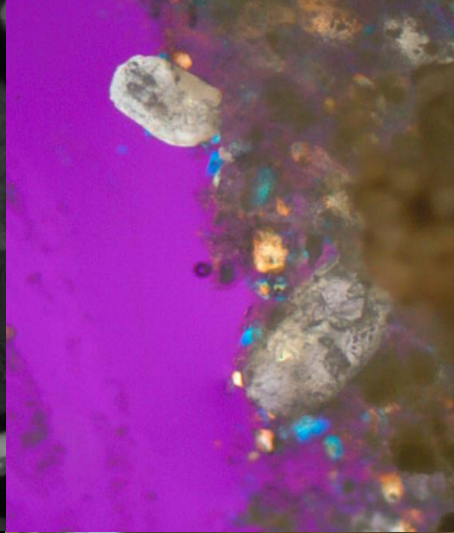
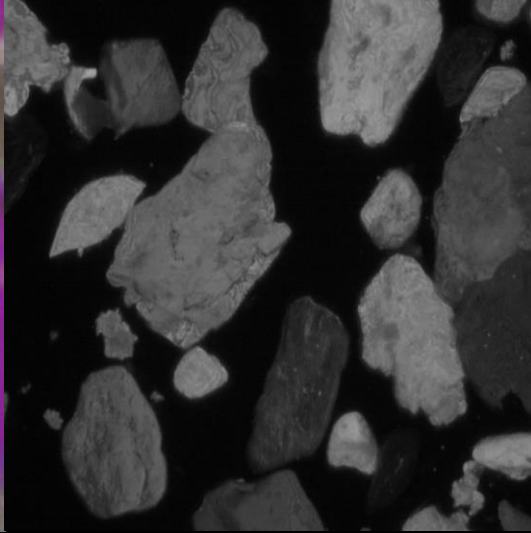
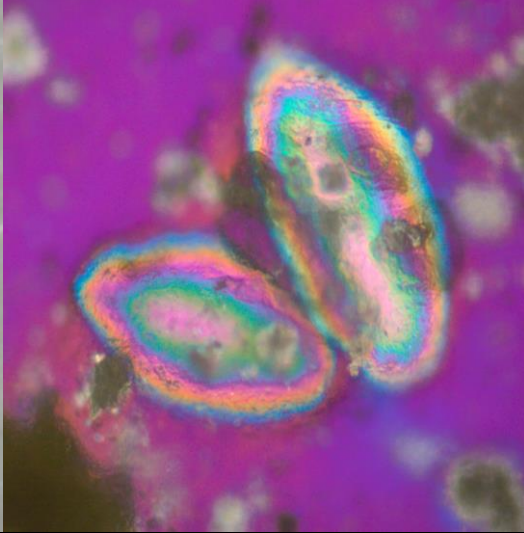
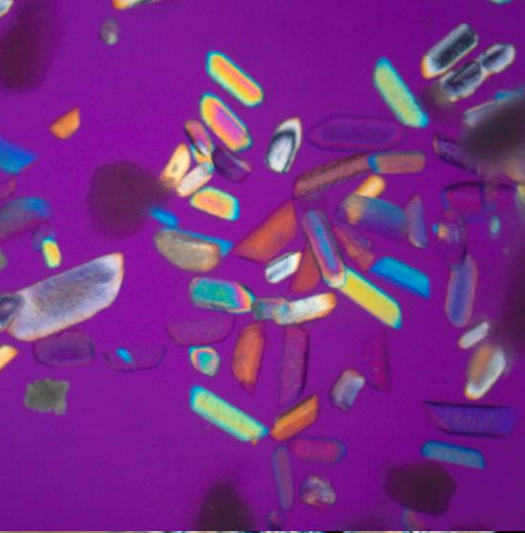
- Washed rind cheese



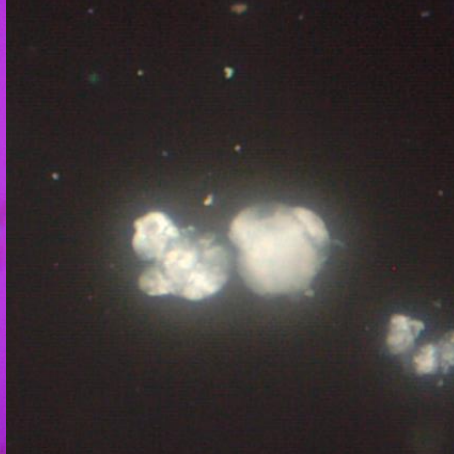
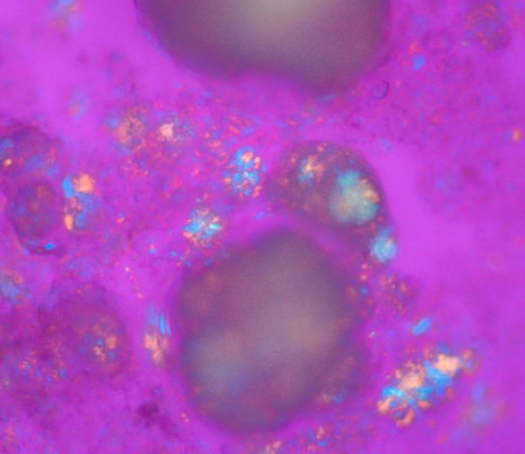
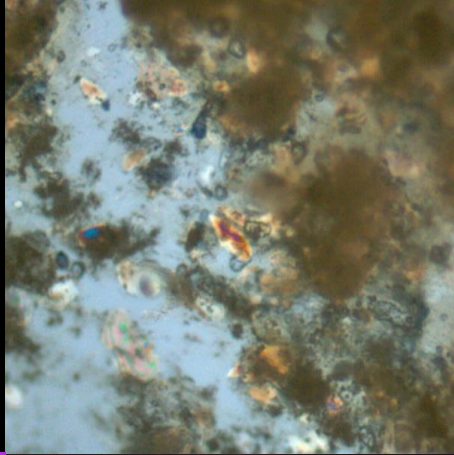
What is a Crystal?



The University of Vermont



A **crystal** is a solid material with a highly ordered microscopic structure



Crystalline Forms

Amorphous

- No order



© Wikipedia

Polycrystals

- Regional order



Single Crystals

- Global order



The image features a white background filled with numerous blue circles of varying sizes and positions. The circles are scattered in a non-repeating, irregular pattern, which visually represents an amorphous material. In the bottom-left corner, there is a black rounded rectangle containing white text.

Amorphous

no order

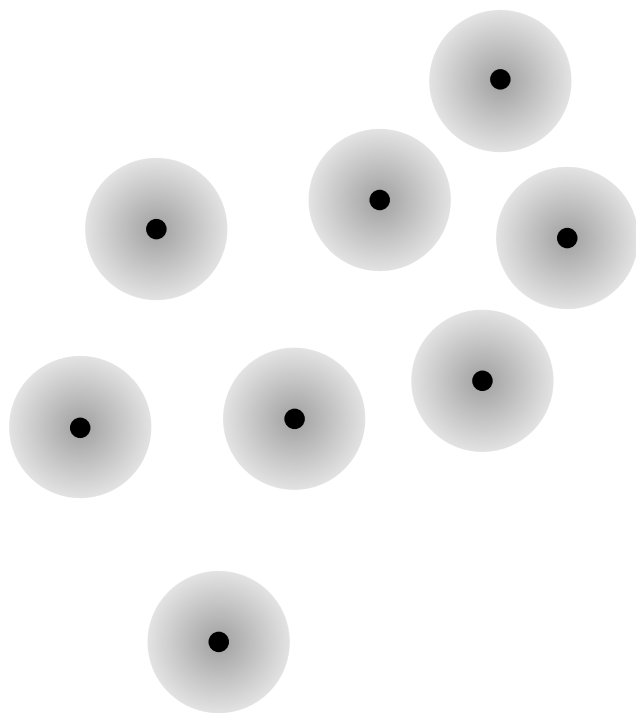


Polycrystalline
regional order



Single Crystal
global order

Crystal Aggregates



**Crystal
nucleation**

**Crystal
growth**
→
**Loss of
individual identify**



Crystal Growth



Crystal Types in Cheese



The University of Vermont

Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

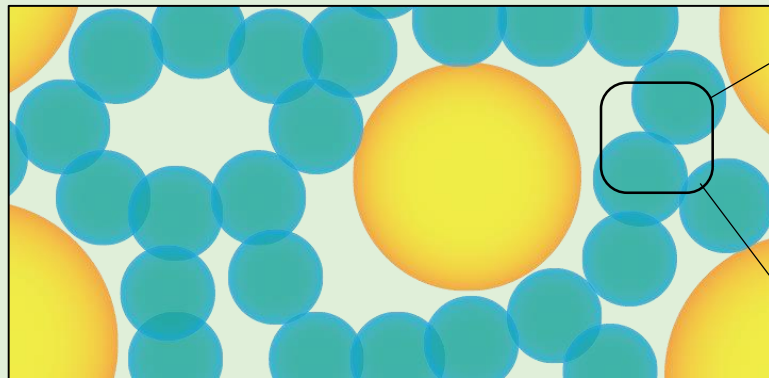
Ikaite

?

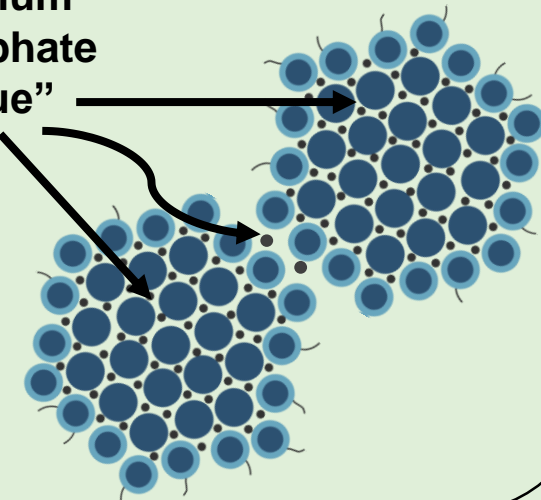
Mineral-
based

Calcium

- **Plentiful in milk and cheese**
- **The “glue” that holds casein together**



Calcium
phosphate
“glue”



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

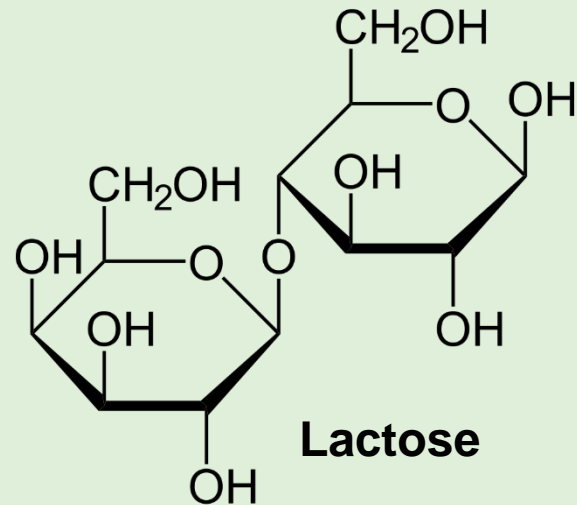
Ikaite

?

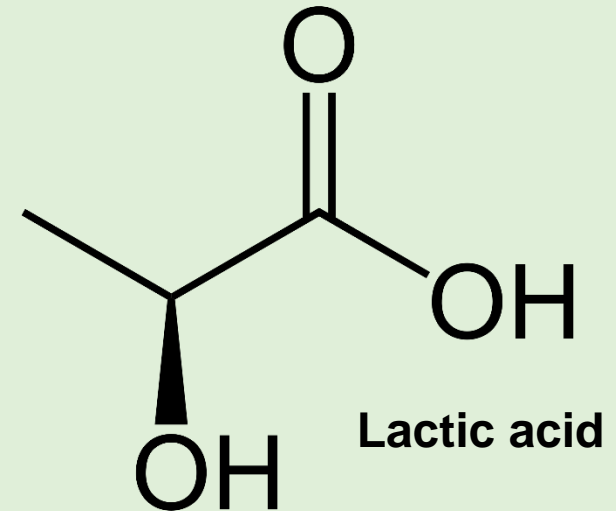
Calcium

Lactate

- Lactate \approx lactic acid
- Formed by the starter culture



Glycolysis
Fermentation



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

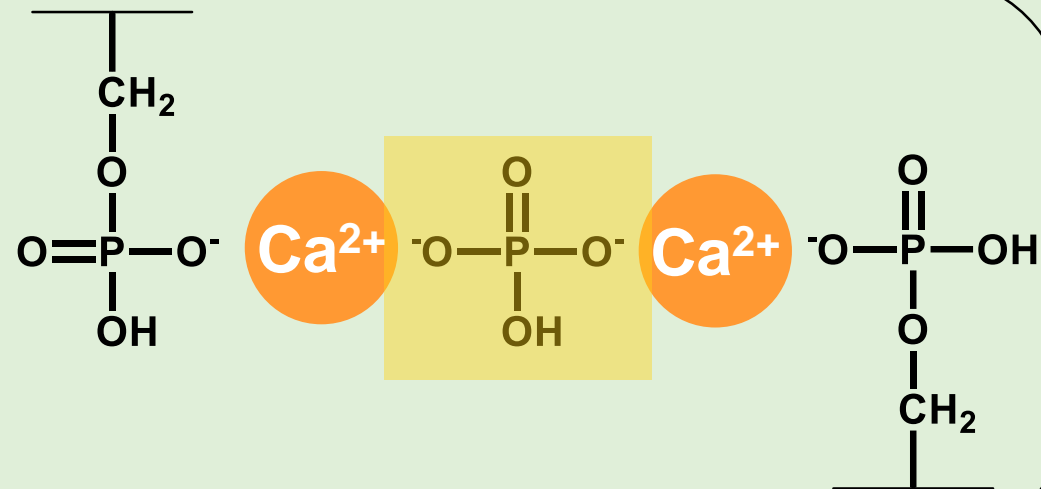
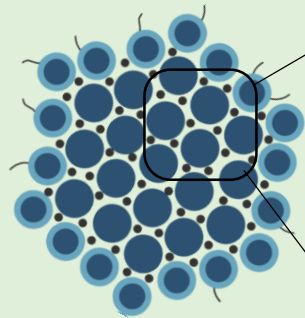
Ikaite

?

Calcium

Phosphate

- Similar story to calcium



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

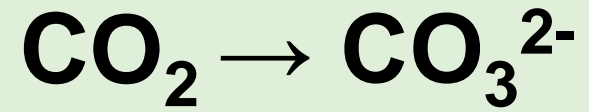
?

Ikaite

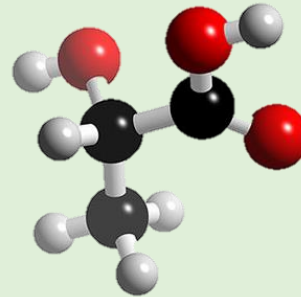
?

Calcium

Carbonate



Smear microbes



Lactic acid

CO₂

Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

Ikaite

?

Mineral-
based

Magnesium

- **Found in milk, salt, and water sources**



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

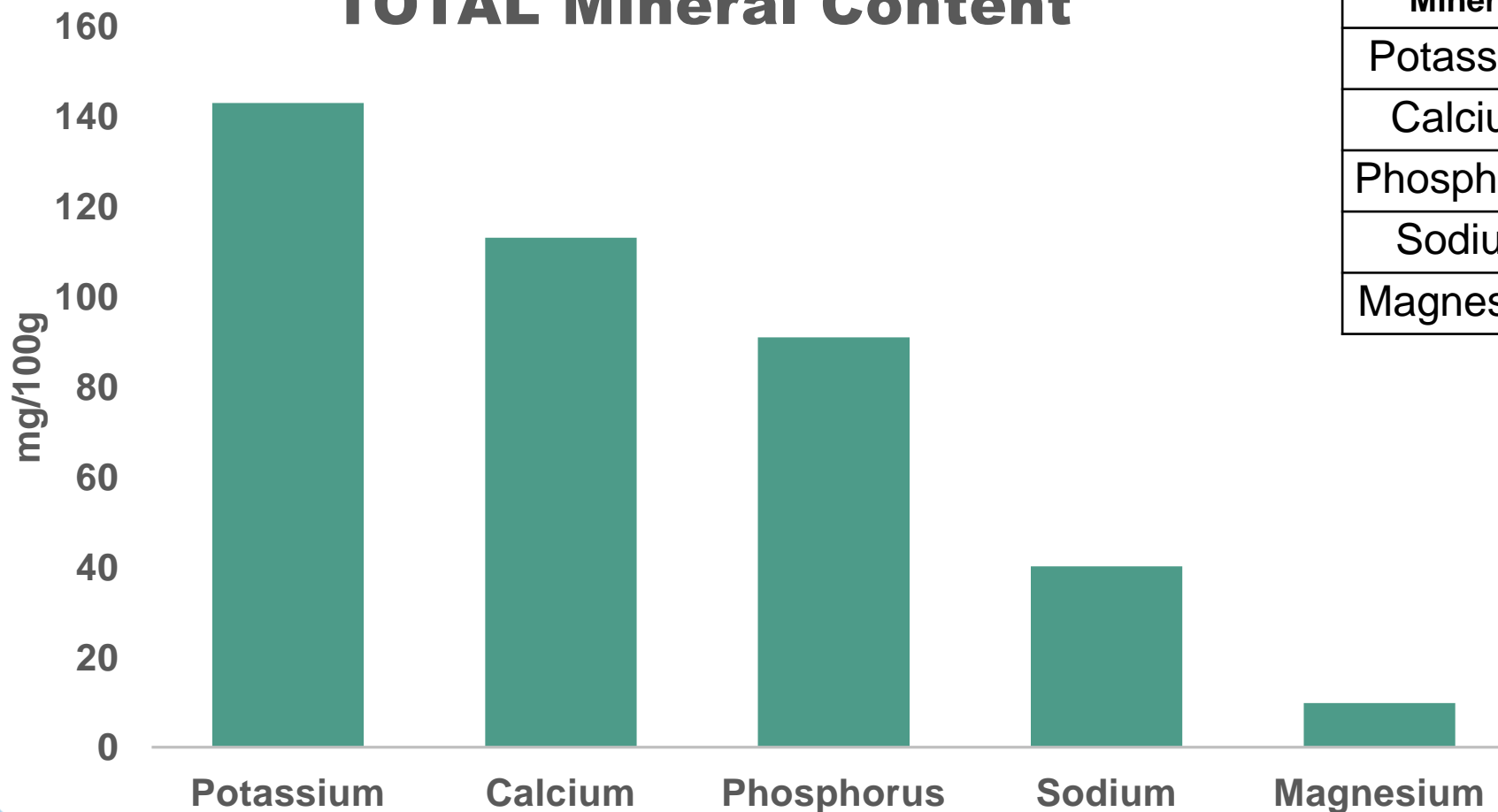
?

Ikaite

?

Minerals in Milk

TOTAL Mineral Content

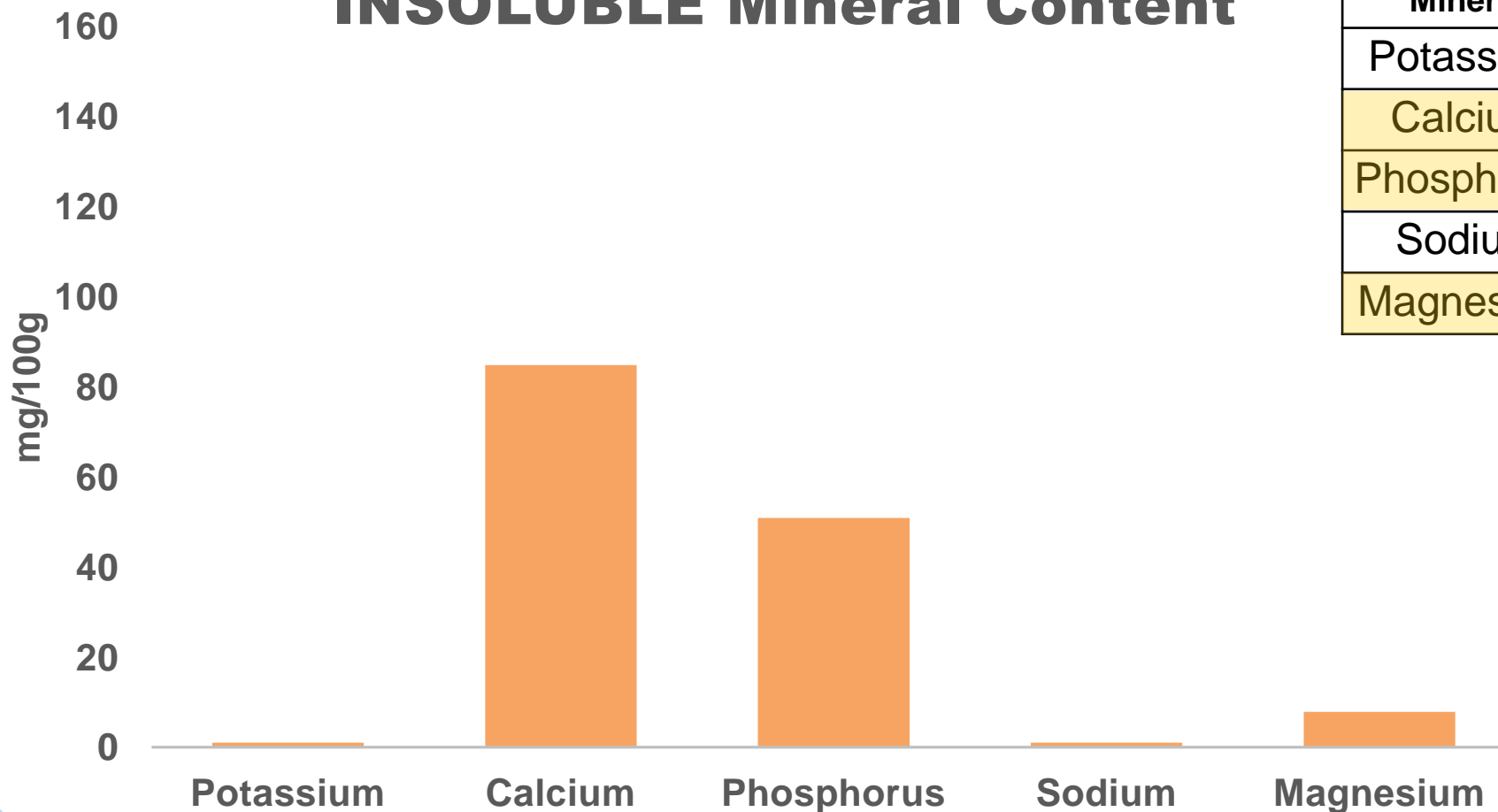


Mineral	Total
Potassium	143
Calcium	113
Phosphorus	91
Sodium	40
Magnesium	10



Minerals in Milk

INSOLUBLE Mineral Content



Mineral	Total	Insoluble
Potassium	143	0
Calcium	113	85
Phosphorus	91	51
Sodium	40	0
Magnesium	10	8



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

Ikaite

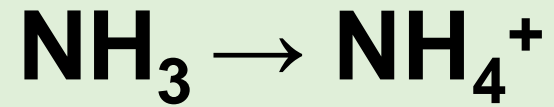
?

based

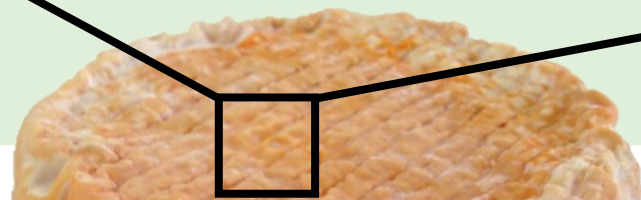
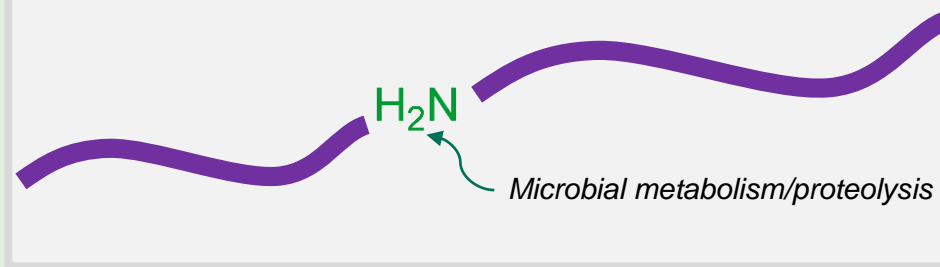
Magnesium

Ammonium

Phosphate



Protein breakdown



Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

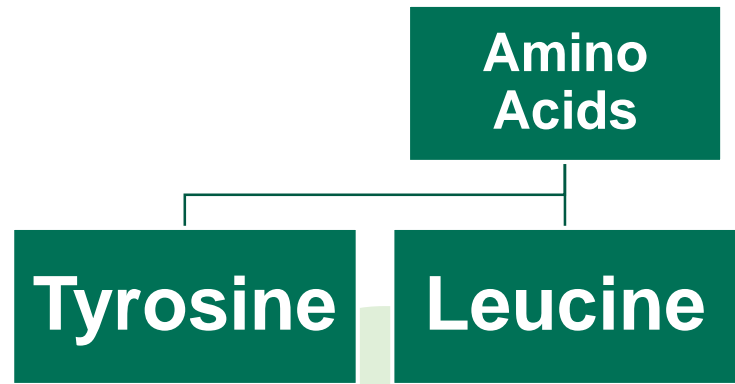
Calcite

D/L - form

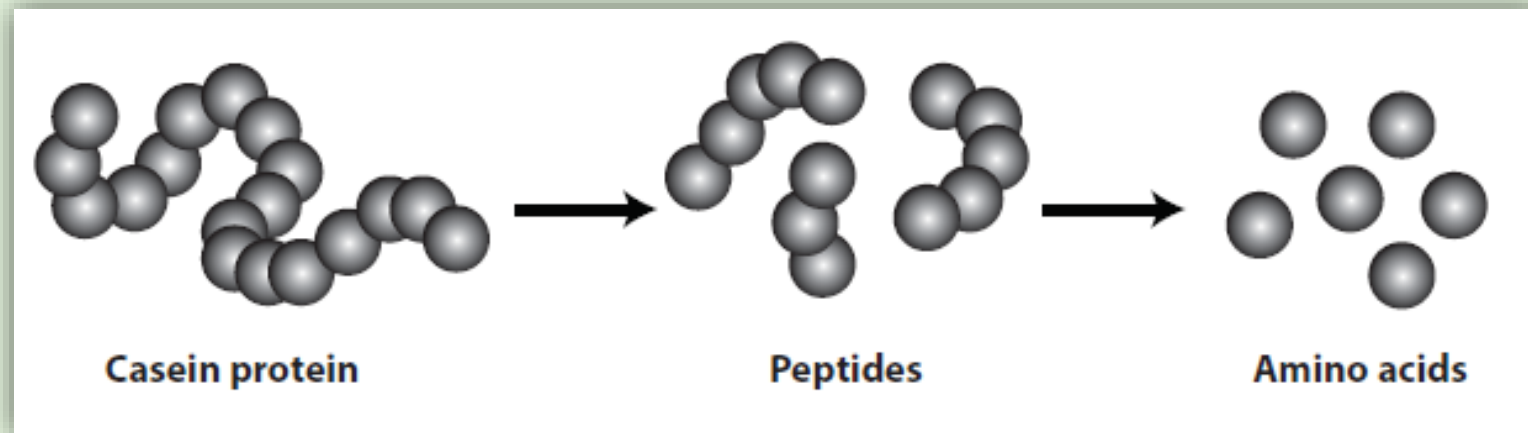
?

Ikaite

?

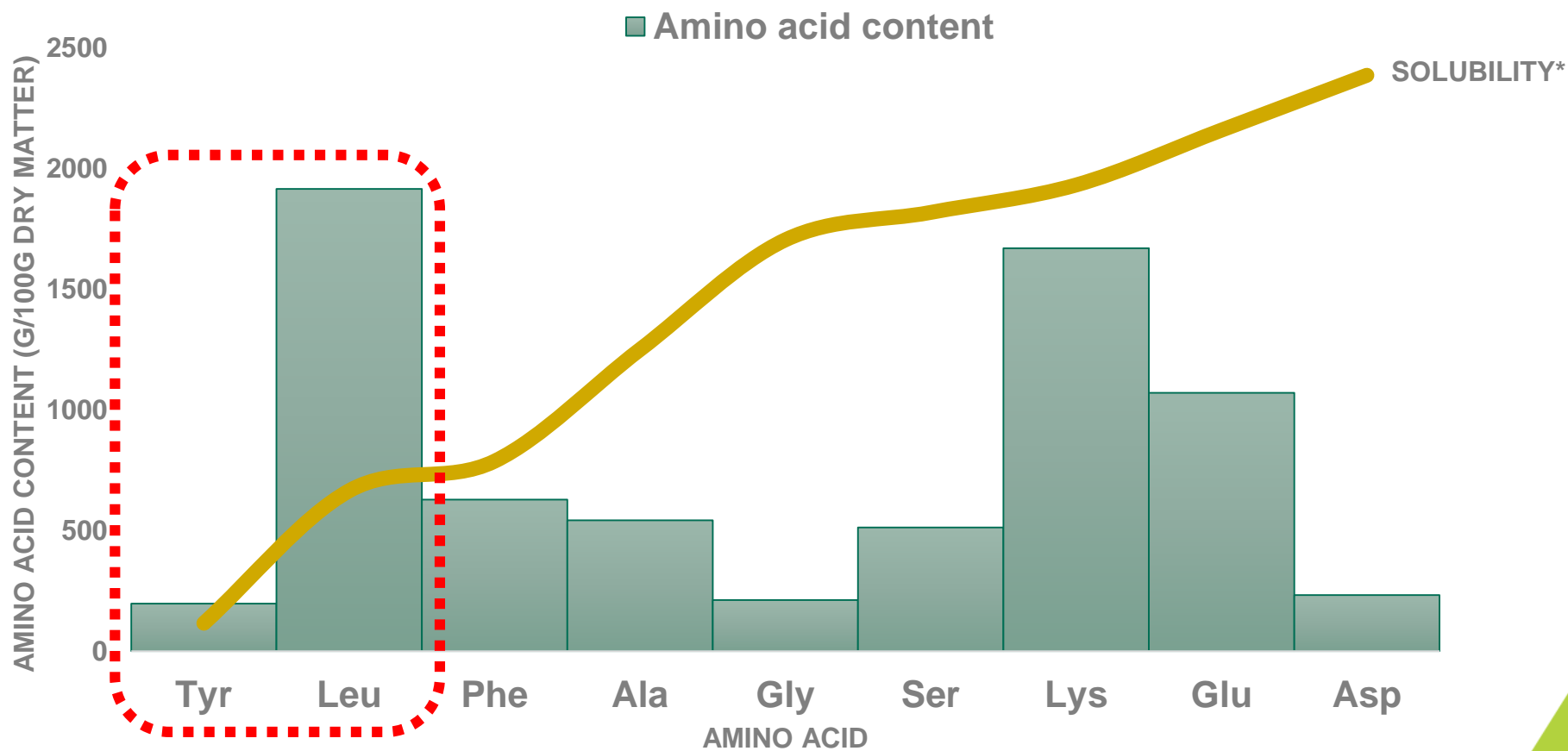


- **Protein breakdown generates free amino acids**



Amino Acids

Free Amino Acids in Parmesan Cheese



*Solubility adjusted to reflect side-chain hydrophobicity at pH~7

Data from
Izco et al. 2012
Monera et al. 1995
The University of Vermont

Mineral-based

Amino Acids

Calcium

Magnesium

Tyrosine

Leucine

?

Lactate

Phosphate

Carbonate

Ammonium Phosphate

L - form

Brushite

Calcite

D/L - form

?

Ikaite

?

Mineral-based

Calcium

Lactate

Phosphate

L - form

D/L - form

Amino Acids

Tyrosine

Leucine

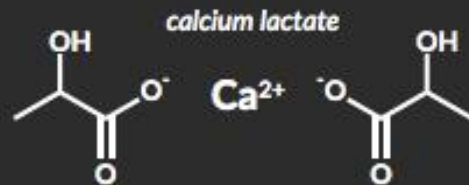
?

The Wonderful World of Cheese Crystals

A variety of crystal types exist across the wide spectrum of cheeses in the marketplace. The most prevalent crystals can come about from **minerals** such as **calcium** and **magnesium**, and **amino acids** such as **tyrosine** and **leucine**.

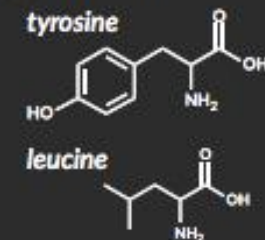
CALCIUM LACTATE

The **white powdery smear** found on many **aged cheddars** are crystals of the compound calcium lactate. Calcium lactate is formed as the **cheese ages when lactic acid reacts with calcium in the cheese**. They don't have any flavor themselves, but usually signify a piece of well-aged cheese that will be flavorful.



TYROSINE & LEUCINE

The crystals found in **aged Italian, Dutch, and Swiss cheese** varieties are usually the **amino acids** tyrosine (distinct specks) and/or leucine (powdery smear, diffuse spots). These are formed as the cheese ages **when the protein breaks down** into its constituent amino acids. They can build up to high concentrations and crystallize out.



CALCIUM PHOSPHATE

Calcium and phosphorus are essential for cheese. Under the correct acidity, **brushite**, a form of calcium phosphate, is found in **rind cheeses** such as brie and **blue cheeses** to name a few.

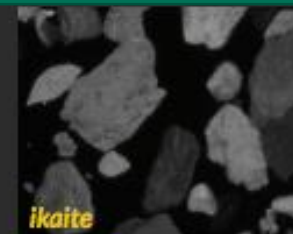


brushite formula
 $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

brushite

IKAITE & STRUVITE

whitened rind cheese is caused by the presence of **ikaite** crystal, and **struvite** is a mineral component of **blue cheese**. The mineral components **ammonium phosphate** and **ammonium carbonate** are used to control surface microbes.



ikaite



struvite

ikaite formula
 $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$

struvite formula
 $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

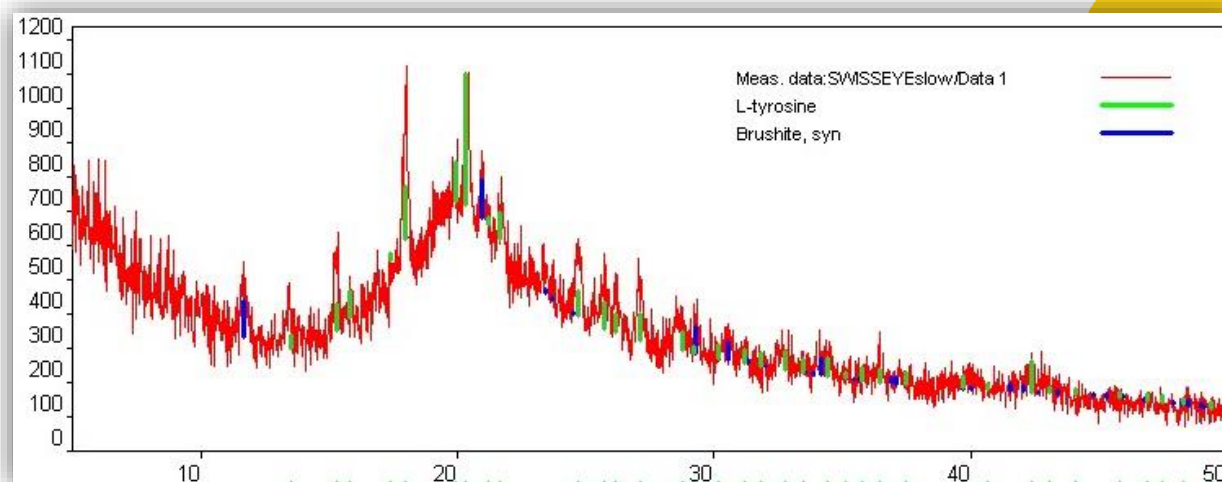
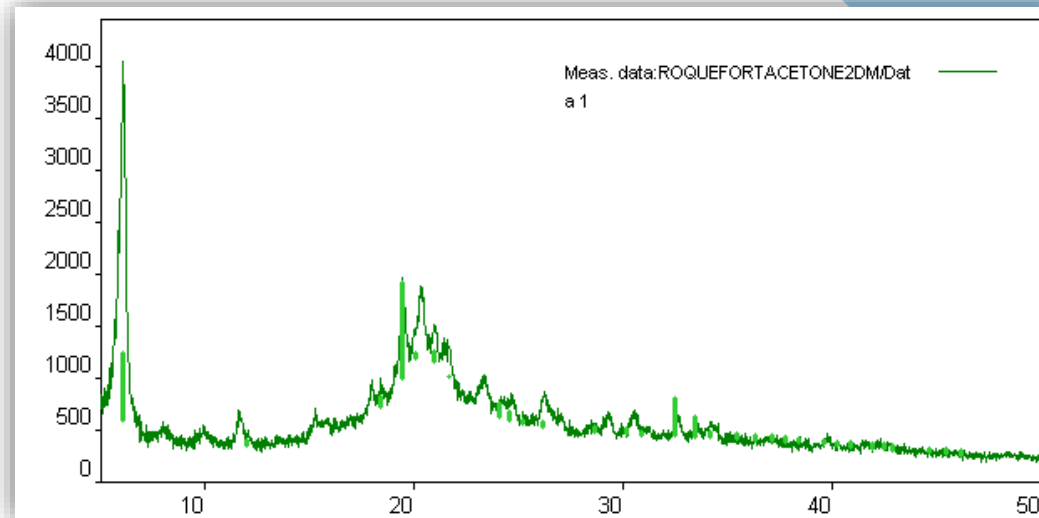
tiny.cc/cheesecrystals

Crystal Analysis in Cheese



The University of Vermont

PXRD

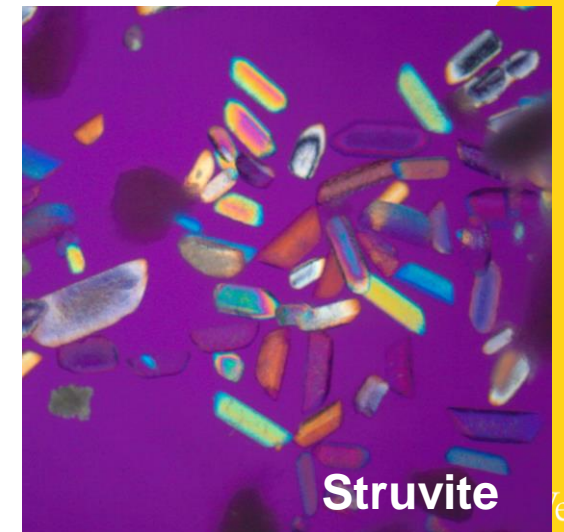
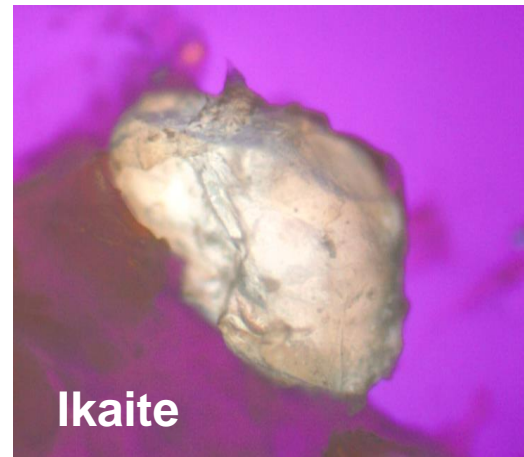


Polarized Light Microscopy (PLM)

Angle of Extinction



Coloring



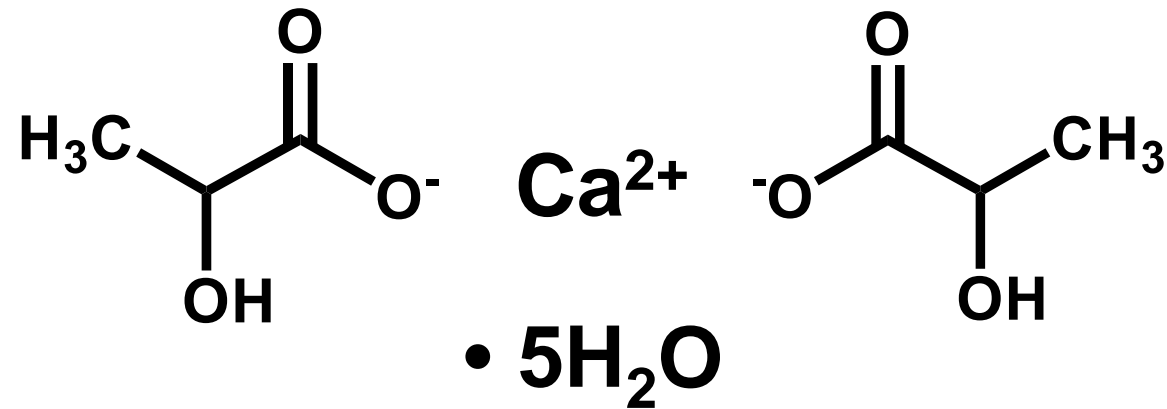
Cheddar Crystals



The University of Vermont

Crystals in Cheddar cheese

- Calcium Lactate Pentahydrate (CLP)

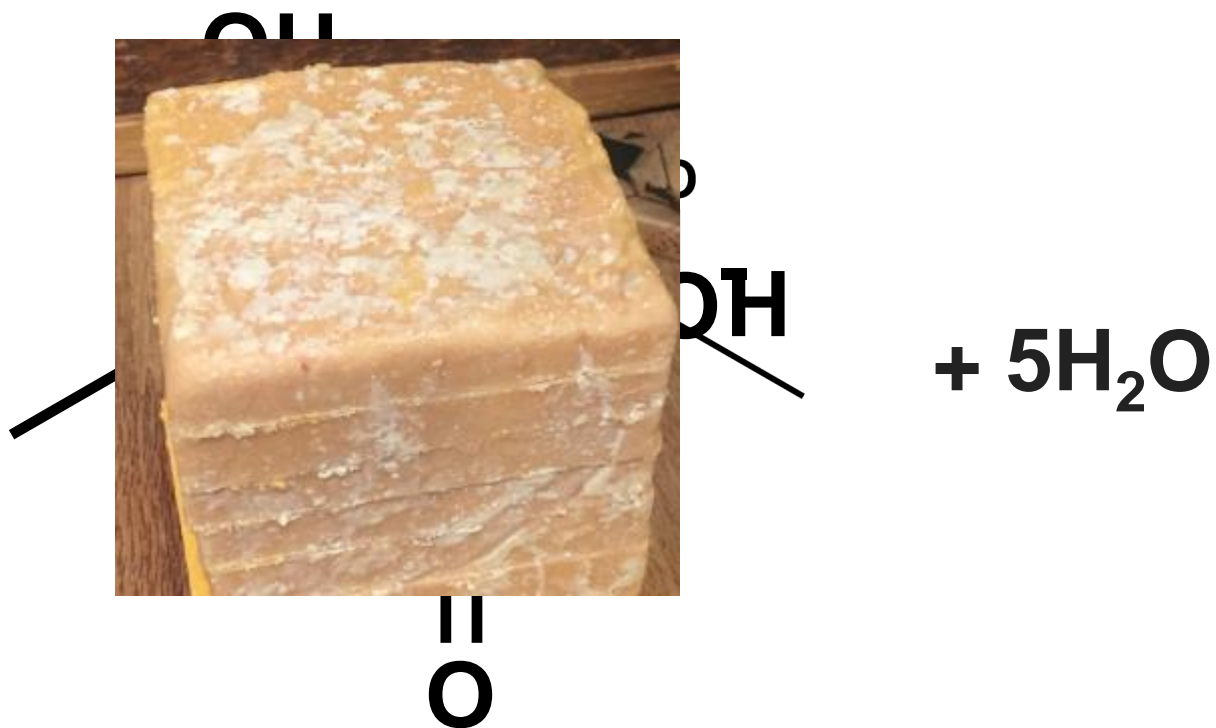


Two possible forms:

- L-CLP (only L-lactate)
- D/L-CLP (both L-Lactate and D-Lactate)



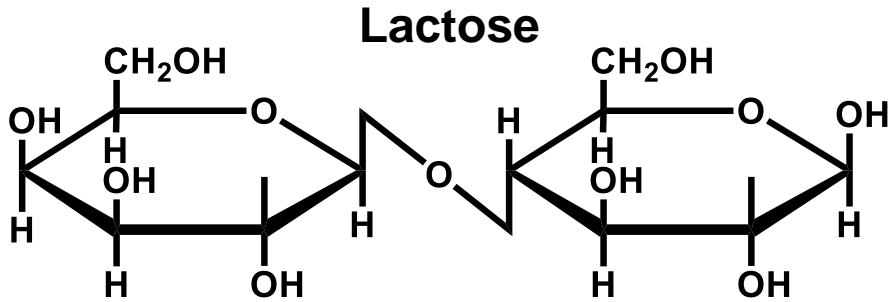
Formation



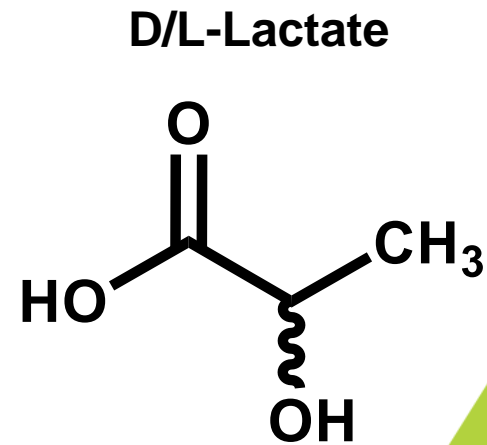
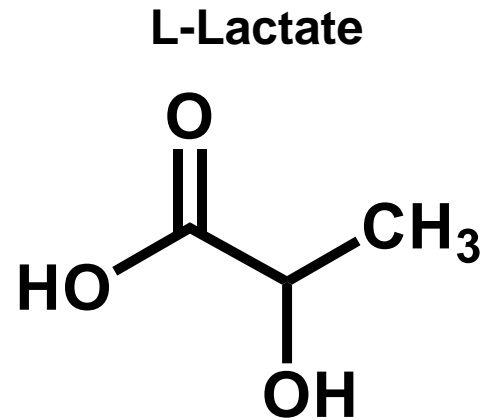
Calcium Acetate Pentahydrate



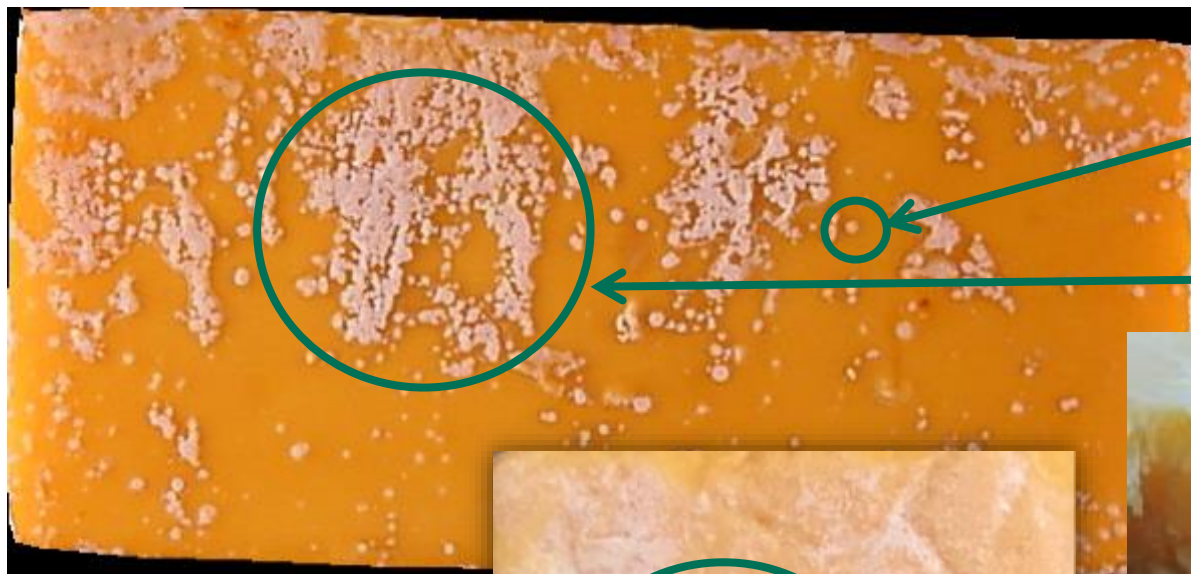
The Path to D/L-Lactate



L-CLP = Very soluble
DL-CLP = Very insoluble



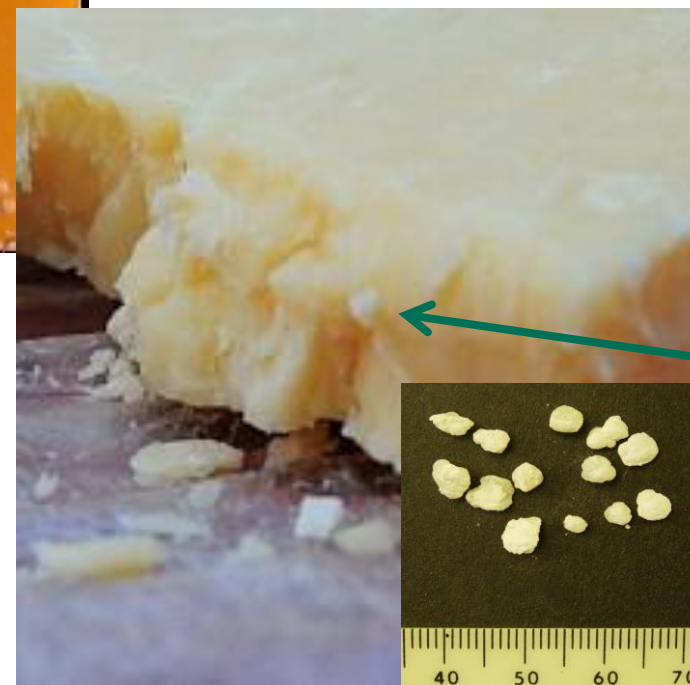
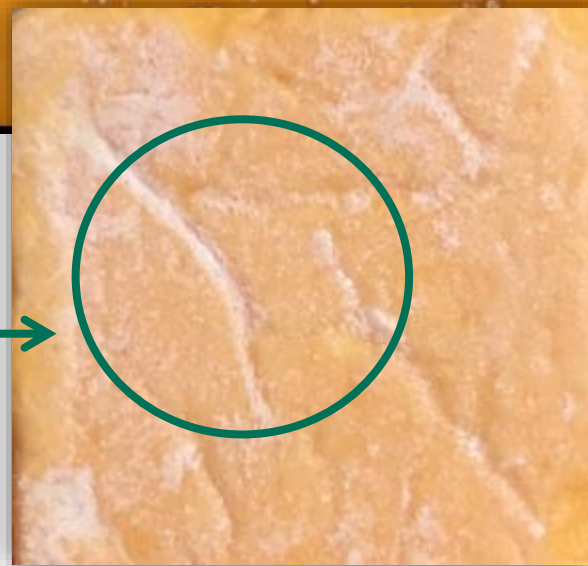
What's it Look Like?



Distinct crystals

Crystal aggregates

Diffuse haze



Internally Embedded



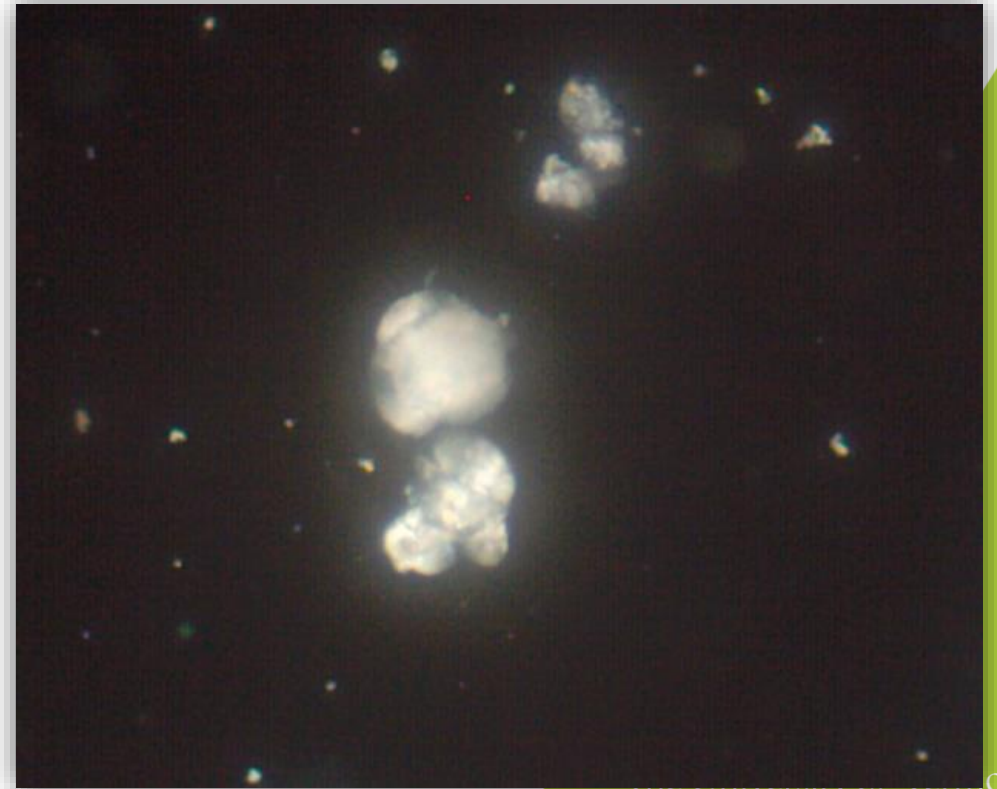
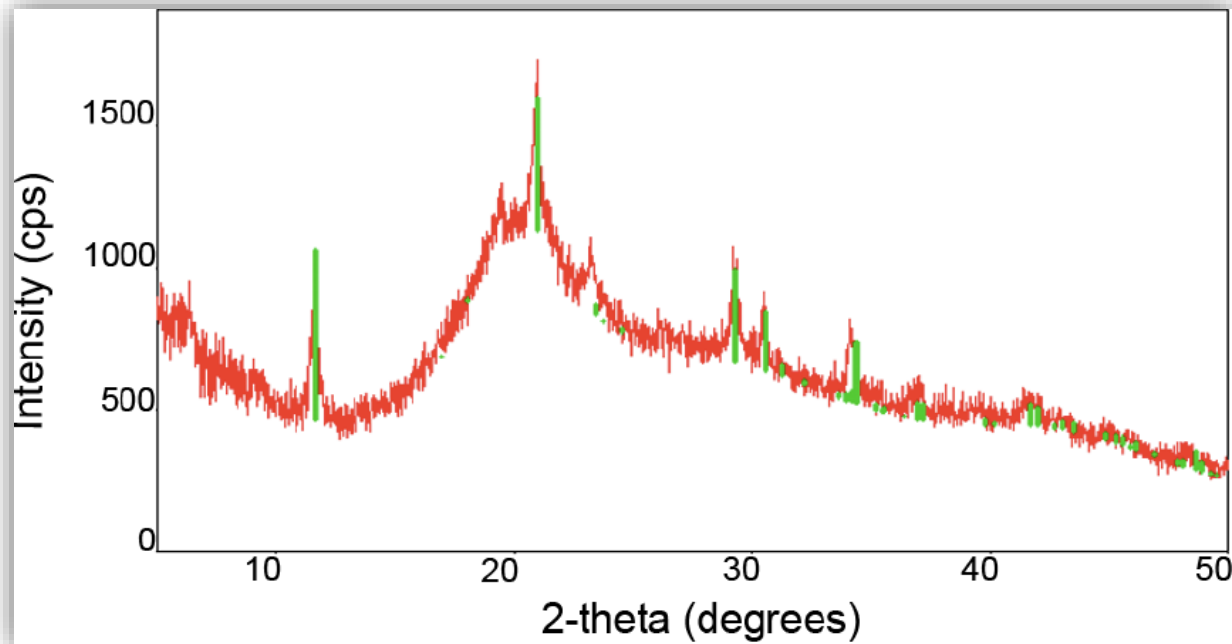
Soft Surface Ripened Cheeses



The University of Vermont

Crystals on Bloomy Rind

Brushite
 $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$





Crystals on Soft Washed Rind Cheeses

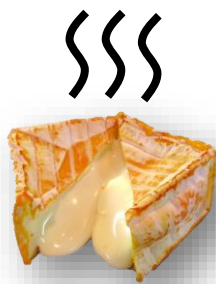
Milk & Cheese

Ca PO_4
Mg



Microbial Ripening

CO_3 NH_4
↑ ↑
 CO_2 NH_3

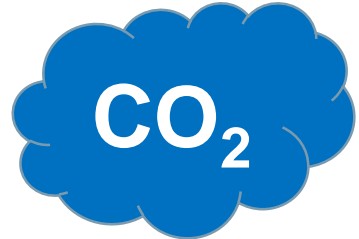


External

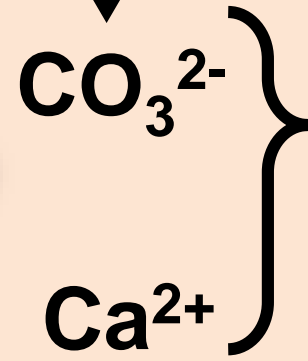
Mg



Ripening atmosphere

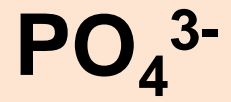
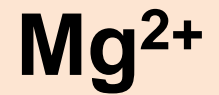


Smear

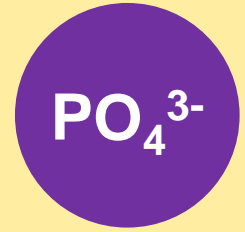


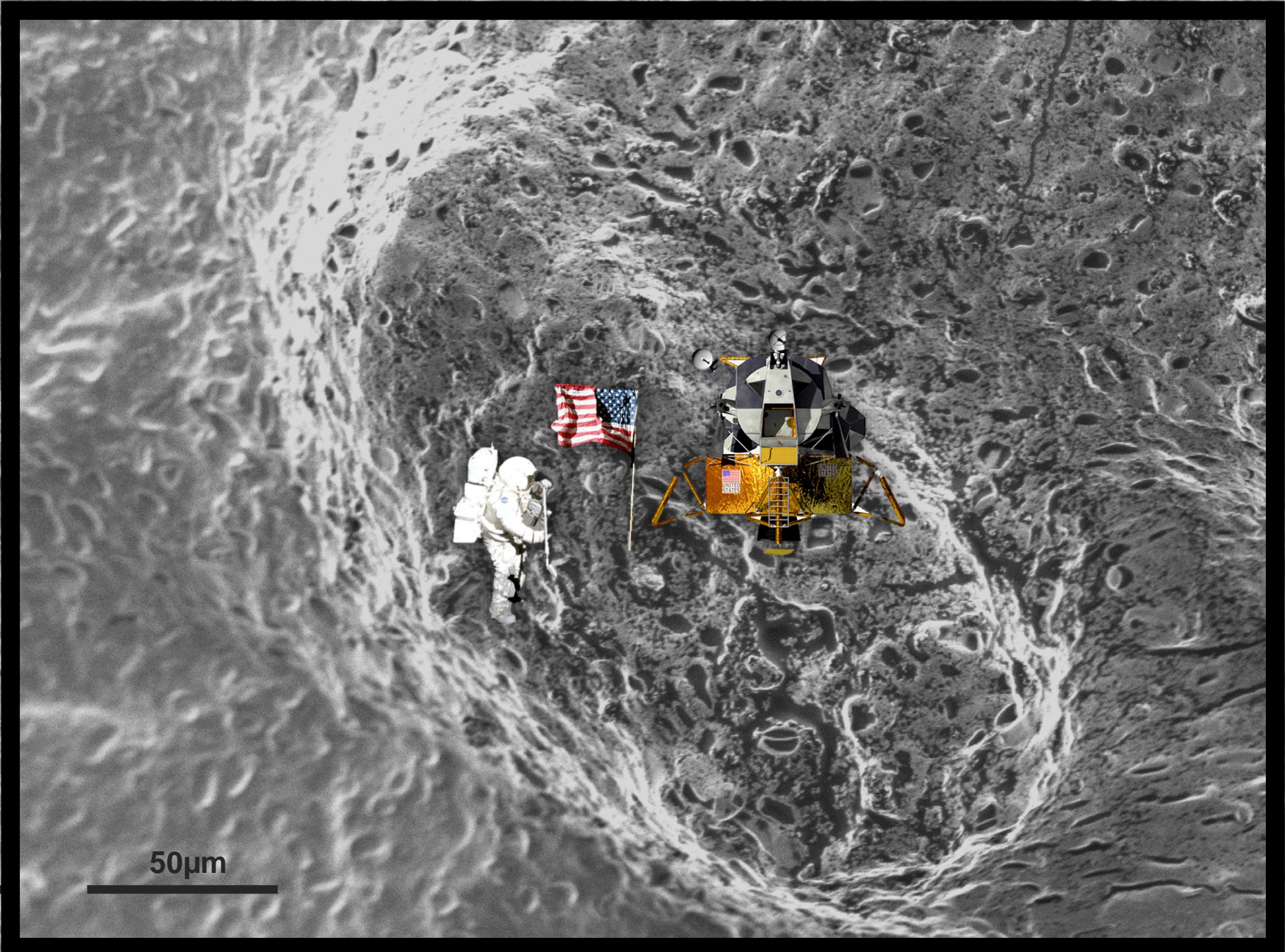
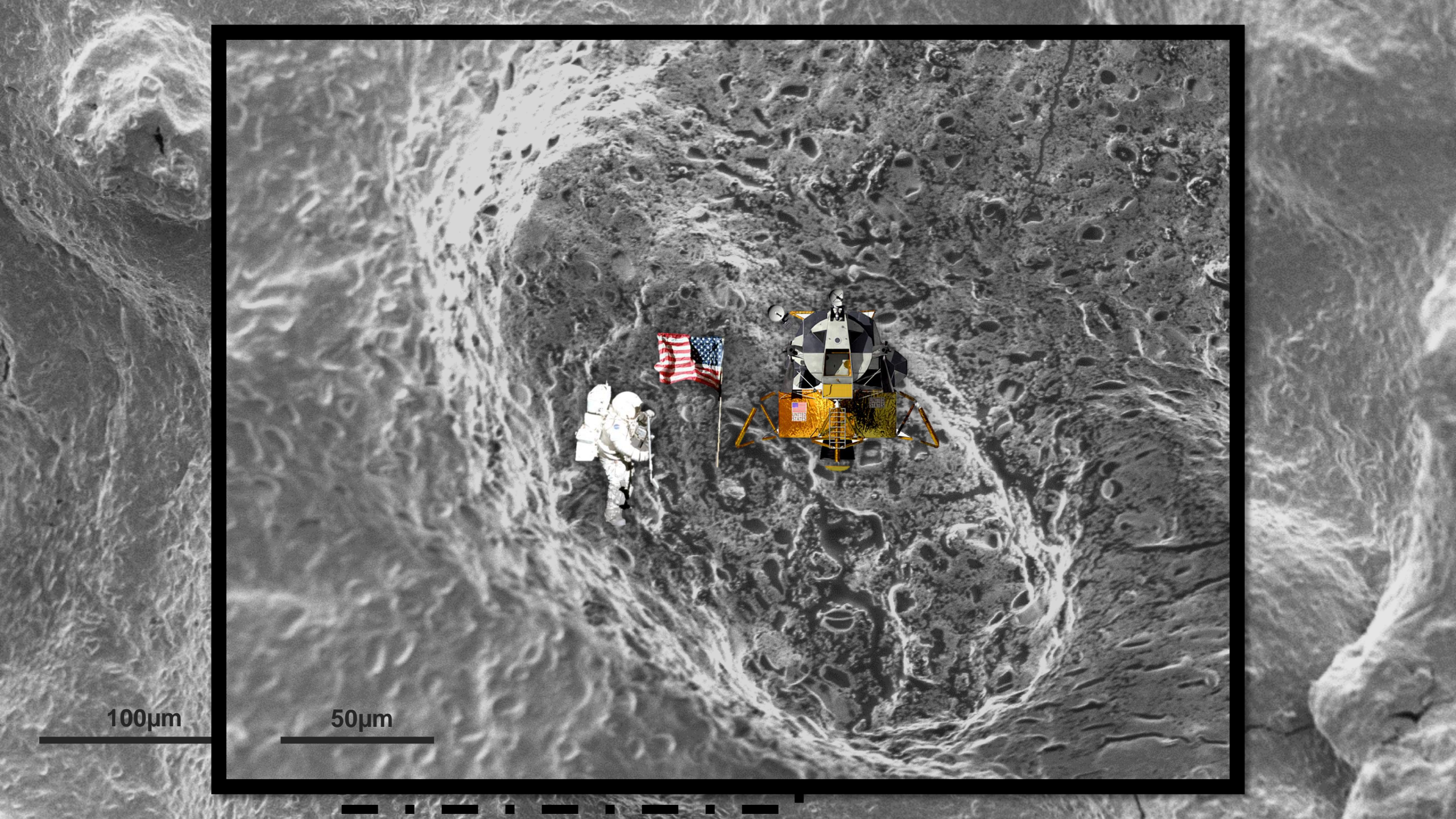
Ikaite

Struvite



Cheese body





100µm

50µm



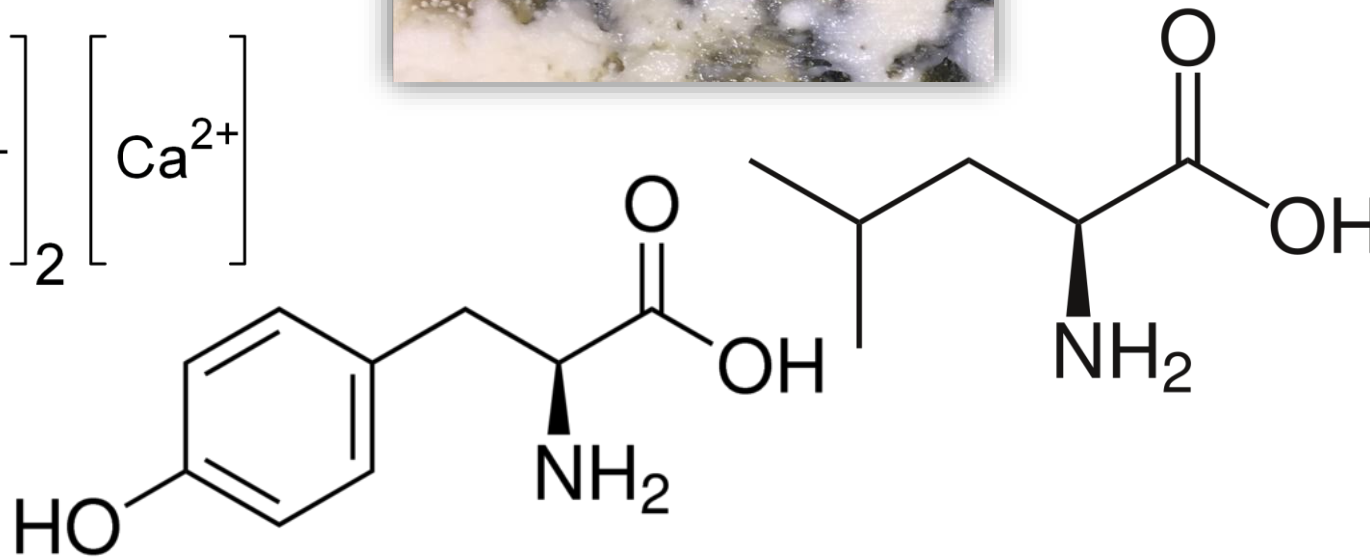
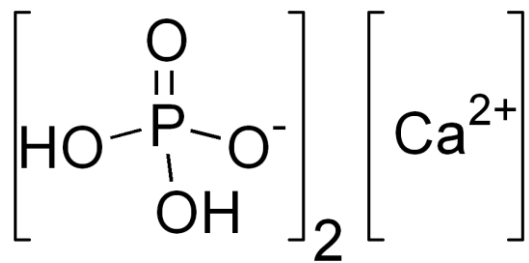
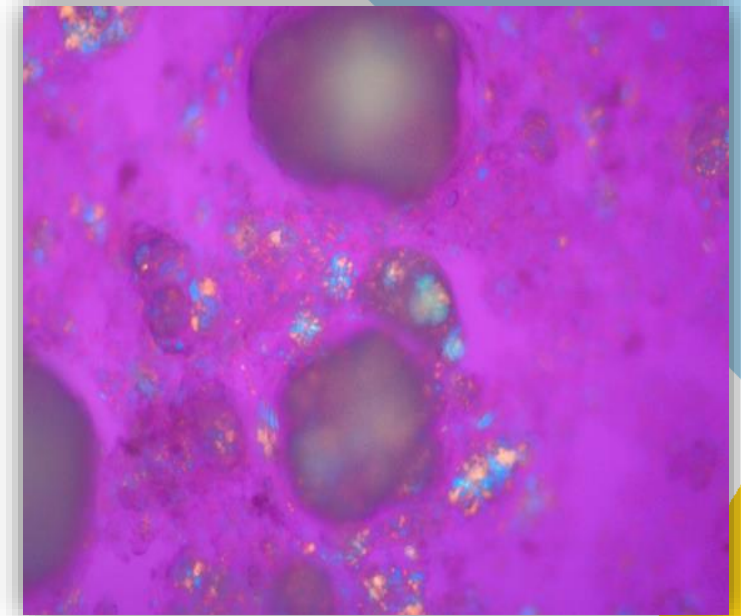
Blue Cheese



The University of Vermont

Crystals in Blue Cheese

- Tyrosine
- Leucine
- Brushite

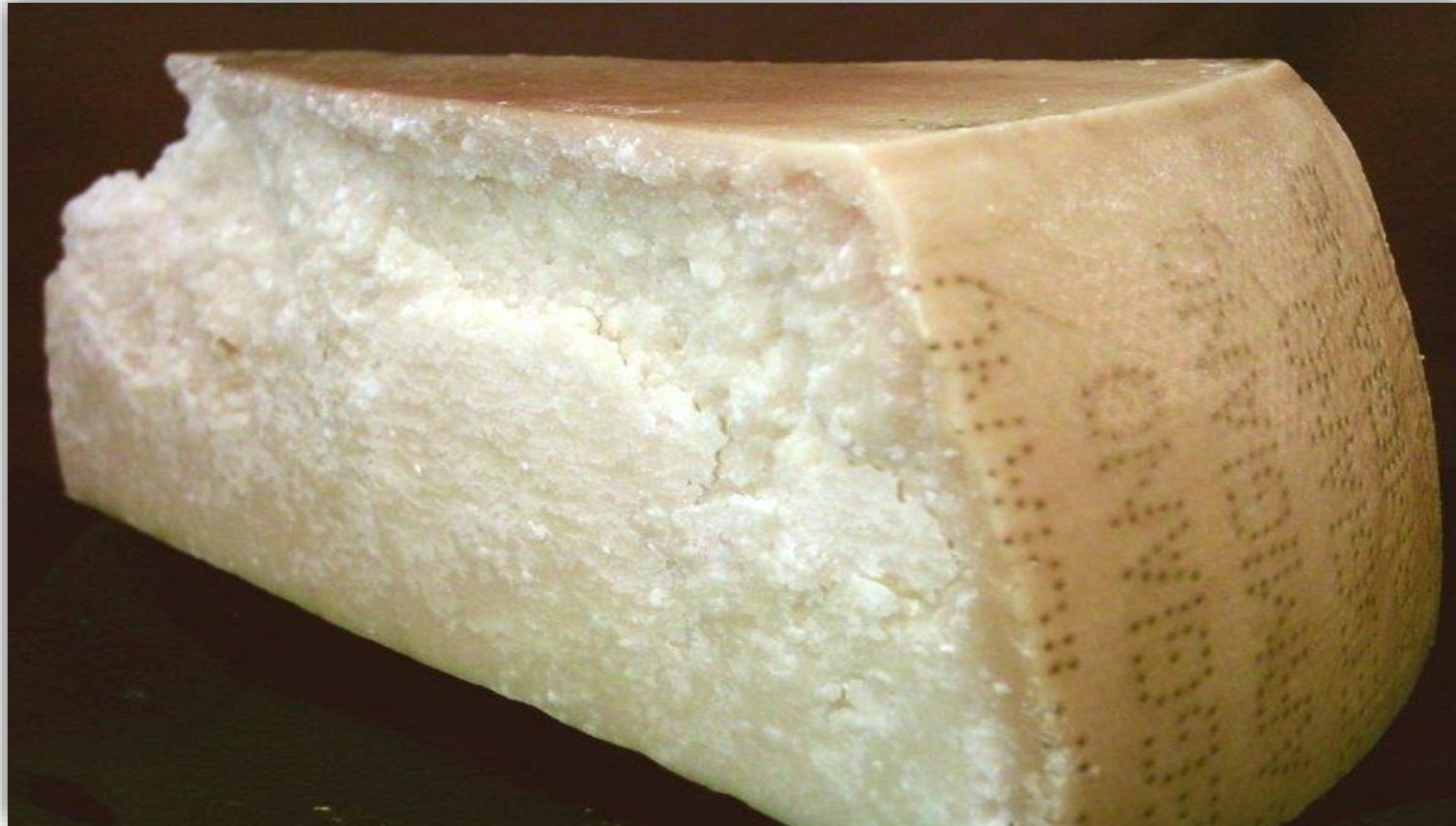


Italian Grana Cheese



The University of Vermont

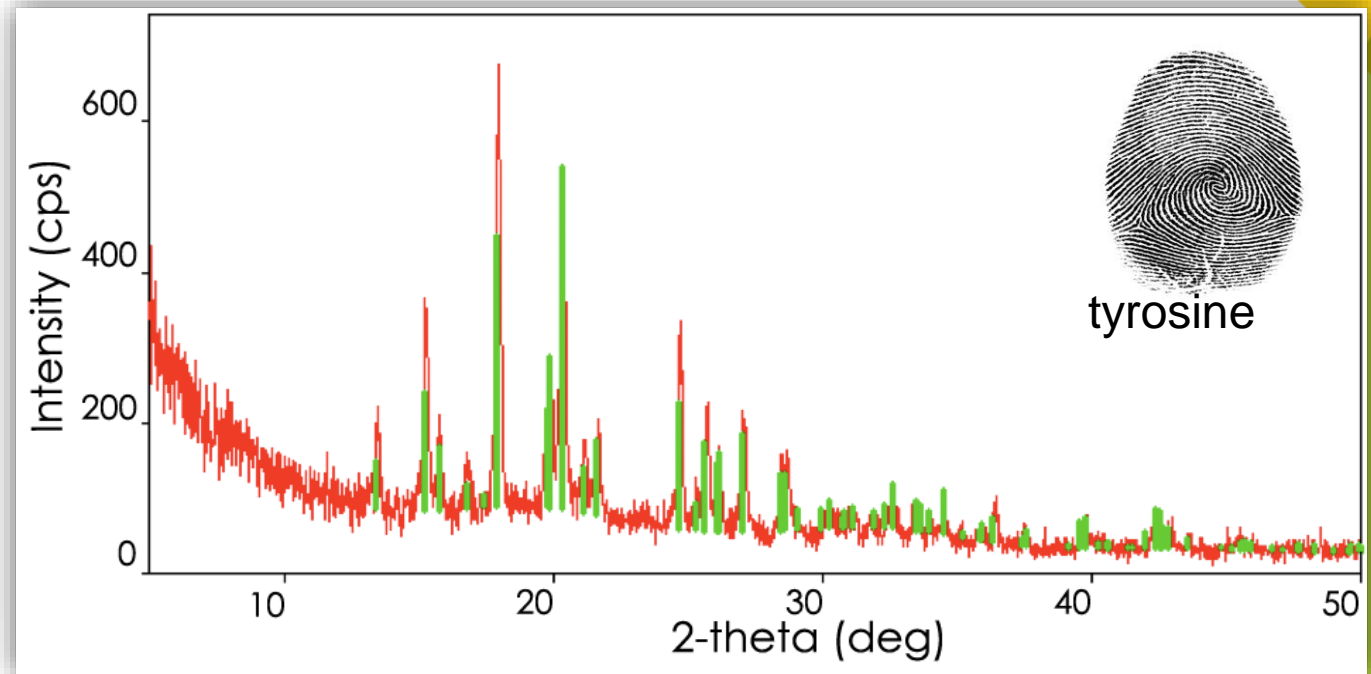
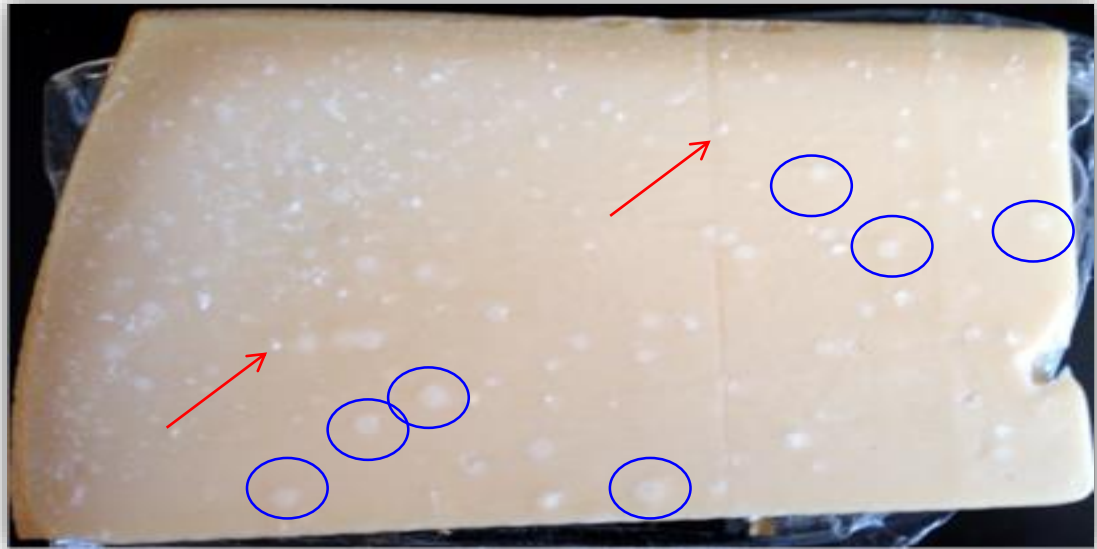
Parmigiano-Reggiano Cheese



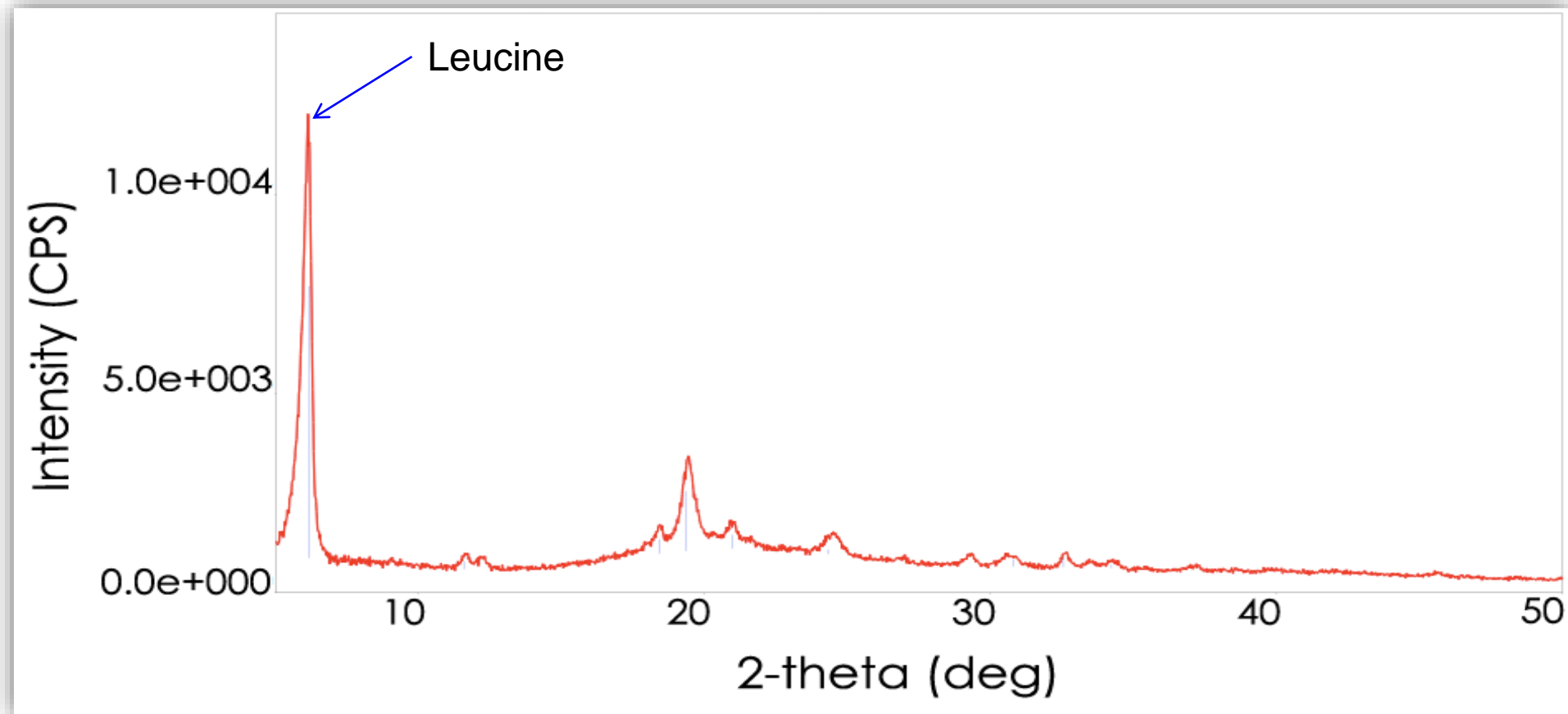
Source: http://en.wikipedia.org/wiki/Parmigiano-Reggiano#mediaviewer/File:Parmigiano_reggiano_piece.jpg



Tyrosine crystals in Parmigiano-Reggiano cheese



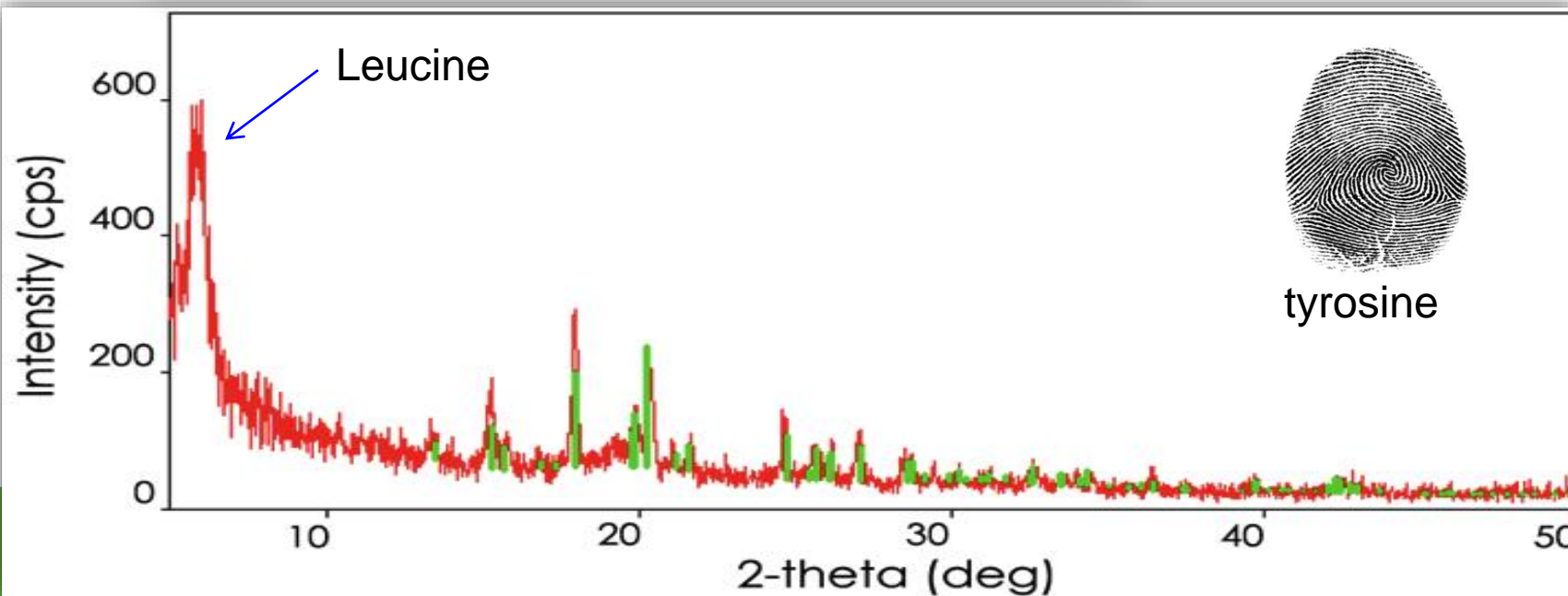
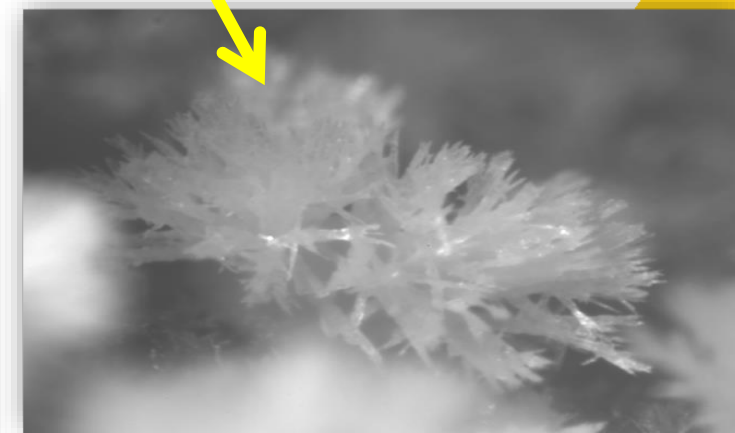
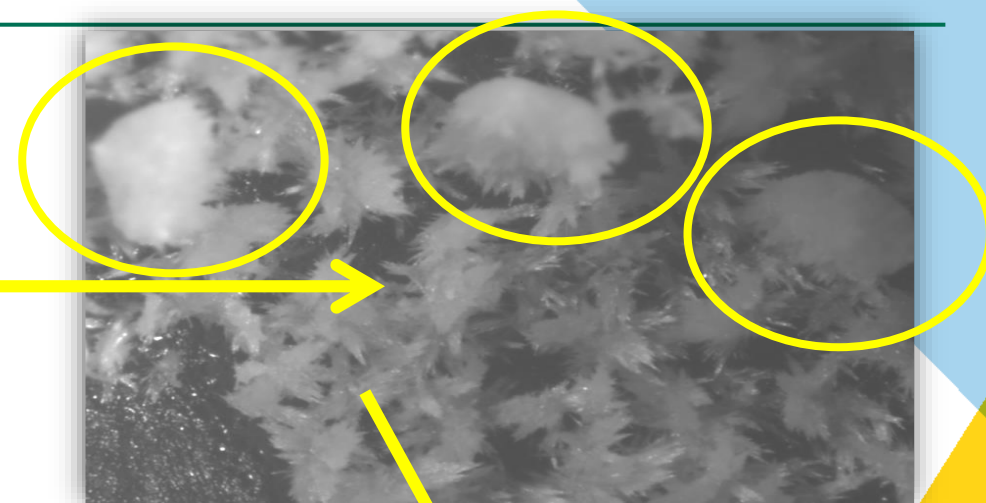
X-ray diffraction pattern of “pearls” in Parmigiano-Reggiano



Dutch Gouda Cheese



Crystal formation in Gouda cheese



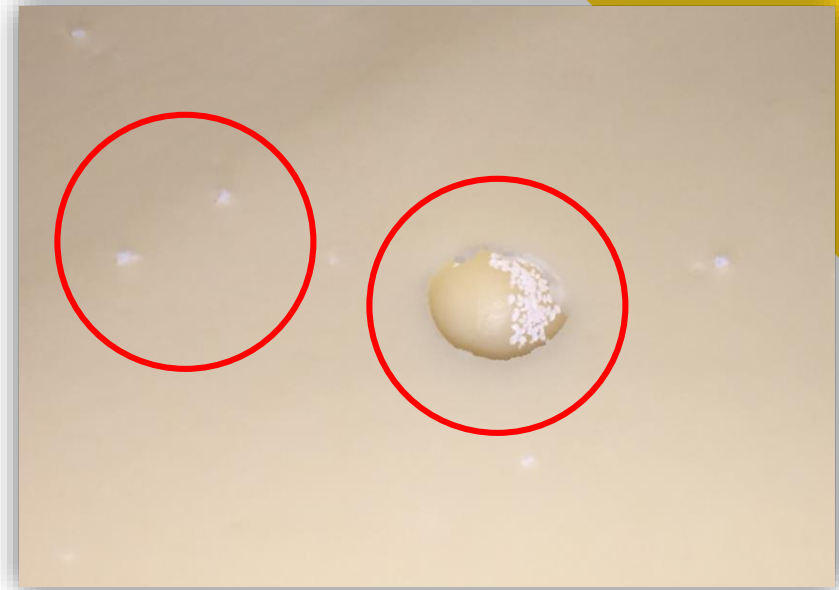
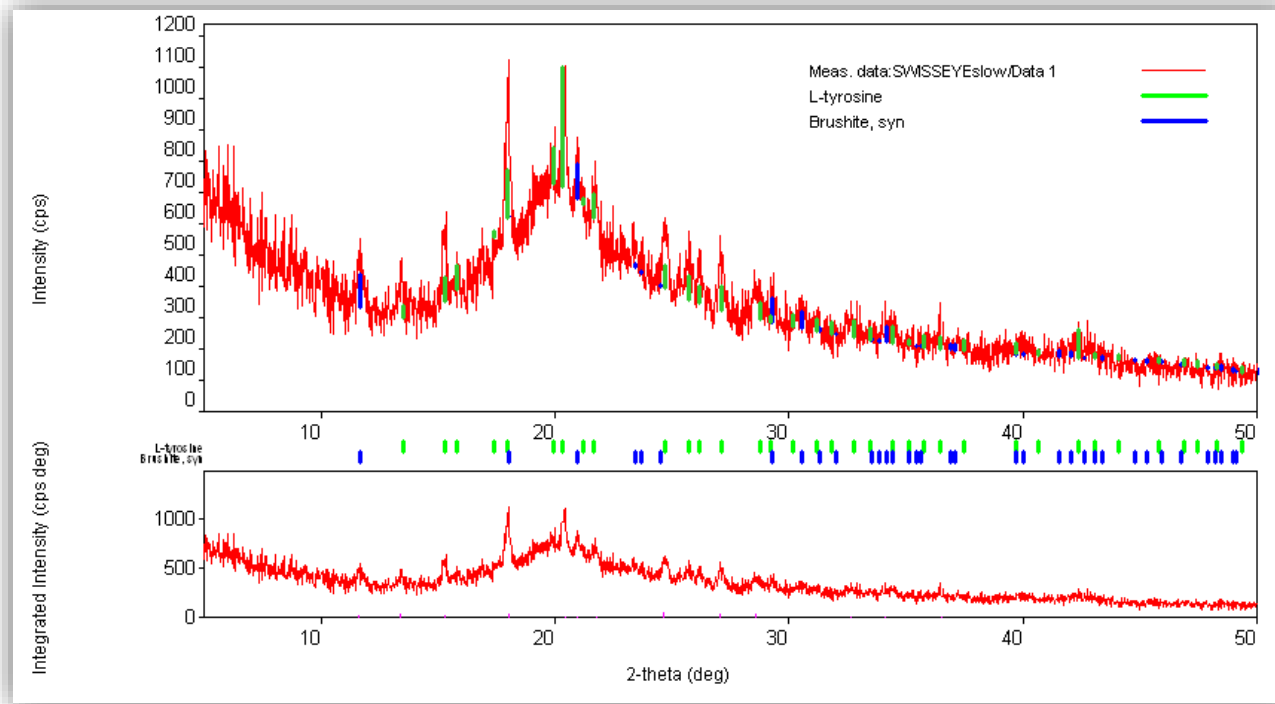
Alpine Cheese



The University of Vermont

Swiss Cheese

- Tyrosine & Brushite



Thank you!



The University of Vermont