Achieving Phase Purity in Nickel Sulfides

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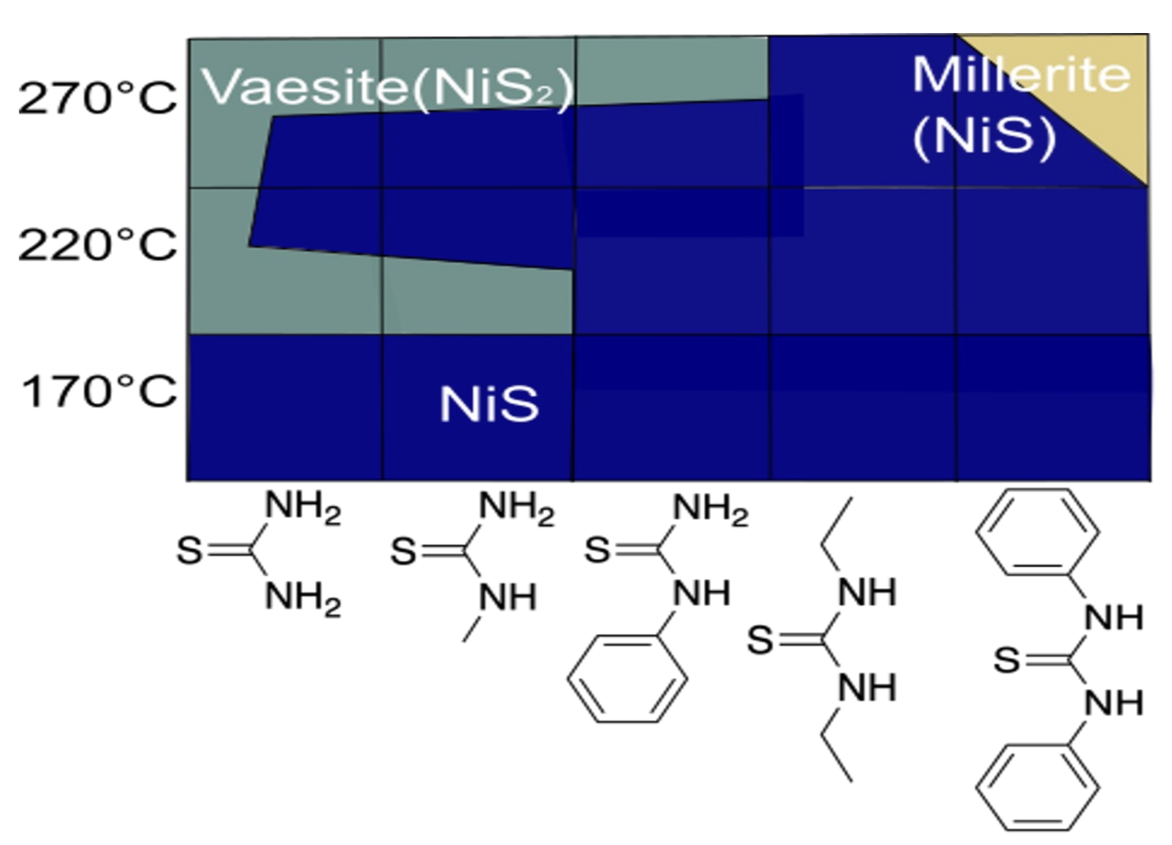
What are Crystalline Phases?

Crystalline phases are made of the same elements, but they are structed differently. These crystalline phases exhibit different behaviors that can lead to them having different applications (i.e., catalysis and semiconductors).



Phase → Form → Function

The effects of precursor reactivity and temperature on nickel sulfide formation have been studied. By using this knowledge, we can produce ways to manipulate the synthesis of the nickel sulfides to obtain the desired phases.

	Phase	Chemical Formula	Space Group	Approximate Sulfur packing	Cation Hole Filling	DS_f (J/mol K)	DH_f (kJ/mol)	Reference Author
★	Vaesite	NiS_2	Pa3	S_2^{2-} in ccp	All Oh	80	-124.9, -128, -133.9	Cemič, Gamsjäger (16, 17)
☑	Millerite	NiS	R3m	S^{2-} in hcp	All Td	53.0	-91.0, -94.0	Cemič, Gamsjäger (16, 17)
★	NiS	NiS	P 6_3/mmc	S^{2-} in hcp	All Oh	60.9	-88.1, -88.1	Cemič, Gamsjäger (16, 17)
★	Godlevskite	Ni_9S_8	I42d	S^{2-} in ccp	Td, Square Pyramidal	481	-760	Gamsjäger (17)
		Ni_7S_6	Bmmb	S^{2-} in ccp	Td, Square Pyramidal	390.2	-582.8, -560.8	Cemič, Waldner (16, 18)
☑	Polydymite	Ni_3S_4	Fdm	S^{2-} in ccp	All Oh, ½ Td (spinel)	191.9	-309.1	Waldner (19)
☑	Haezlewoodite	Ni_3S_2	R32	S^{2-} in bcc	Distorted Td	133.5	-217.24, -215.9	Gamsjager, Waldner (17, 19)

☑ = obtained
★ = obtained phase pure

How can we obtain phase pure Nickel Sulfides?

Synthesis of Nickel Sulfides

1. Place 0.5 mmol Nickel (II) Stearate, 10 mL of ODE, and a stir bar in a 3-neck round bottom flask. In an addition funnel, add the substituted thiourea and 5 mL of ODE.
2. With a Schlenk line, place under vacuum and degas for 30 mins at 60°C.
3. Switch to nitrogen or argon and heat the 3-neck round bottom flask to 170°C-270°C and the addition funnel to 170°C.
4. Stir for 1 minute-4 hours.
5. After stirring, let cool down to room temp and remove from Schlenk line.
6. Suspend particles in chloroform and ethanol and place in centrifuge.

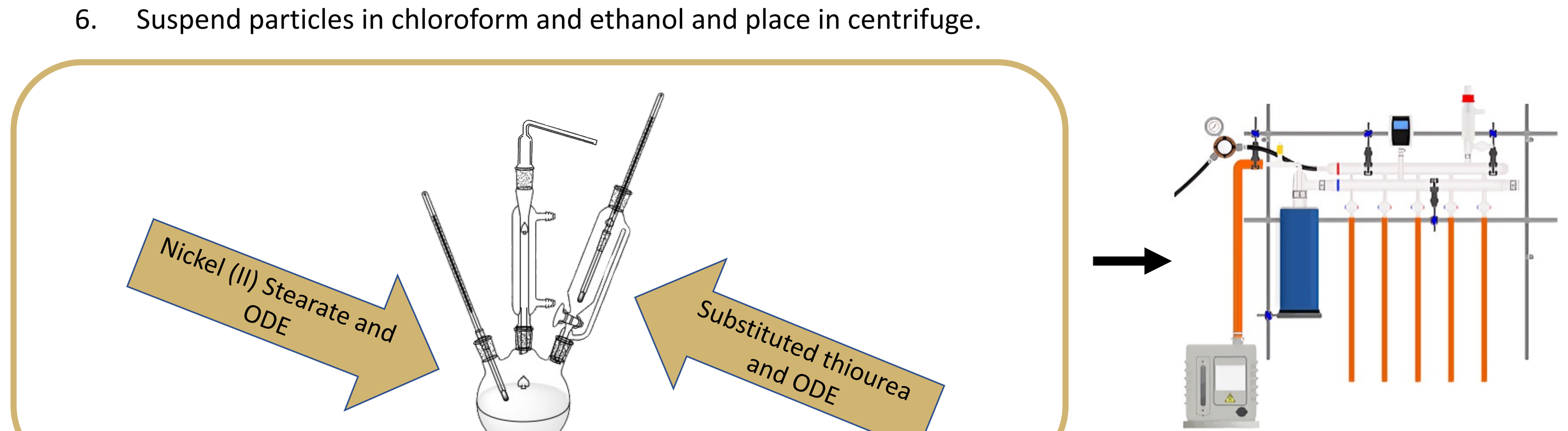
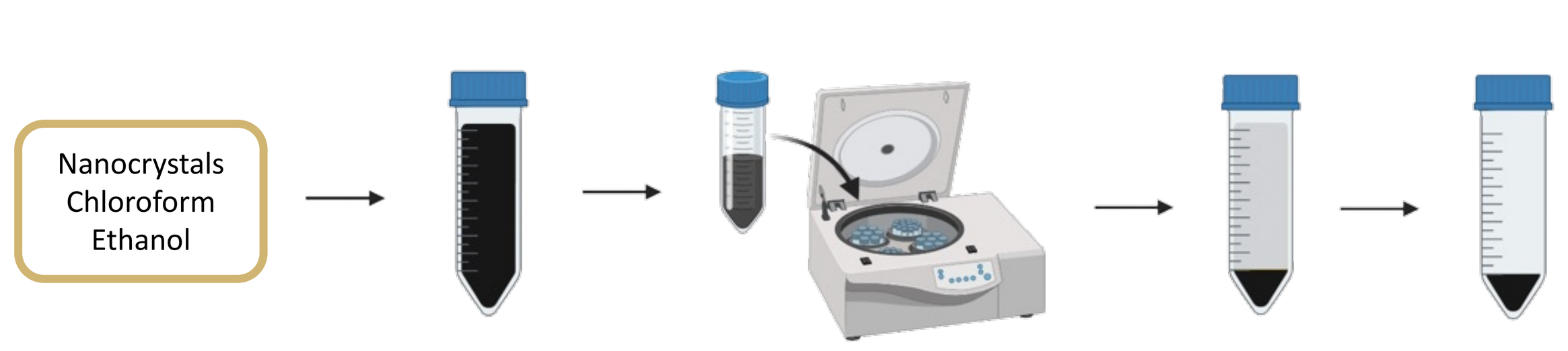


Image from: https://schlenklinesurvivalguide.com/assembly/



X-ray Diffraction (XRD) is a way to characterize the nanocrystals that are synthesized. The XRD instrument shoots X-ray at the sample, which then measures the intensities and scatter angle that come from the sample.

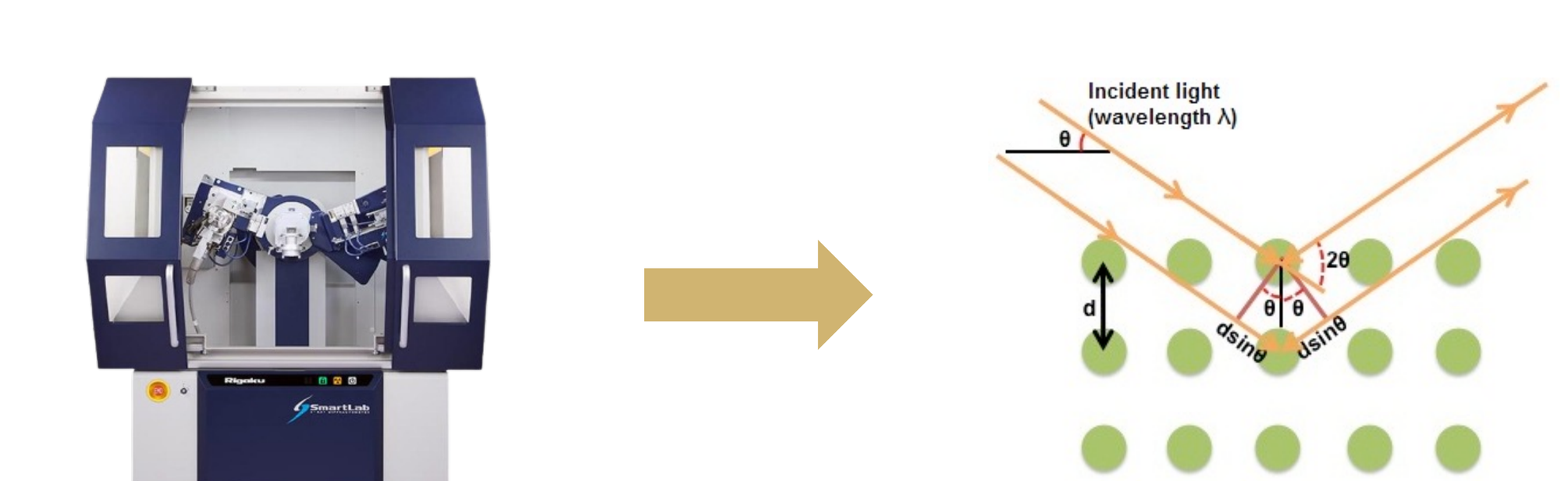
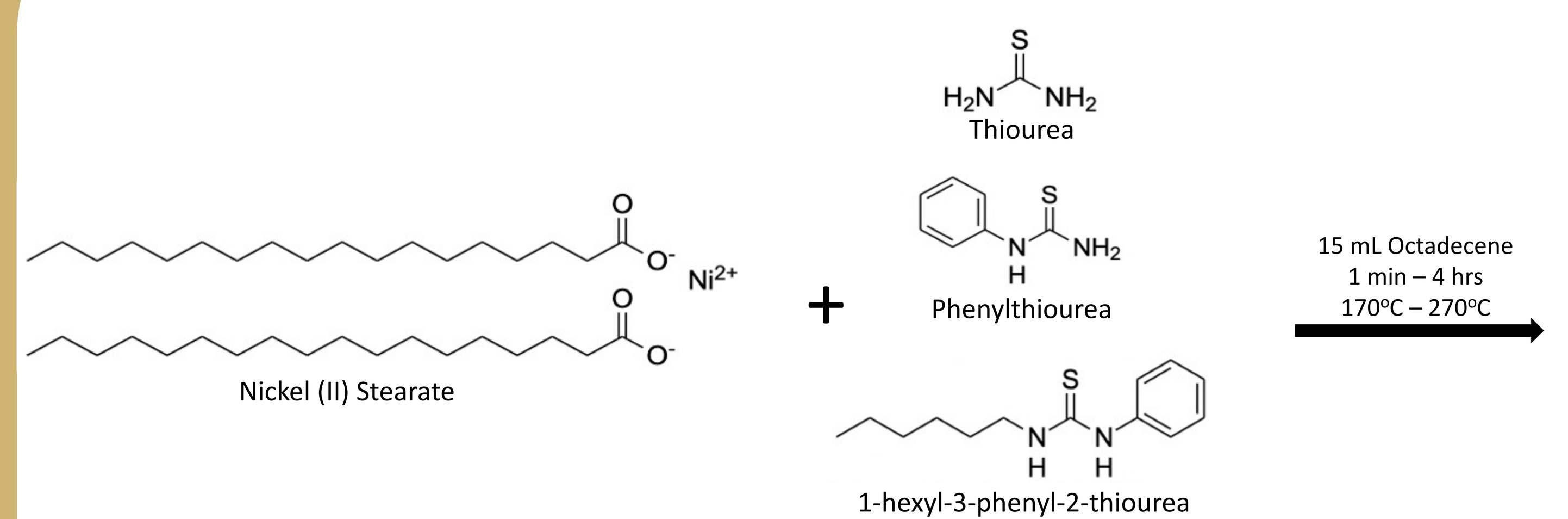


Image from: https://covalentmetrology.com/techniques/x-ray-diffraction-xrd/

Image from: https://chem.libretexts.org/... An-Introduction-to-Single-Crystal-X-Ray-Crystallography

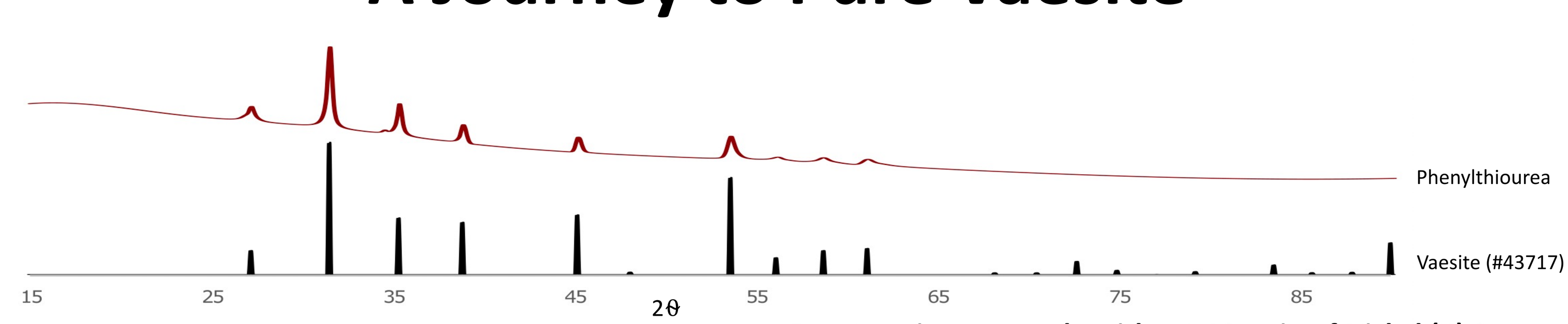
Manipulating the Synthesis of Nickel Sulfides



By changing four components of the nickel sulfide synthesis process, different phases can be obtained. The four components are:

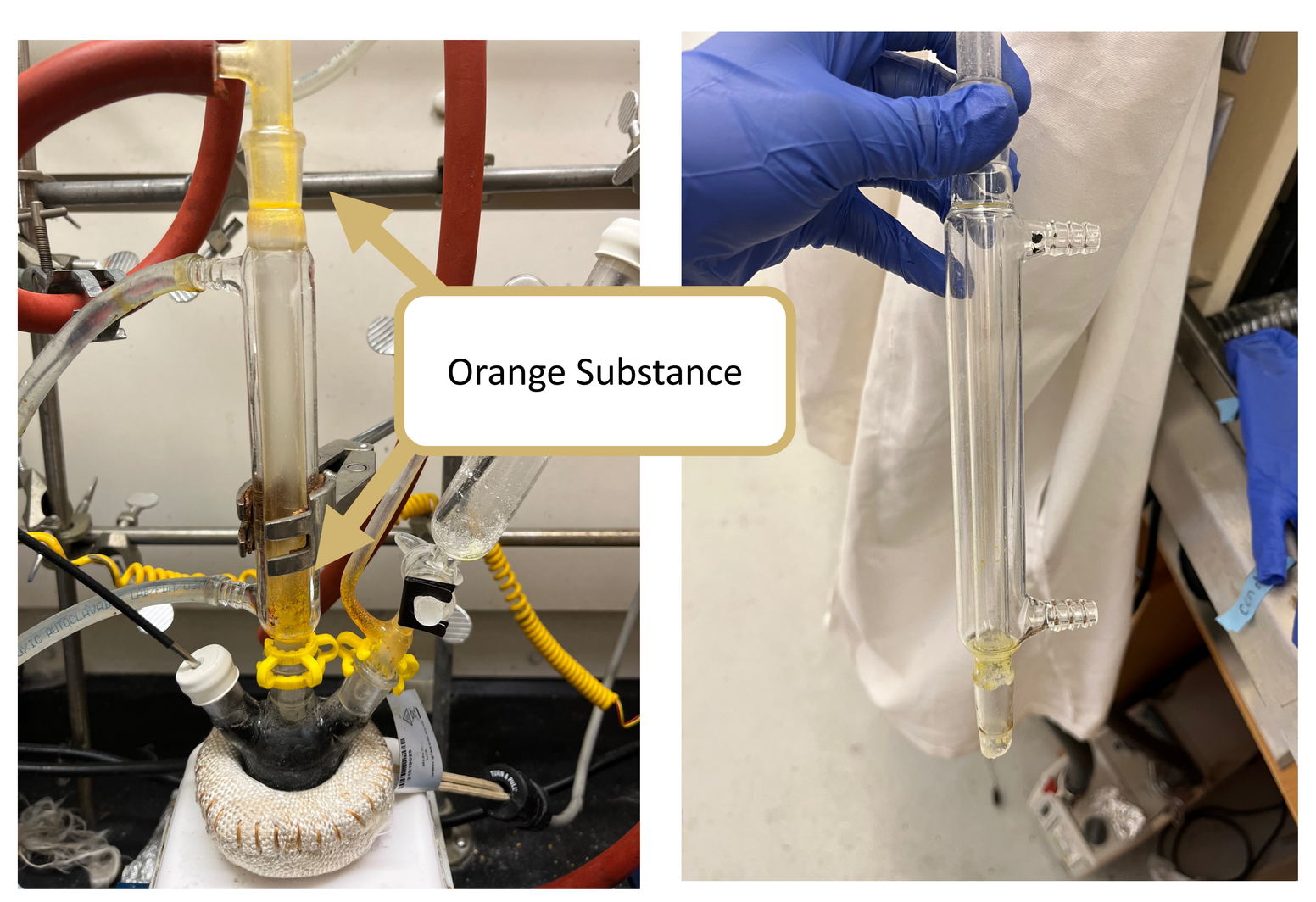
- The substituted thiourea used
- Ratio between nickel (II) stearate and the substituted thiourea
- Amount of time the reaction is being stirred at
- The temperature it is being stirred at

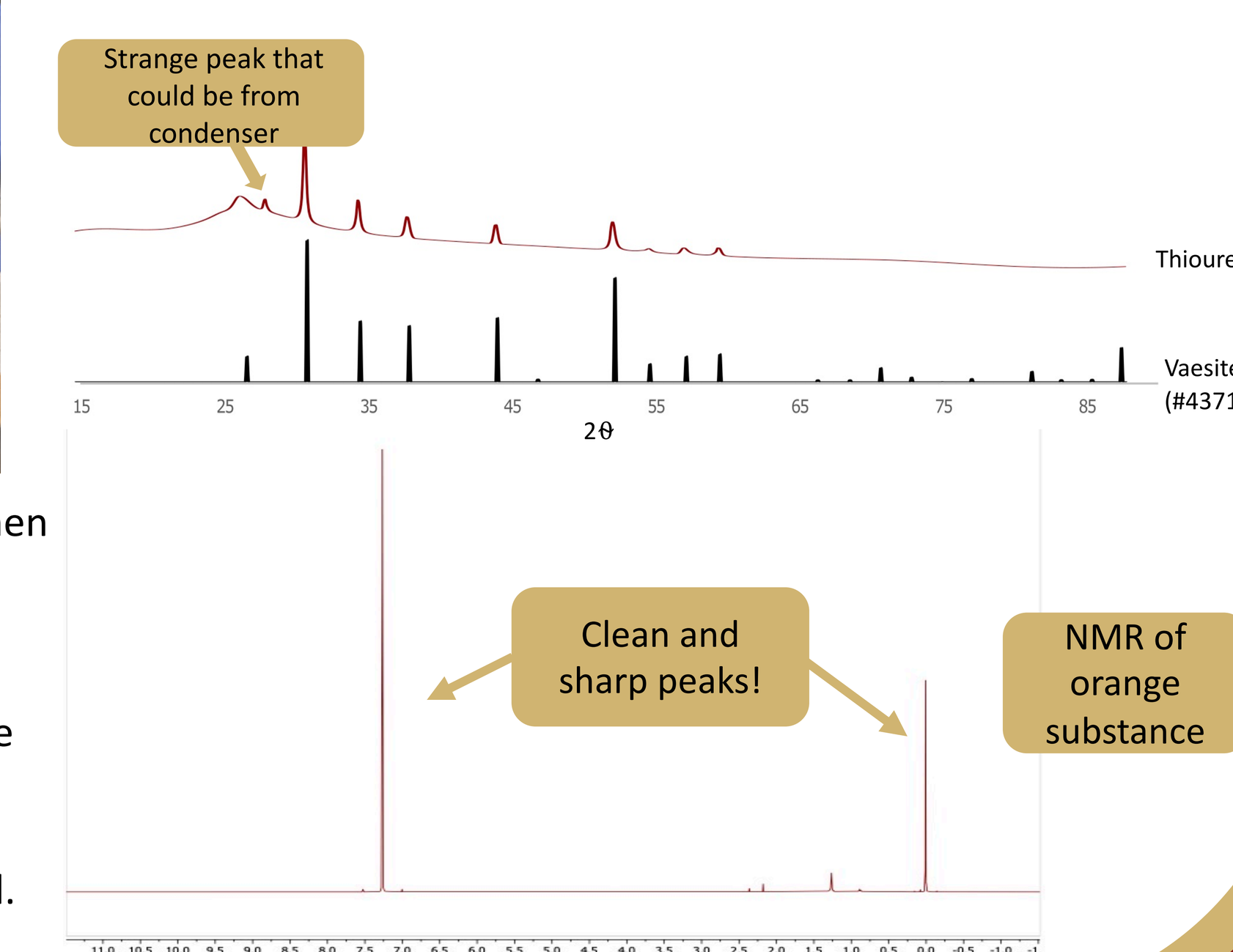
A Journey to Pure Vaesite



Pure Vaesite was made with a 1:18 ratio of Nickel (II) Stearate to Phenylthiourea and stirred for one hour at 220°C.

- This shows that high ratios of phenylthiourea synthesizes Vaesite because phenylthiourea is slower at releasing sulfur into the system, when compared to thiourea.
- Pure Vaesite could also be found in a range of temperatures of 220°C to 270°C.

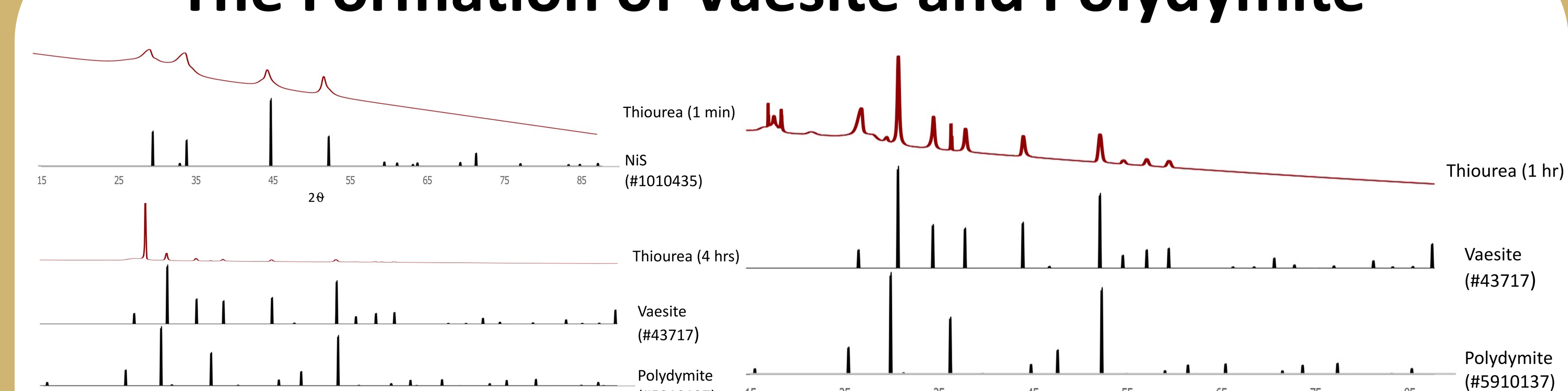




Noticed an orange substance forming on the condensers when using high ratios of thiourea.

- The picture on the left shows the substance on the condenser, while the picture on the right shows the condenser after synthesizing pure Vaesite with no orange substance.
- The NMR to the right shows clean and sharp peaks. This could entail that the orange substance contains no nickel.

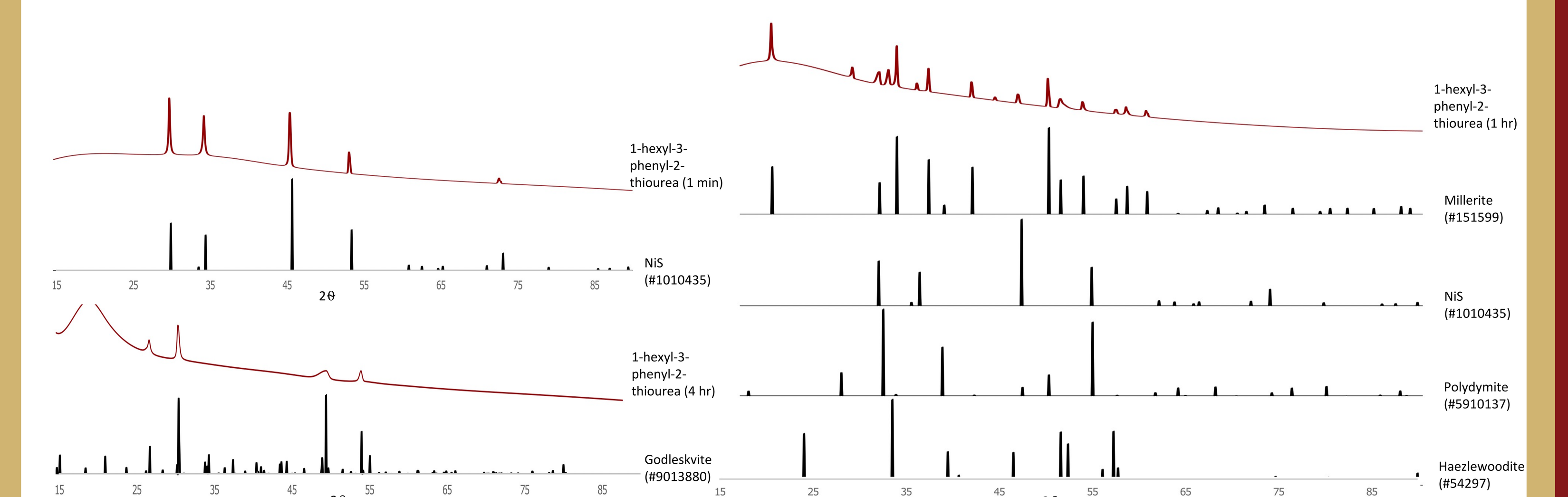
The Formation of Vaesite and Polydymite



These reactions were made with a 1:24 ratio of nickel (II) stearate to thiourea and stirred at 270°C and various amounts of time to understand the formation of Vaesite and Polydymite.

- The one-minute synthesis shows that the nanocrystals nucleate as NiS. After an hour it grows into 90% Vaesite and 10 % Polydymite.
- After four hours, the amount of Polydymite seemed to decrease more significantly than Vaesite. The condenser also formed an orange substance, which could explain the unmatched peak in the 4-hour XRD.

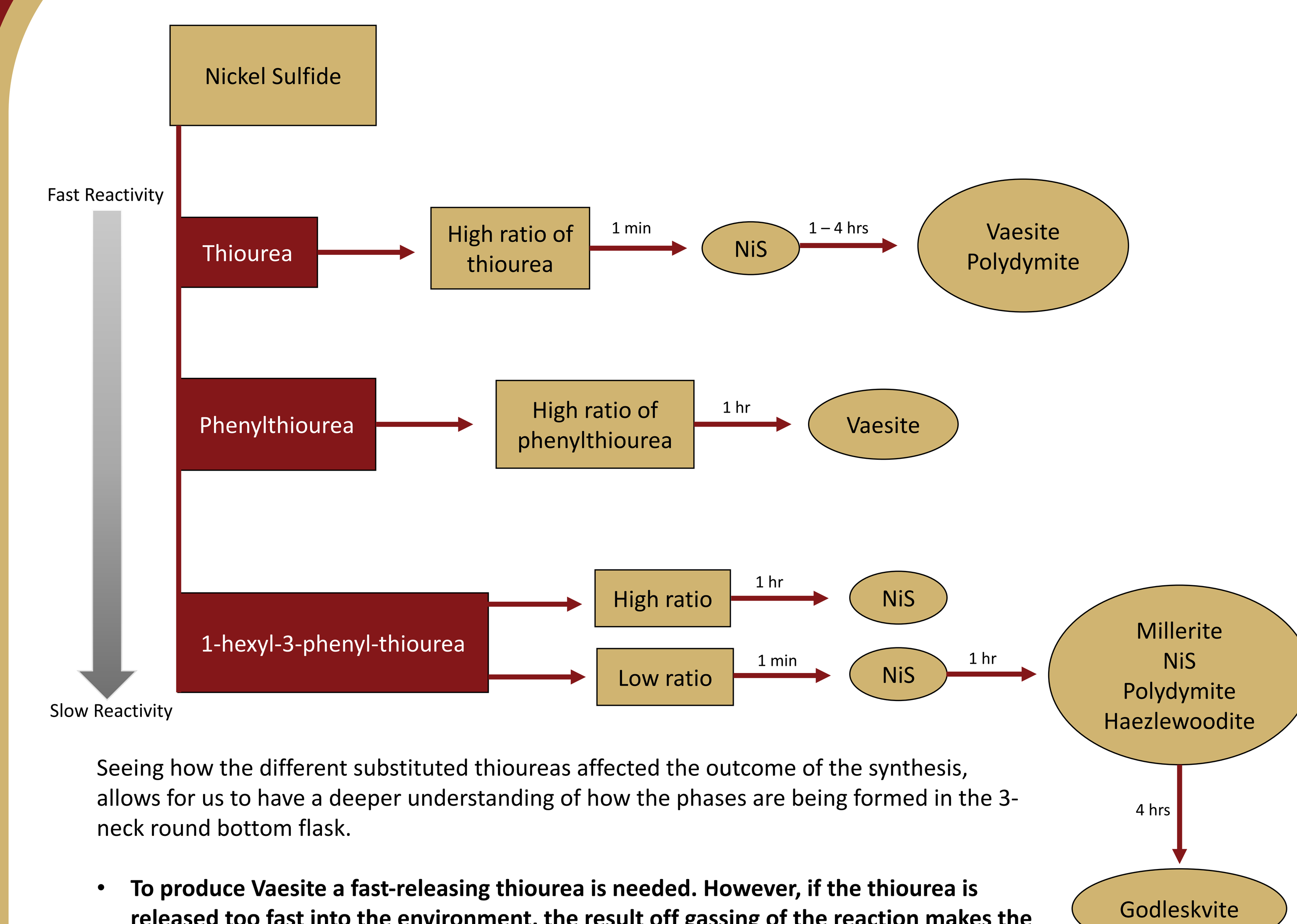
Exploring Sulfur Deficient Environments



A 1:1 ratio is explored while using 1-hexyl-3-phenyl-2-thiourea, which is the slowest releasing thiourea that was used.

- One-minute synthesis shows that the nanocrystals nucleate as NiS.
- After an hour, they stay as NiS and grow into Millerite, Polydymite, and Haezlewoodite.
- After four hours, the XRD shows that the nanocrystals form into mostly Godleskvite.

Conclusion



Seeing how the different substituted thioureas affected the outcome of the synthesis, allows for us to have a deeper understanding of how the phases are being formed in the 3-neck round bottom flask.

- **To produce Vaesite a fast-releasing thiourea is needed. However, if the thiourea is released too fast into the environment, the result off gassing of the reaction makes the nanocrystalline synthesis much less reproducible; phenylthiourea is the perfect candidate to form pure Vaesite because it is slower at releasing sulfur into the system, but fast enough to pack the nanocrystals correctly.**
- **It is possible that Vaesite transforms into Polydymite at very high temperatures.**
- **When the environment is flushed with a high concentration of slower sulfur-releasing thiourea, only NiS is formed, but when a lower concentration is used, many different phases are formed. If reacted long enough, these phases become Godleskvite.**

Acknowledgements

I would like to give a huge thanks to everyone in the Macdonald lab for helping me throughout the summer. Especially, my mentors, Jeremy Espano and Alexandra Koziel. I would also like to thank the NSF VINSE REU program for giving me this opportunity.

- NSF-DMR 1852157
- CHE-603057

NSF