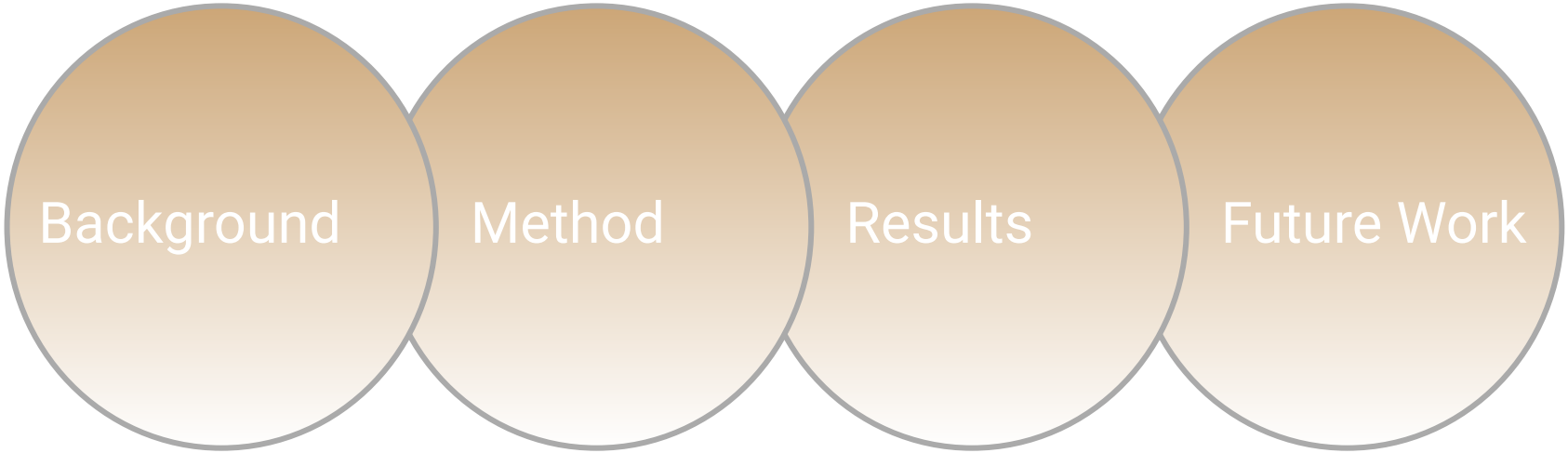
Multi-Scale Structures of Starch as Revealed by Scattering Techniques: From Unit Cell to Nanostructure

Amy Musser, University of Maryland
NCNR SURF 2022
Mentors: Yimin Mao and Susana Teixeira

Overview



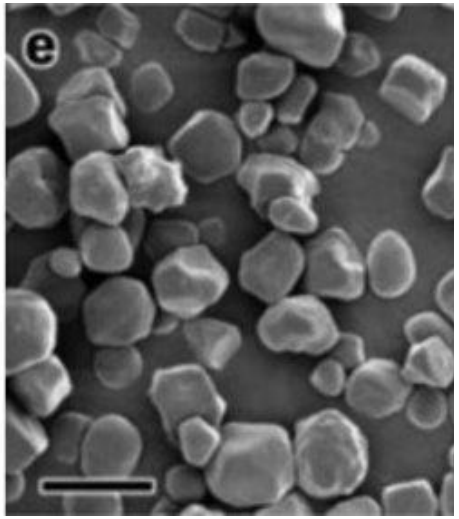
Starch

Sample preparation, SAXS, WAXS

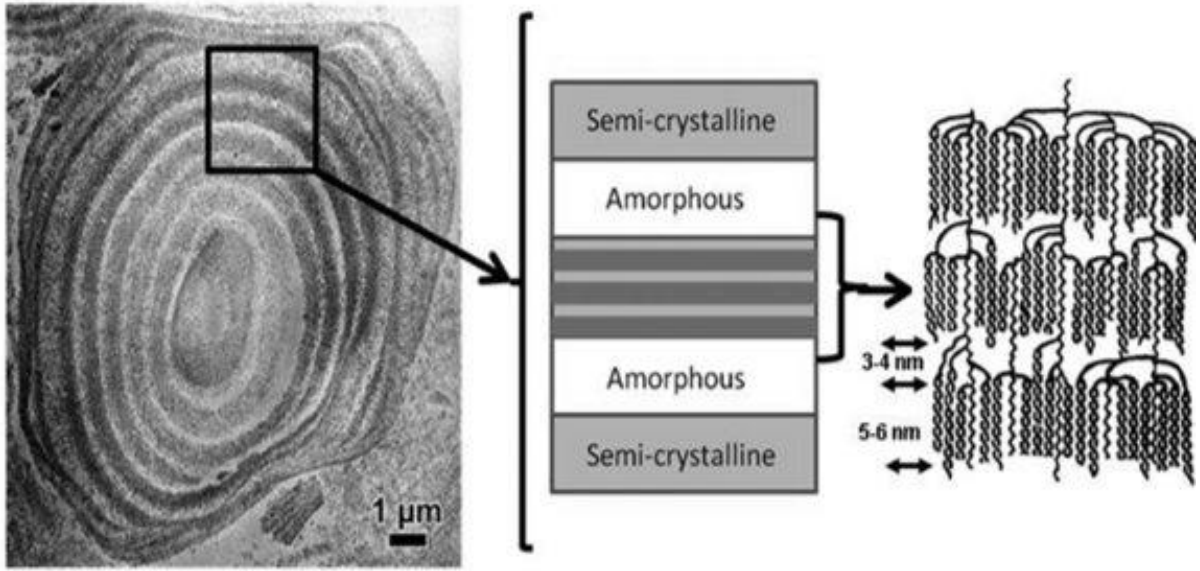
Graphical analysis

SANS for future work

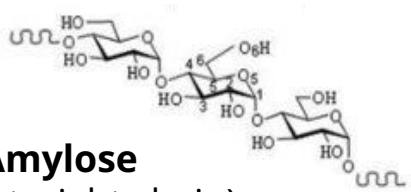
What is starch?



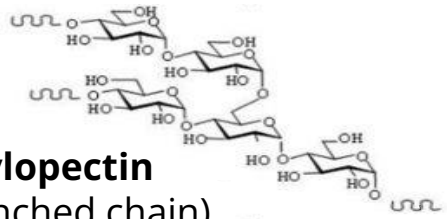
Scanning electron microscopy of corn starch granules. Scale bar 20 μm



Starch granule growth rings (left) semi-crystalline and amorphous layers (center), branching of amylopectin (right)



Amylose
(straight chain)



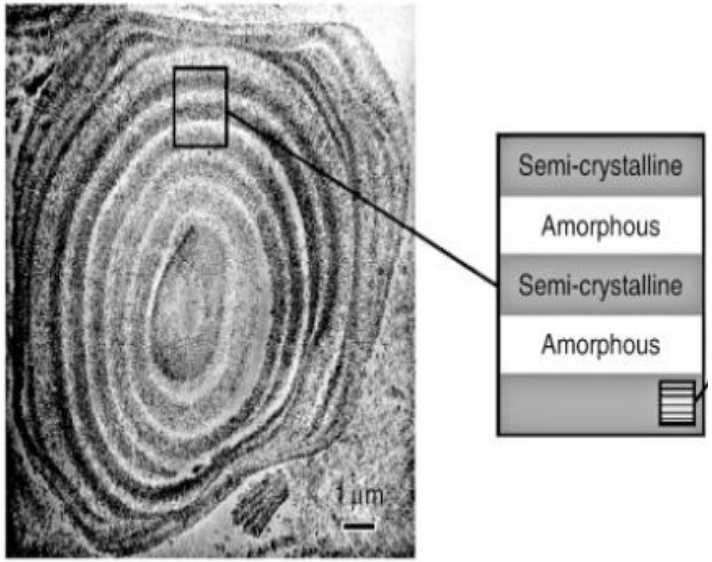
Amylopectin
(branched chain)

DOI 10.1002/star.201000013

Experimental Objective

Question: How does addition of water within hydrated starches affect the structure of type A and type B starches?

Objective: Use small angle scattering (SAS) and contrast variation techniques to determine the effect of water on structure in hydrated starch samples in both type A and type B crystals



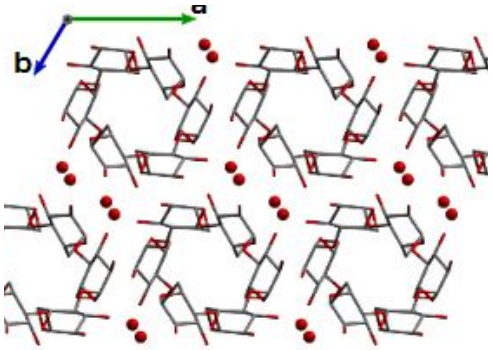
Starch granule growth rings (left), semi-crystalline and amorphous layers (right). Scale bar 1 μm

DOI 10.1071/CH07168

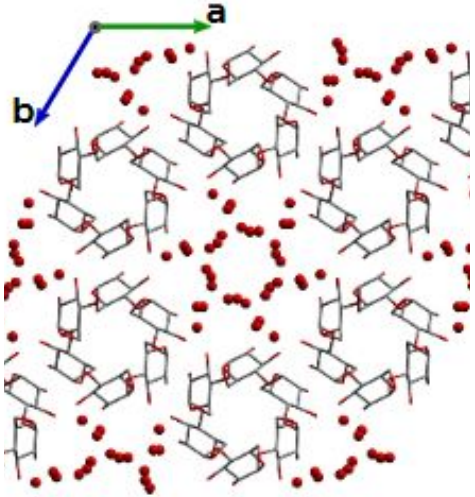
Type A and B Crystals

		Amylose Percent	Crystalline Type
1	Waxy Maize (WM)	0	A
2	Normal Maize (NM)	26	A
3	High Amylose Maize (HAM)	70	B
4	Pea	30-40	C

Type A



Type B



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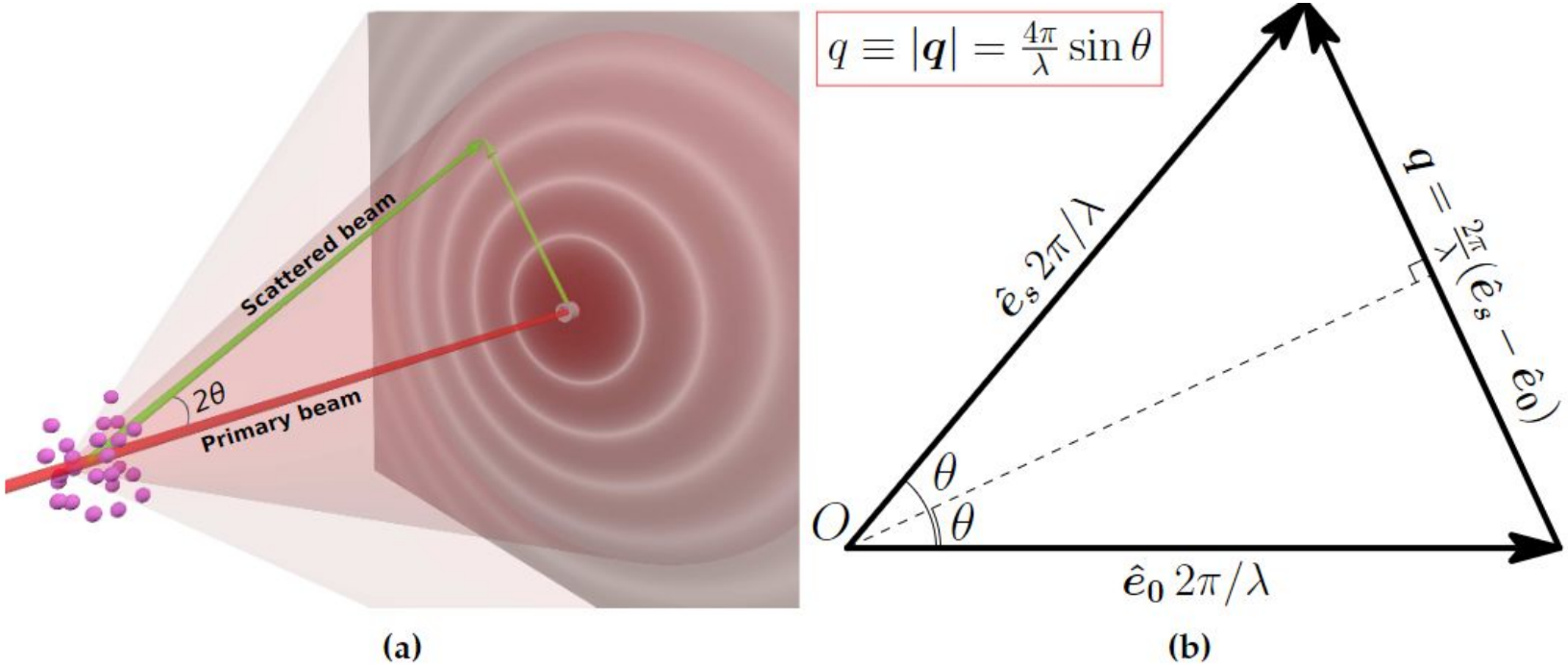
Small and Wide Angle Scattering



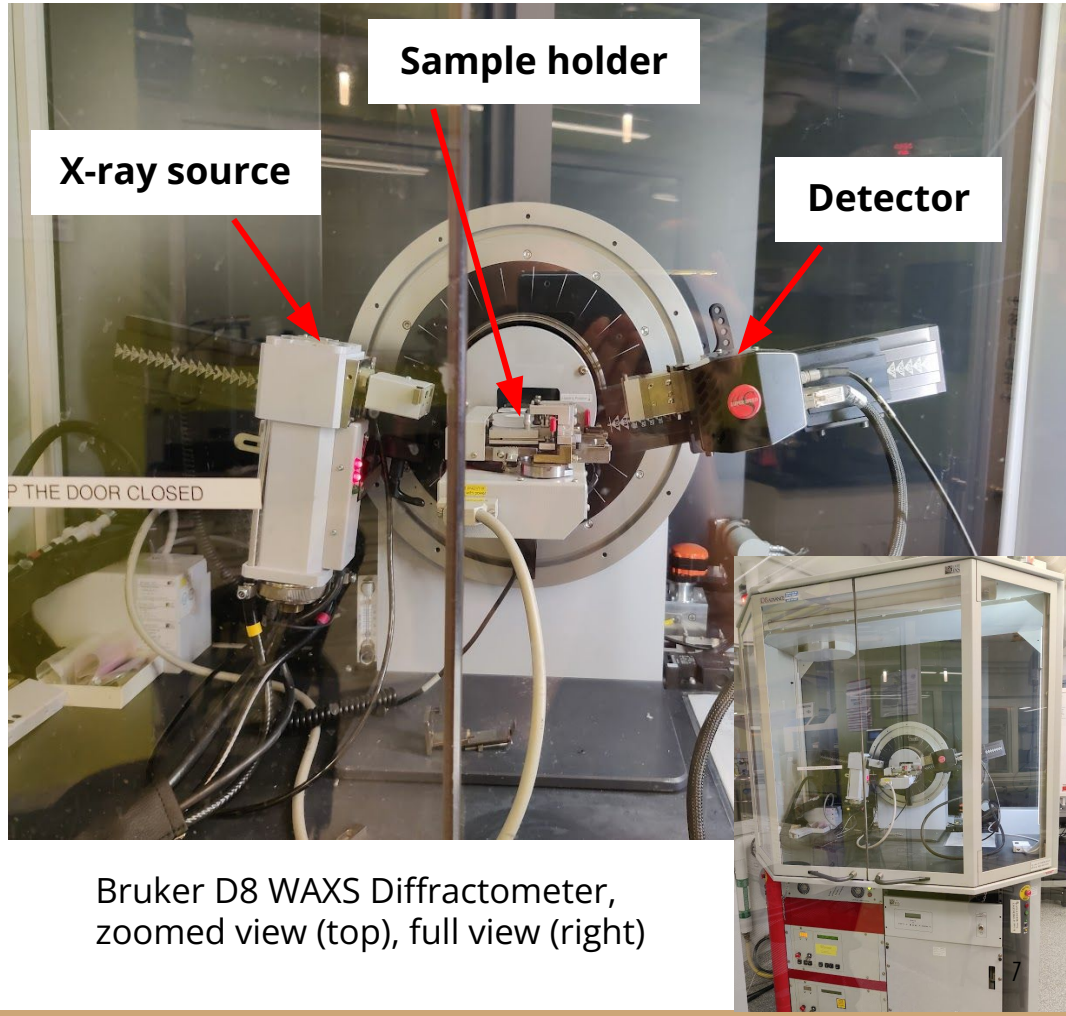
(a) Simplified scattering experiment and (b) scattering geometry which defines scattering vector ***q***

Y. Mao, *Scattering 101: A Heuristic Treatment for the Impatient,* UMD/NIST (2022)

Wide Angle Scattering

- Bruker D8 Diffractometer
  - UMD X-ray Crystallography Center
- X-rays from copper
  - Wavelength: 1.54 Å
- Software for data processing: Topaz

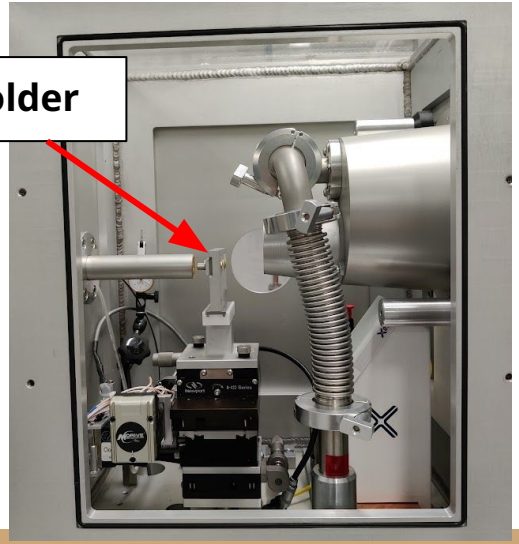
Sample	Exposure Time
Dry	20 minutes per sample
Wet	5 minute increments for 20 minutes, 2x, no significant difference between rounds

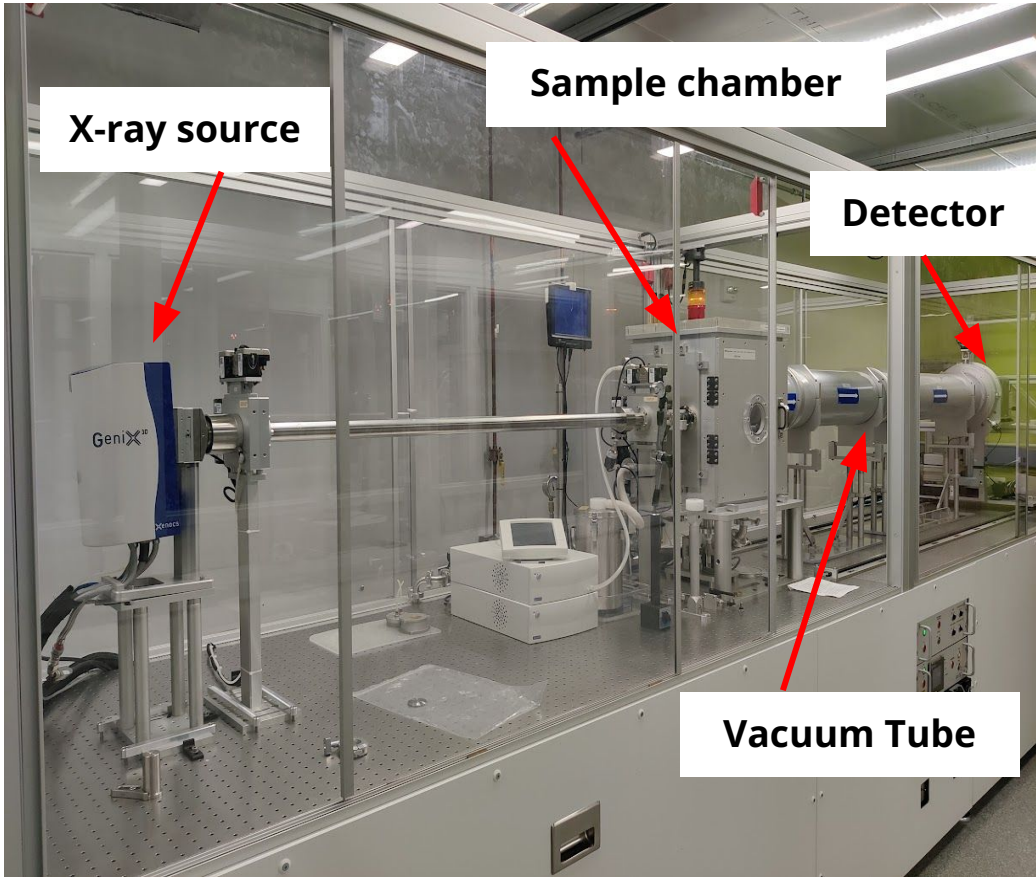


Bruker D8 WAXS Diffractometer, zoomed view (top), full view (right)

Small Angle Scattering

- Xeuss SAXS/WAXS System
  - UMD X-ray Crystallography Center
- X-rays from copper
  - Wavelength: 1.54 Å
- Software for data processing: Igor Pro 8





Xeuss system (top), sample chamber (left)

SAXS Data Processing Parameters

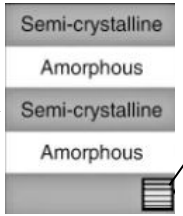
- Detector: Pilatus 300k
- Sample holder thickness (mm): 0.8
- CCD pixel size (mm): 0.172
- Beam size (mm): 0.8
- Calibration standard: AgBe
- Background: Kapton
- Plotting: Q-dot, 300 points and circular average
- Data from two sample to detector distances (SDD) stitched together

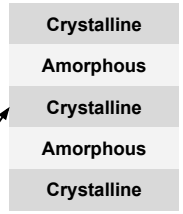
SDD (mm)	**Exposure Time**
2500	20 minutes, 2x for starches; 10 minutes, 1x for kapton
590	15 minutes, 2x for starches; 15 minutes 1x for kapton

Sample Preparation

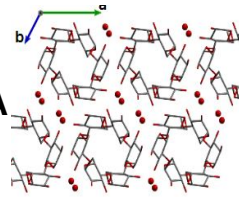
		Crystalline Type	Dry Moisture (%)	WAXS Wet Moisture (%)	SAXS Wet Moisture (%)
1	Waxy Maize (WM)	A	13	49.9	50.0
2	Normal Maize (NM)	A	13	50.0	50.0
3	High Amylose Maize (HAM)	B	12	49.7	50.0
4	Pea	C	13.58	50.0	50.0

SAXS Results

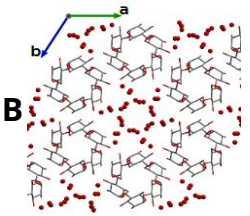


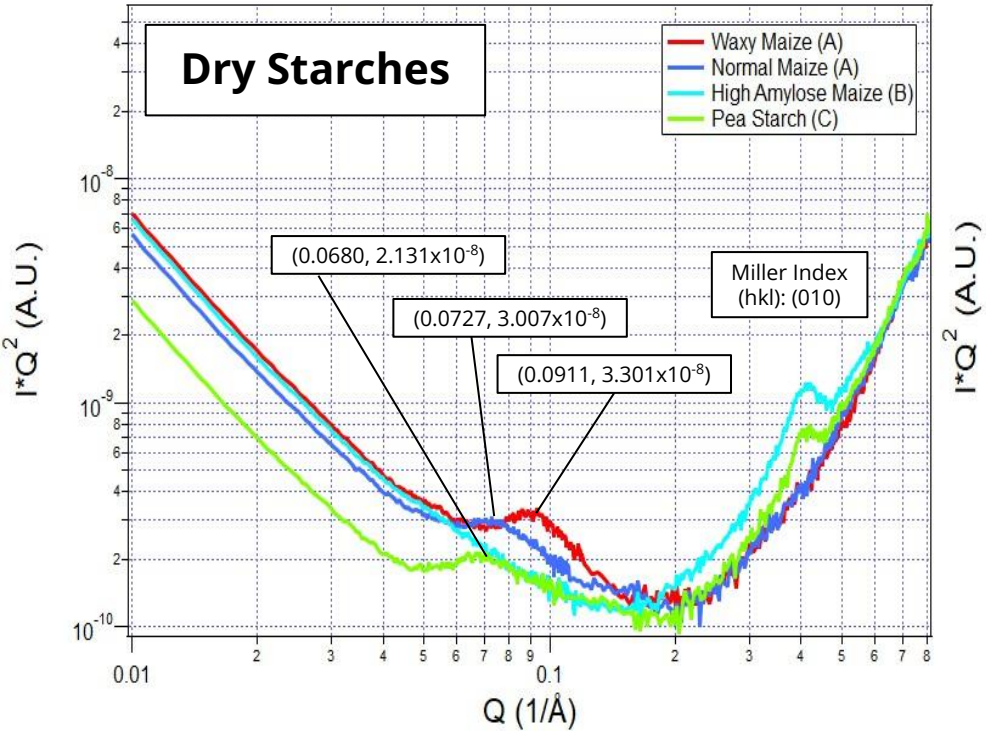


Type A

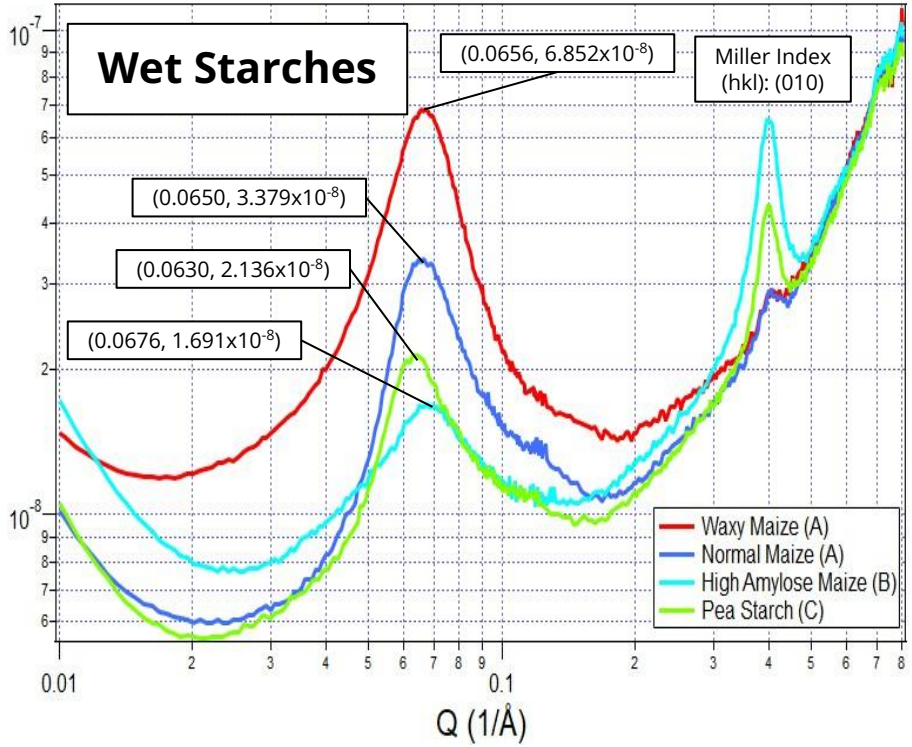


Type B



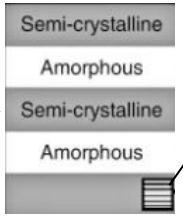


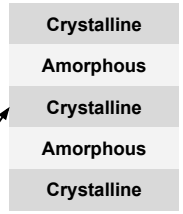
SAXS of dry starches. Data at SDD 2500 and 590 mm stitched. Log scale



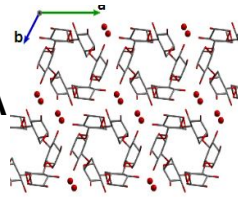
SAXS of wet starches (50% hydration). Data at SDD 2500 and 590 mm stitched. Log scale.

SAXS Results

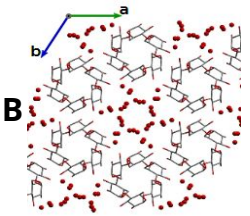




Type A



Type B



Crystalline and Amorphous Interlamellar Distance (d)

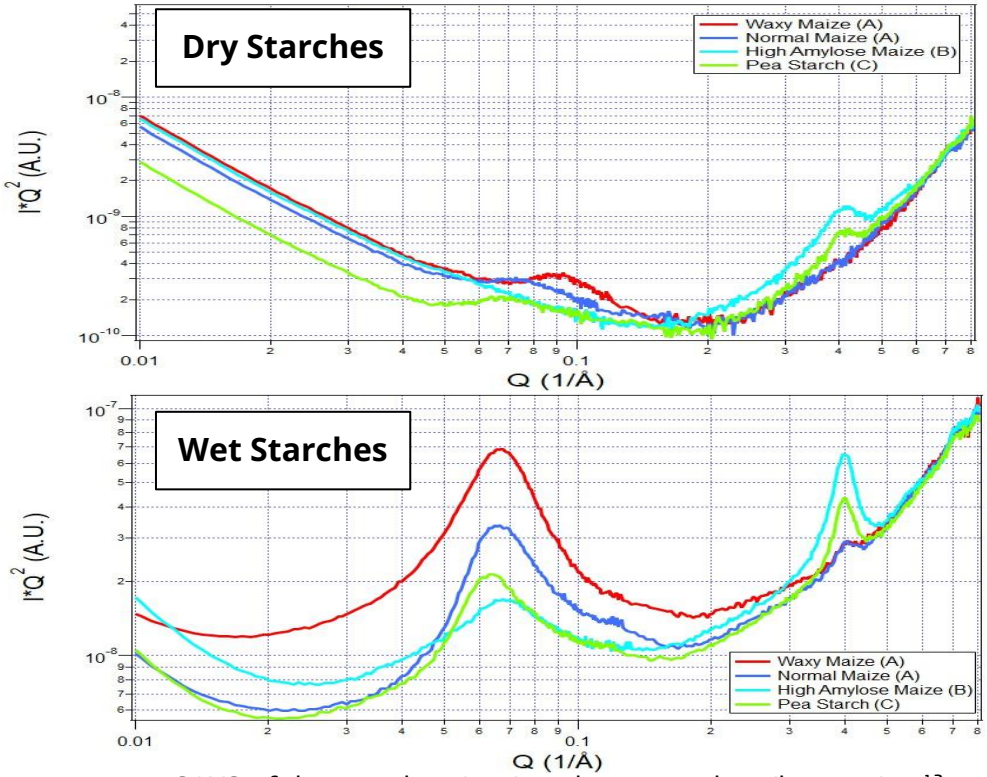
$$d = \frac{2 \times \pi}{q}$$

Starch	Crystal Type	Amylose (%)	d (dry) (nm)	d (wet) (nm)
Waxy Maize	A	0	6.90	9.58
Normal Maize	A	26	8.64	9.67
High Amylose Maize	B	70	--	9.27
Pea	C	30-40	9.24	9.98

Peak Width

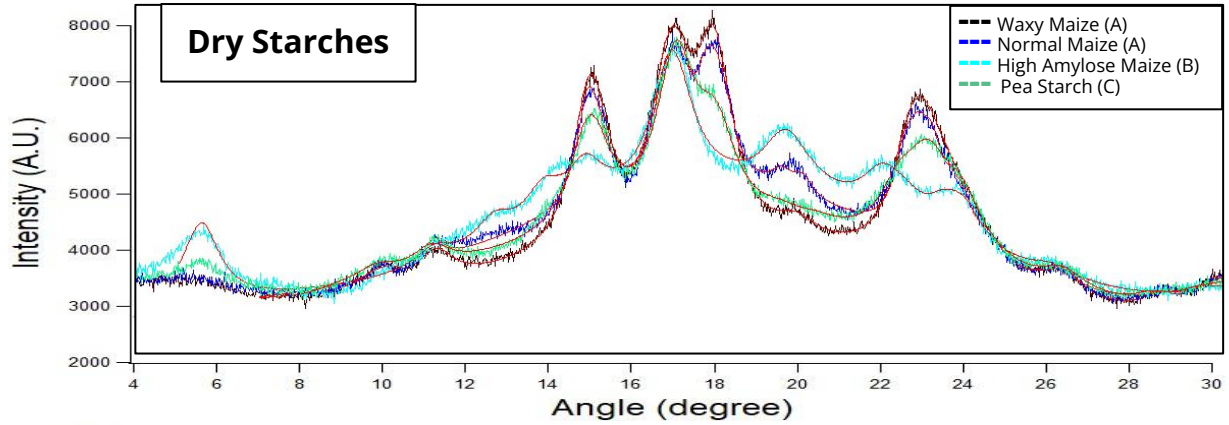
Water increases degree of organization

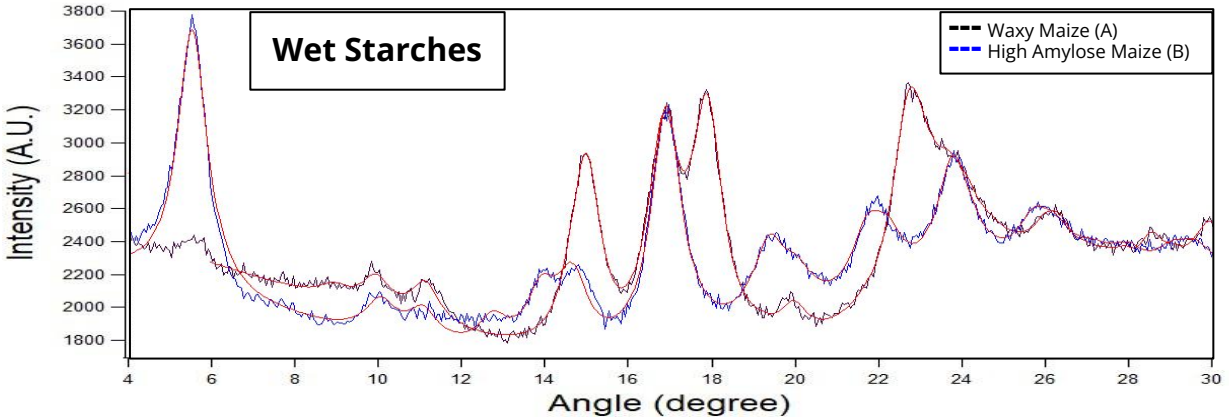
- Waxy Maize (most sharp)
  - Most ordered
- High Amylose Maize (least sharp)
  - Least ordered



SAXS of dry starches (top) and wet starches (bottom). Data at SDD 2500 and 590 mm stitched. Log scale.

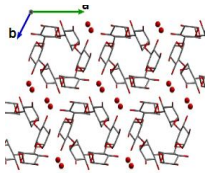
WAXS Results



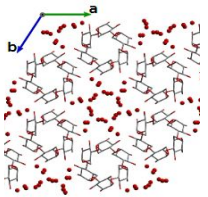


WAXS of dry starches (top) and wet (50% hydration) starches (bottom). Data fitted using TOPAZ and crystal unit cell parameters.

Type A



Type B



Parameters

Crystal	Type A	Type B
Symmetry Space Group	B112	P61
Cell Length A (Å)	20.83	18.52
Cell Length B (Å)	11.45	18.52
Cell Length C (Å)	10.58	10.57
Gamma (degrees)	122.0	120.0

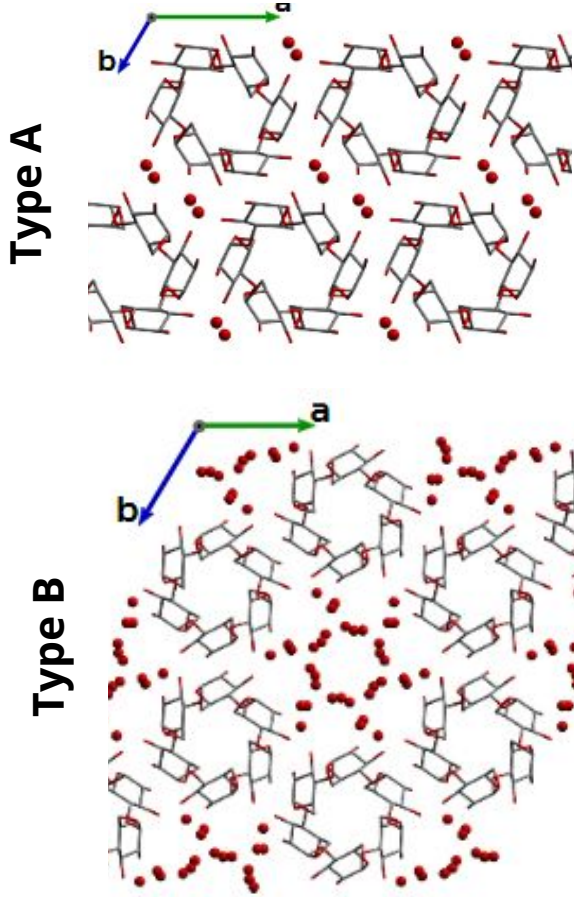
Hydrated samples show narrow, exaggerated peaks

Future Work: Analysis of wet normal maize and pea starch

Conclusions

Hydrated Starch

- Swells crystalline and amorphous inter-lamellar distance (nm scale)
- Increases organization of crystalline and amorphous lamella (nm scale)
  - Type A starch more so than Type B starch
- Increases crystallinity of unit cells (μm scale)
  - Type B starch more so than Type A starch



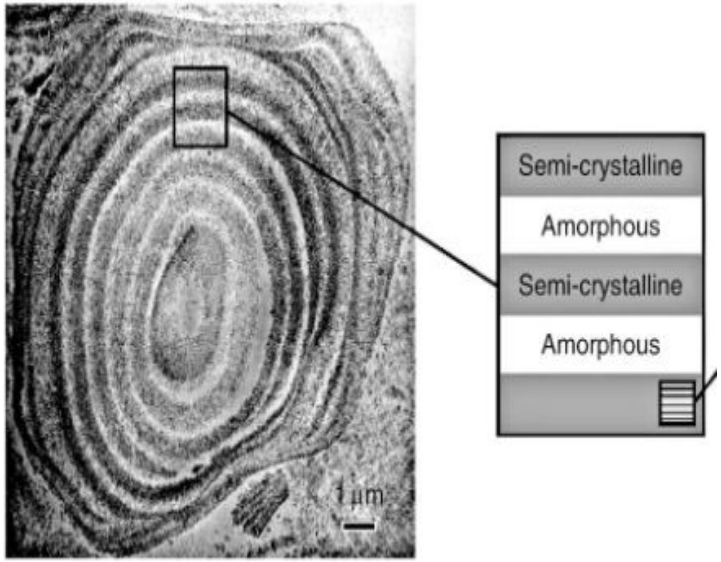
Y. Mao, *Surf Project Introduction: Starch and Pickering Emulsions,* UMD/NIST (2022)

Future Work

Question: How does addition of water within hydrated starches affect the structure of type A and type B starches?

Objective: Use SAS and contrast variation techniques to determine the primary location water in hydrated starch samples in both type A and type B crystals

Purpose: Knowledge of starch structure can inform measurement techniques and choices in composition and corresponding applications in the food and nonfood industry (e.g. paper making, clothing, etc)



DOI 10.1071/CH07168

Acknowledgements

NIST SUMMER UNDERGRADUATE RESEARCH FELLOWSHP SURF

NSF CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NIST

UNIVERSITY OF MARYLAND

NIST CENTER FOR NEUTRON RESEARCH

- Yimin Mao
- Susana Teixeira
- Robert Briber
- Joe Dura
- Paul Butler
- Susan Krueger
- Brandi Tolivar
- Mary Ann Fitzgerald
- Natalie Schwab