PNNL SA-210593

Molten Salt Reactor PROGRAM

Fluid inclusions in chloride salts – characterization and mitigation

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Molten Salt Reactor Campaign Annual Review
22-24 April 2025

Argonne NATIONAL LABORATORY · INL Idaho National Laboratory · Los Alamos NATIONAL LABORATORY · OAK RIDGE National Laboratory · Pacific Northwest NATIONAL LABORATORY · Sandia National Laboratories · U.S. DEPARTMENT of ENERGY Office of Nuclear Energy

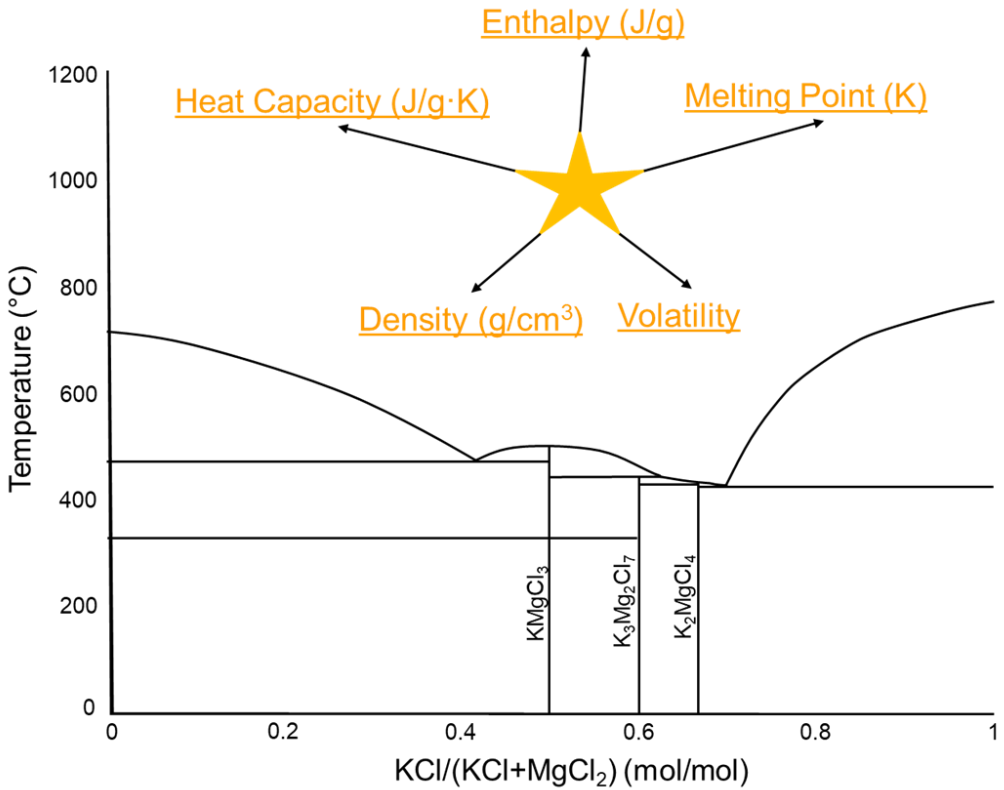
Outline

- Introduction to fluid inclusions
- Presence of fluid inclusions in salts
- Preliminary vacuum oven experiment
- Preliminary quantification results of fluid inclusions: Imaging of salts

Introduction

- Use PNNL expertise to perform thermophysical property measurements
  - ➢ Density via TMA
  - ➢ Heat Capacity via Drop Calorimetry
  - ➢ Volatility via XRD and EGA

- Achievements to date:
  1. Improvement of sample preparation methodology for thermophysical property data
  2. Density and volatility method development
  3. Thermophysical property data collection on the KCl-$MgCl_2$ binary system
  4. Error analysis for drop calorimetry using principles of the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM 100:2008)
  5. **Salt fluid inclusion characterization**



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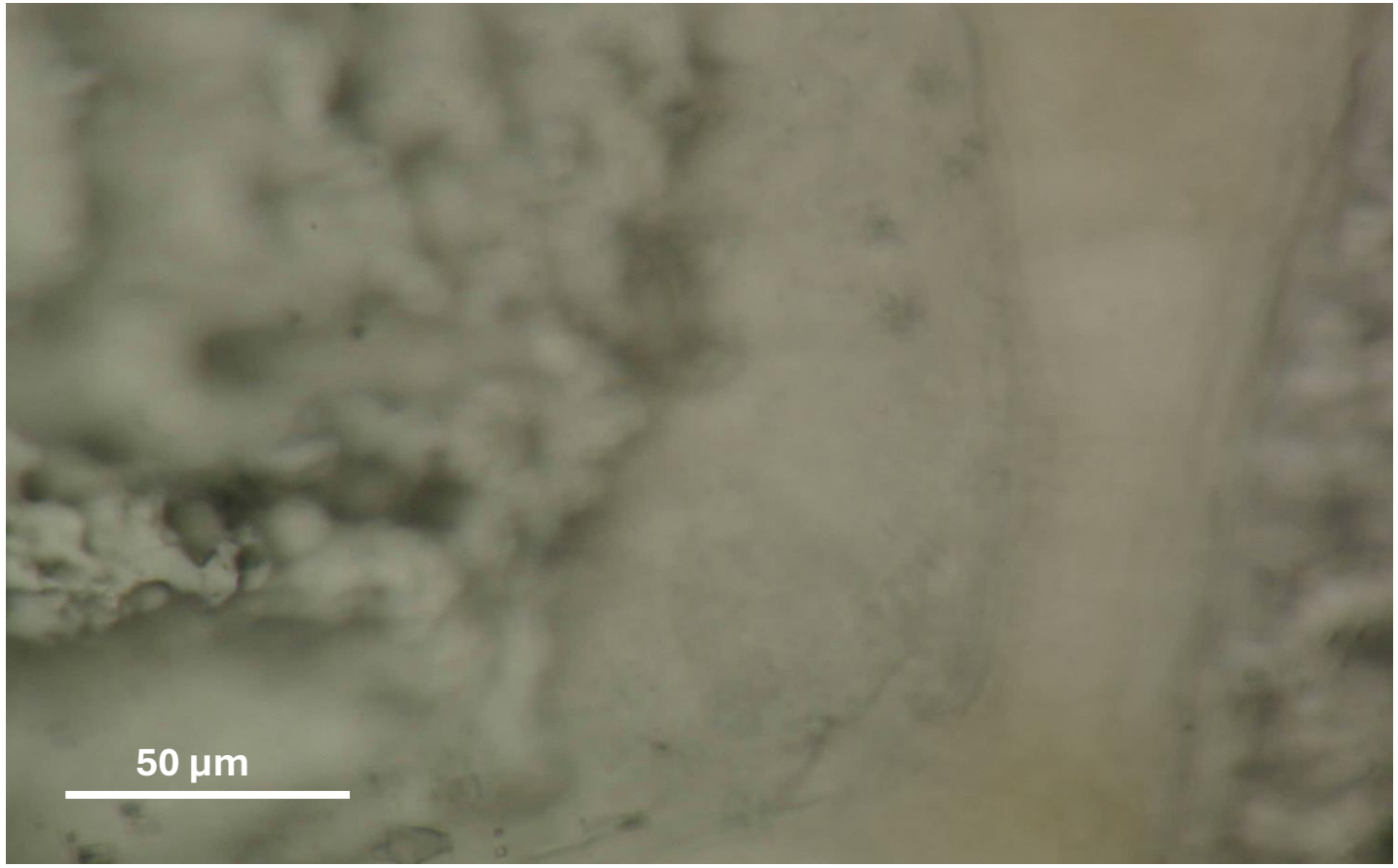
Fluid Inclusions

American Elements KCl 99.999% pure (metals basis)



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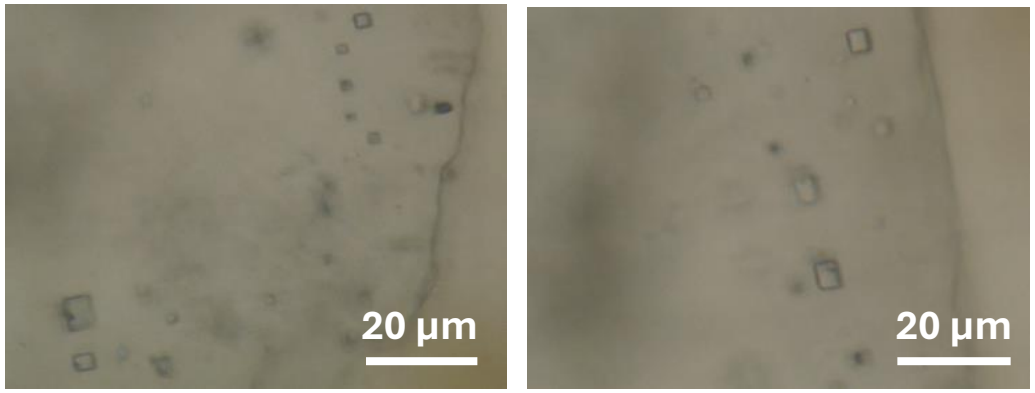
Formation of Fluid Inclusions

- Skeletal growth of crystals
  - Lack of nutrients at crystal center relative to edges
  - Undercooling
- Constitutional supersaturation
- Rapid crystal growth
- Favorable wetting characteristics

American Elements KCl 99.999% pure



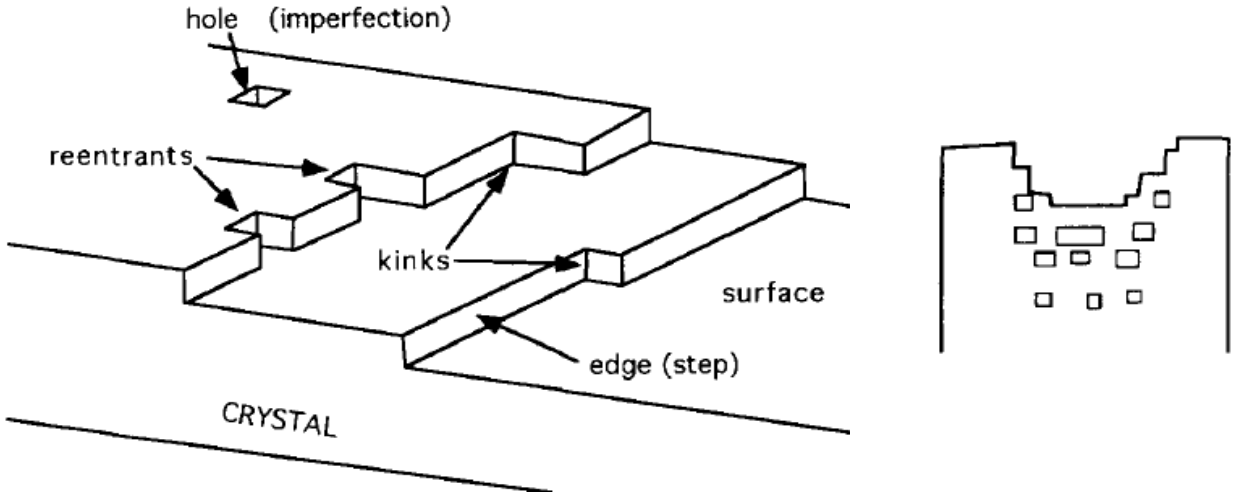


Figure from Goldstein and Reynolds (1994)

Preservation of Fluid Inclusions

- Preserved at elevated temperatures
- However, fluid may escape if pressures induced by expansion (e.g., heating or decompression) exceed elastic modulus of the host mineral

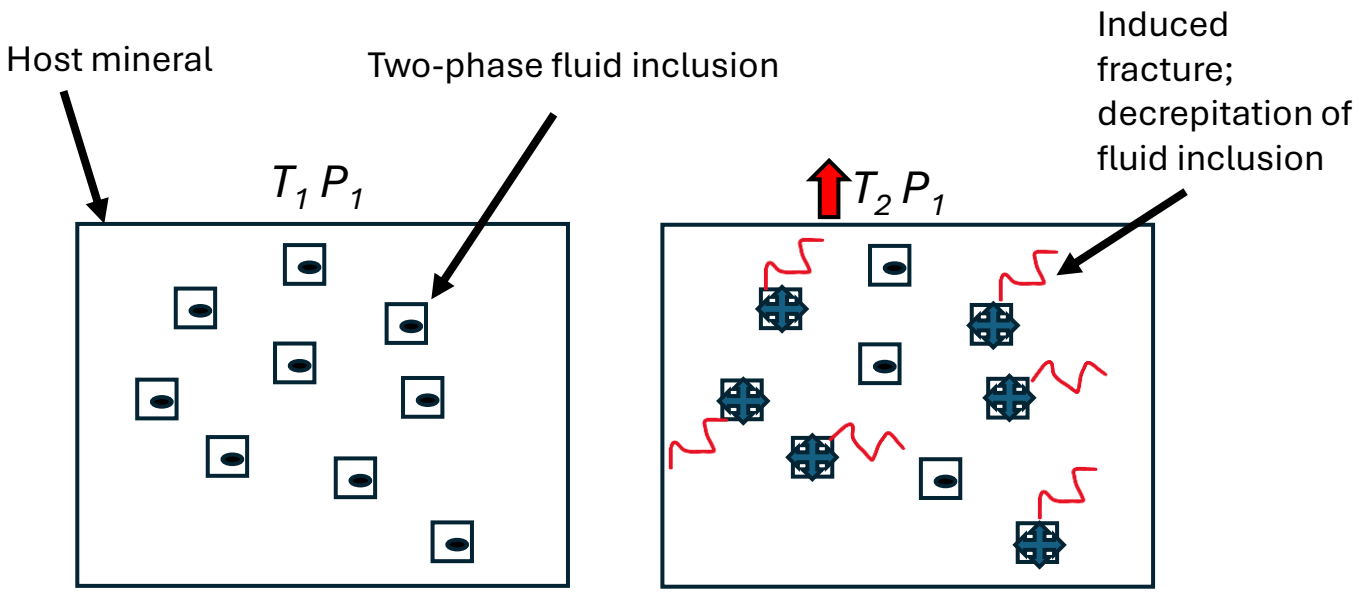
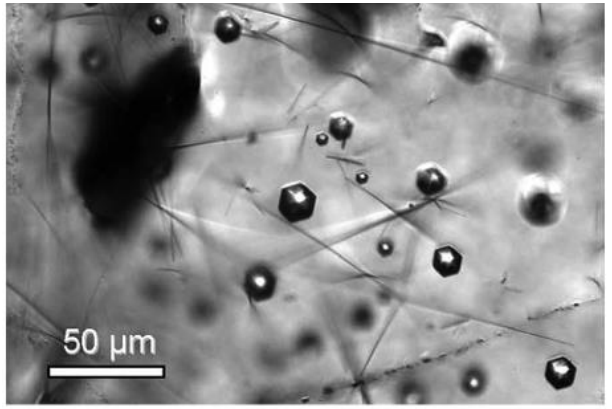


Figure from Kerkhof et al. (2014)



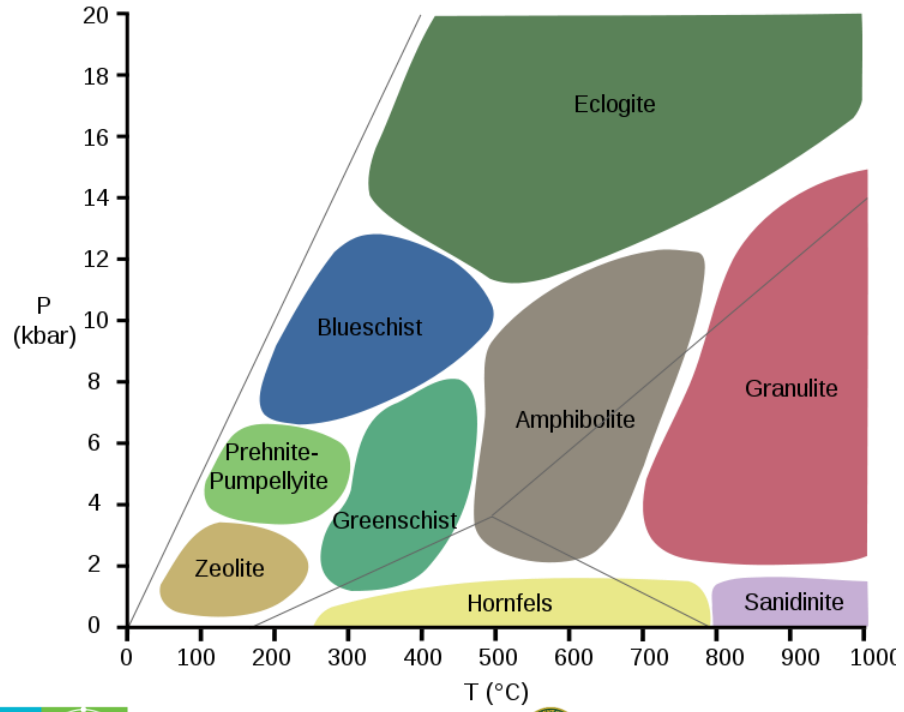


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Diagram from: https://commons.wikimedia.org/wiki/File:Metamorphic_Facies_Diagram.png

Presence of fluid Inclusions in Salts

- Likely in all salts precipitated from an aqueous solution

- Absolute number of inclusions depends on:
  - Kinetics of crystal formation
  - Thermodynamic conditions at solution-crystal interface
  - Wetting characteristics
  - Diffusivity of nutrients in aqueous solution (e.g., K, Na, etc.)

Decrepitation Study on SiO_2; 0.5% by volume!

Size range	average diameter	inclusions/gram	total volume cc
1-5 *u*	2 *u*	1394 million	$1.4 * 10^{-3}$
5-10 *u*	7 *u*	80 million	$2.8 * 10^{-4}$
10-20 *u*	15 *u*	42 million	$3 * 10^{-4}$
>20 *u*	25 *u*	20 million	$2.5 * 10^{-4}$
TOTAL		**1536 million**	**$2.23 * 10^{-3}$**

https://www.appliedminex.com/decrep/general/ficalc.htm

Questions to Answer

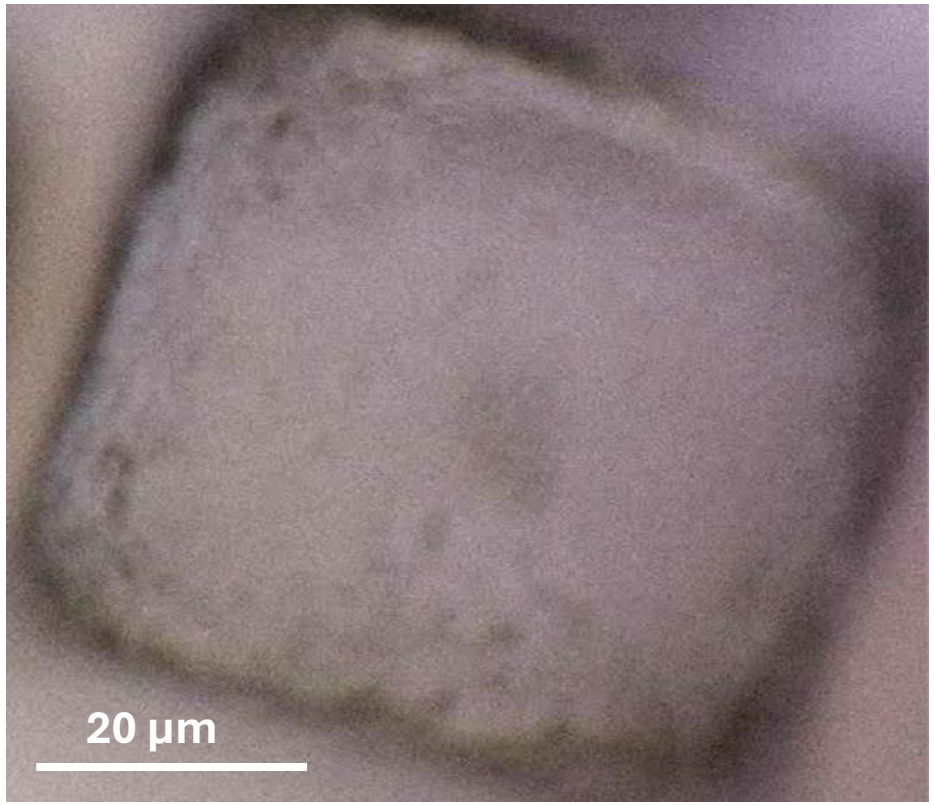
1. What salt species originate from aqueous precipitation?
   - Process driven?
   - Manufacturer specific?
2. Can the process of manufacture be tailored towards conditions unfavorable for the creation of fluid inclusions?
3. Alternatively, for the end-user of the salts, is post-processing of salts to remove fluid inclusions:
   - Possible?
   - More economical?
4. The million-dollar question- how have fluid inclusions affected the results of previously measured thermophysical properties and how do we mitigate their effects on future lab-scale measurements?

Preliminary Vacuum Oven Experiment

- American Elements 99.999% pure (metals basis) KCl and NaCl
- 1 g weighed and transferred into 20 mL scintillation vial

- Experiment 1- hold for 8 hr at 100 °C
- Experiment 2- using same salt, hold for 8 hr at 200 °C

NaCl Post 200 °C



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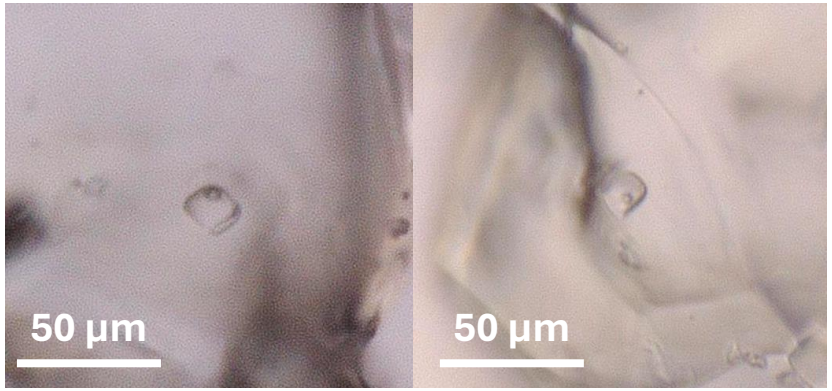
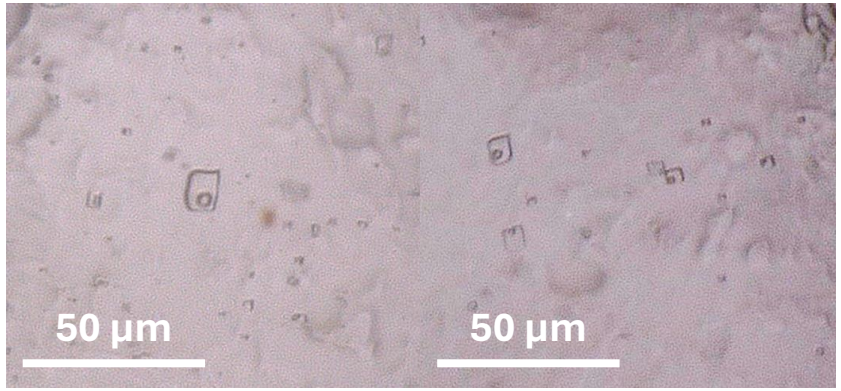
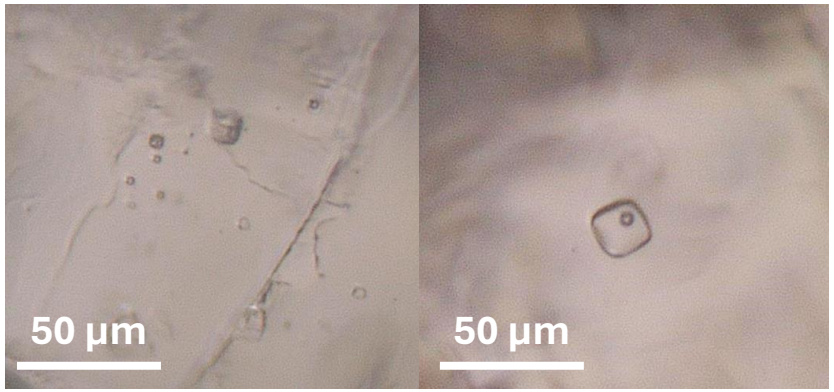
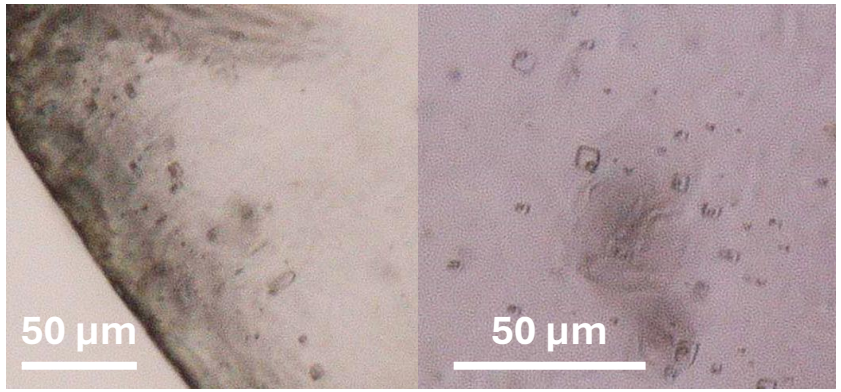
Preliminary Vacuum Oven Experiment

	KCl	NaCl
Experiment 1 100 °C for 8 hr		
Experiment 2 200 °C for 8 hr		

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Fluid Inclusions in Stages of Growth

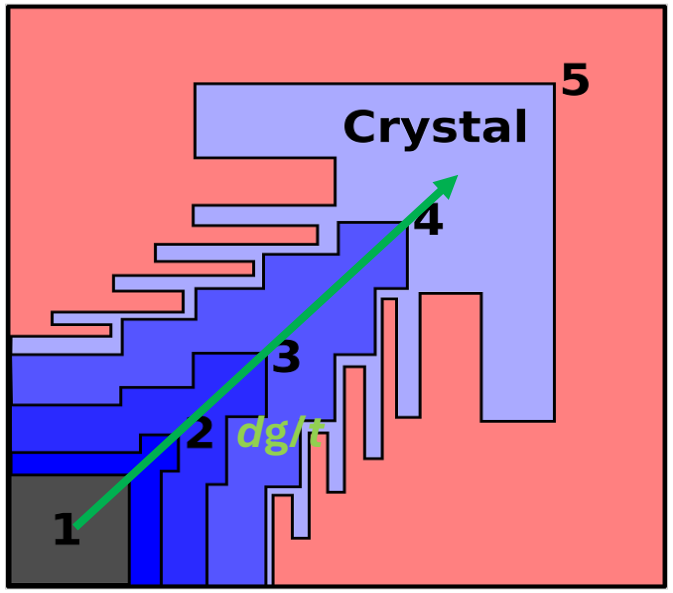
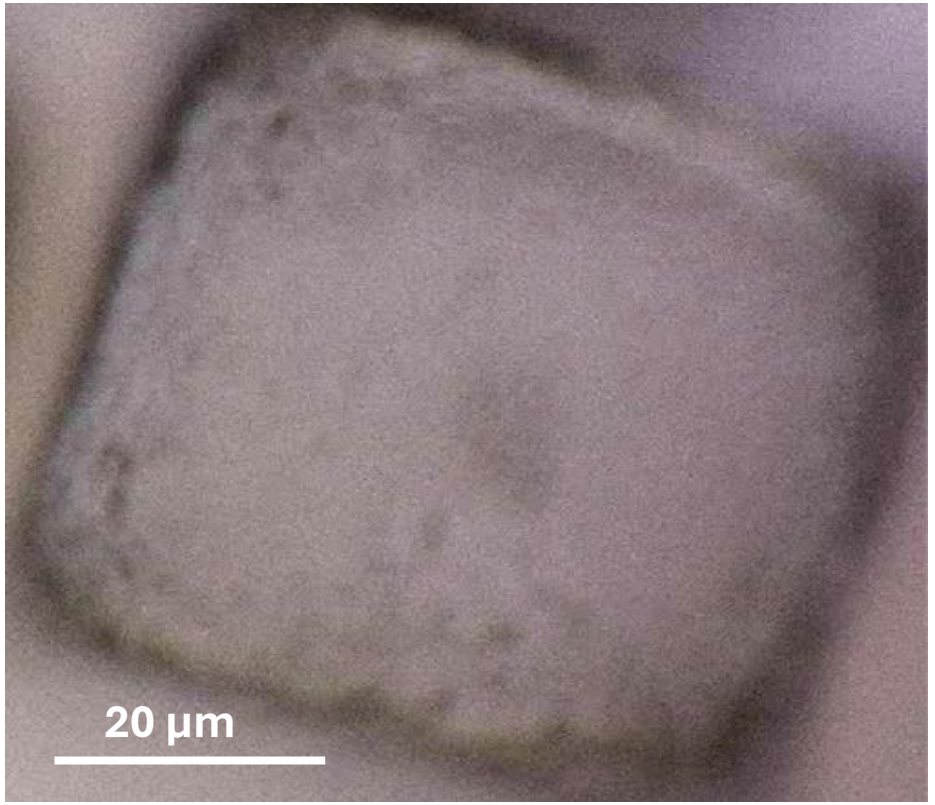


Figure modified from Kretz (2003) and
https://www.alexstrekeisen.it/english/vulc/skeletal.php

NaCl Post 200 °C

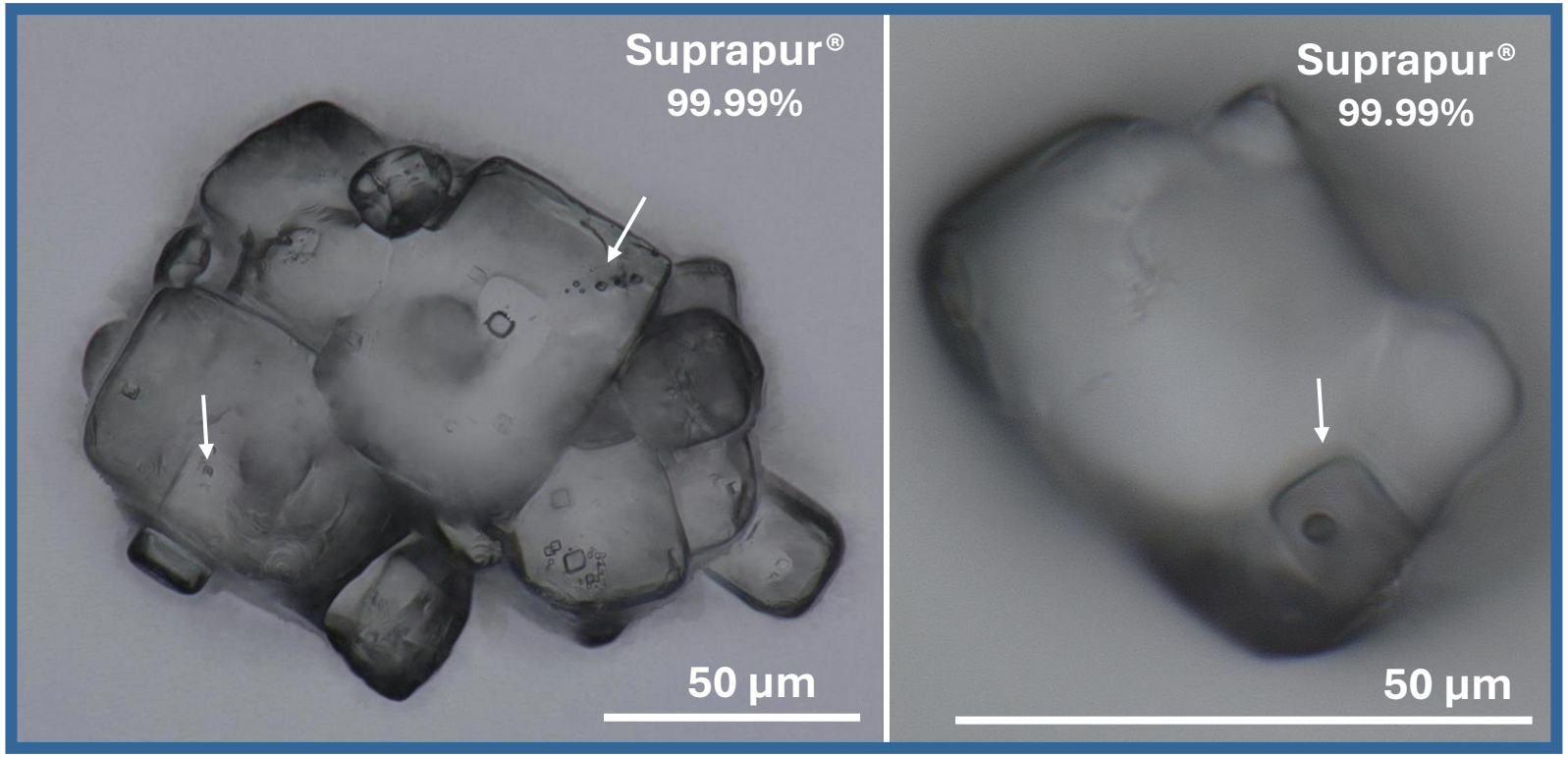


Capturing Fluid Inclusions in Salts

- Keyence VHX-7000
  - Transmitted light
  - Depth profile (z-height)
  - ImageJ for inclusion size
- Three samples of NaCl and KCl from three different vendors and timeframes
- One in-house synthesized $PuCl_4$-KCl
- Only analyzing two-phase (liquid-gas) inclusions

NaCl

- SPEX
  - Purity not listed
  - 1992
- Suprapur® Millipore
  - 99.99%
  - 2019
- Thermo Fischer Ultra Dry
  - 99.99% metal basis
  - 2019



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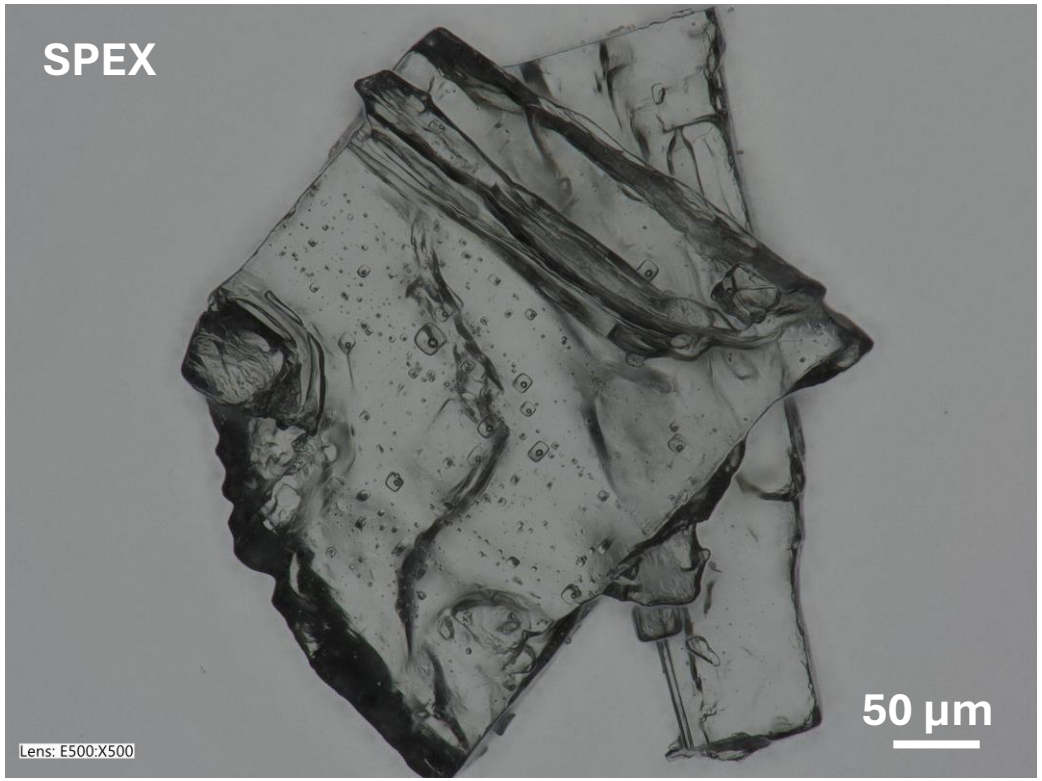
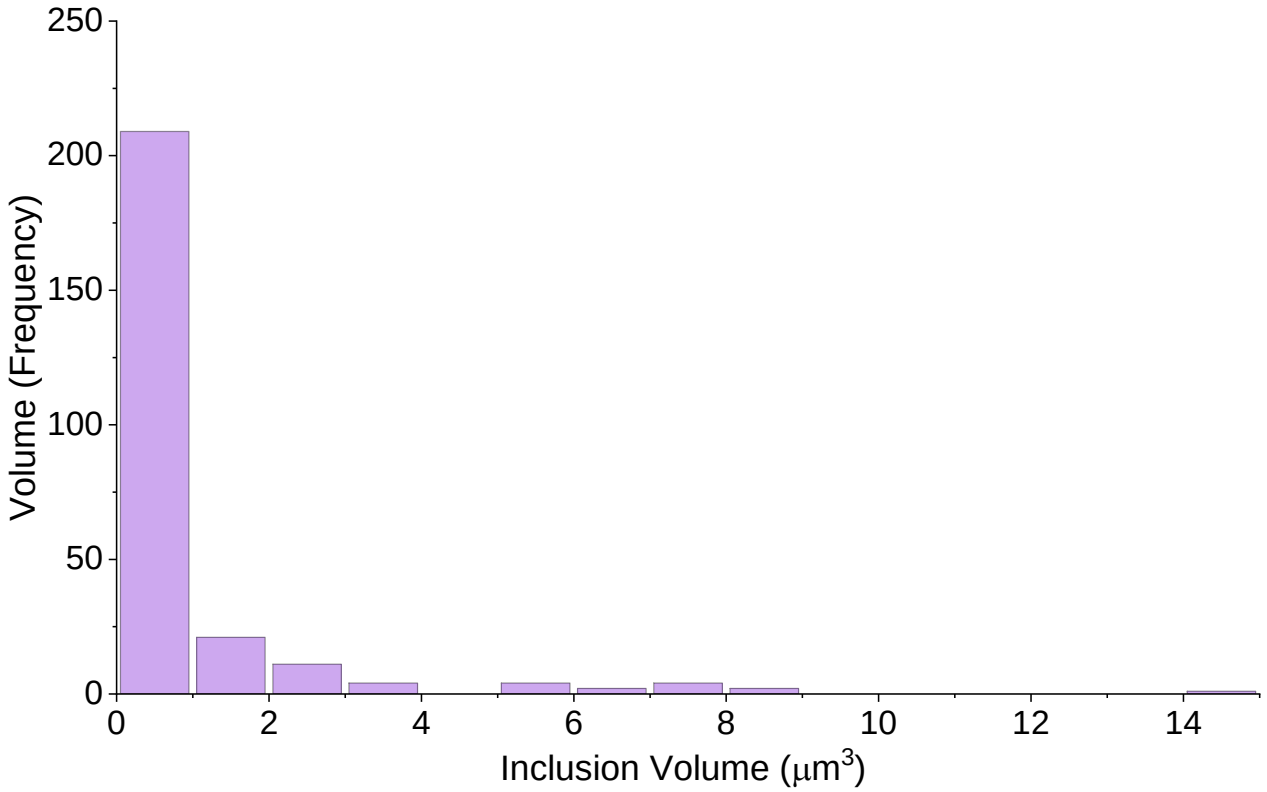
NaCl





crystal volume (cm³)	10362.55
total water (cm³)	201.6
wt% of water	1.95%

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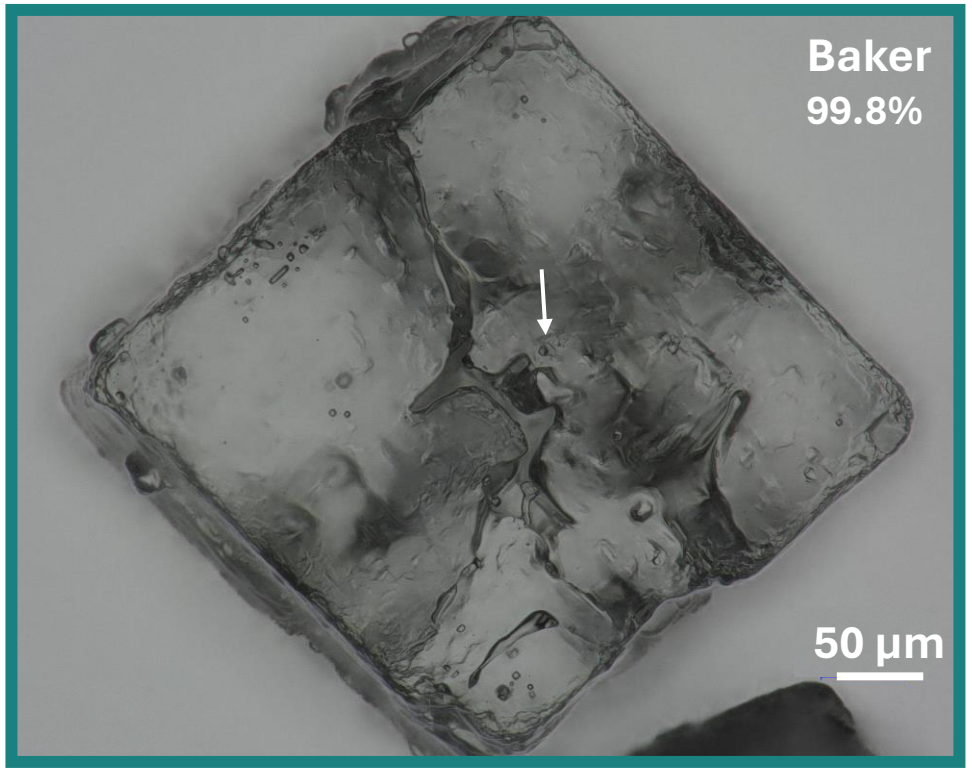
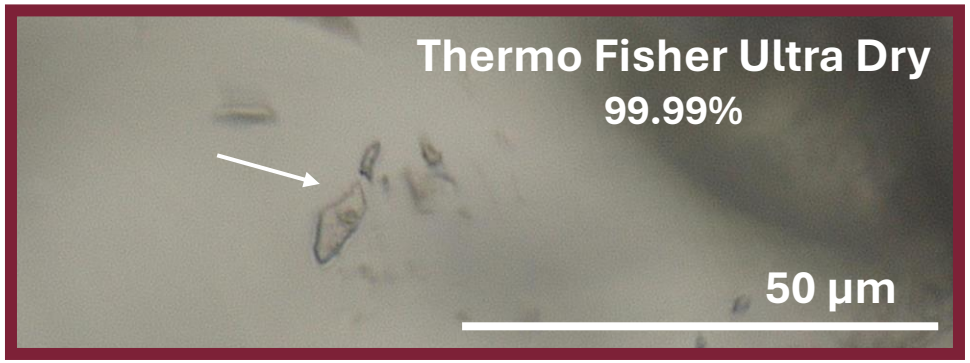
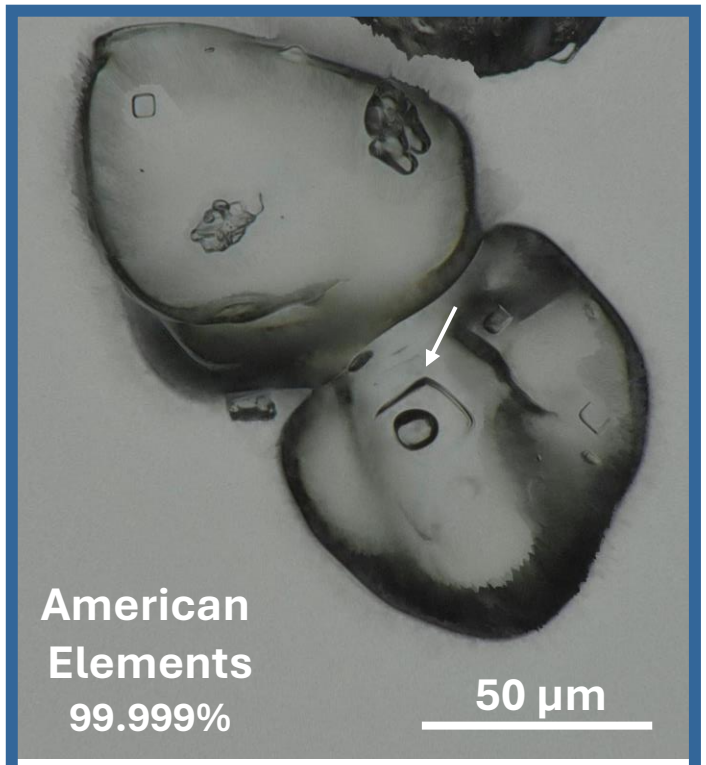
KCl

- Baker Analyzed
  - 99.8% metal basis
  - 1998
- American Elements
  - 99.999% metal basis
  - 2019
- Thermo Fisher Ultra Dry
  - 99.99% metal basis
  - 2024







American Elements	
crystal volume (cm^3)	3535.03
total water (cm^3)	55.1
wt% of water	1.56%

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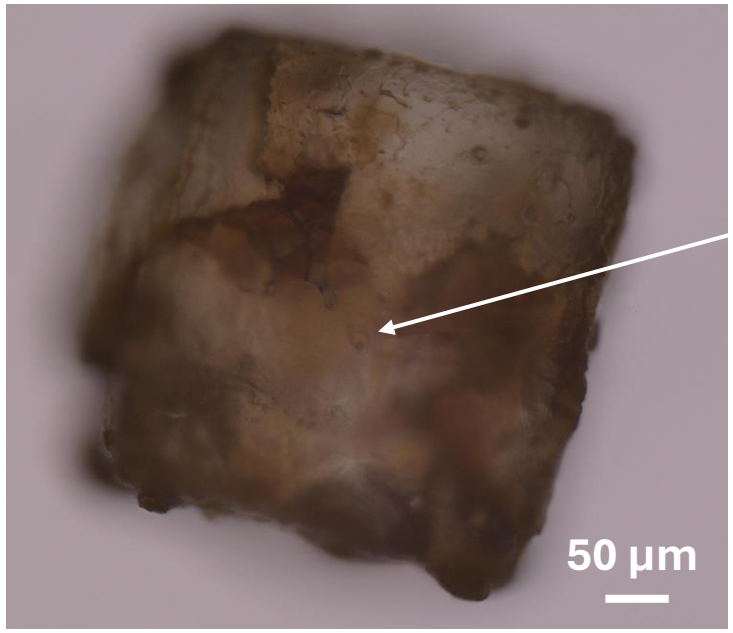
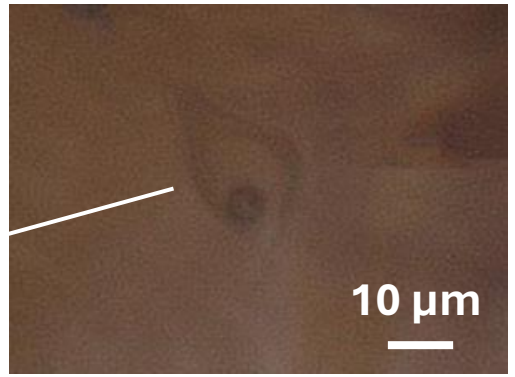
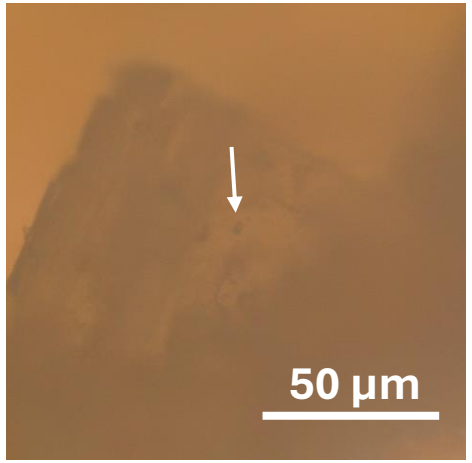
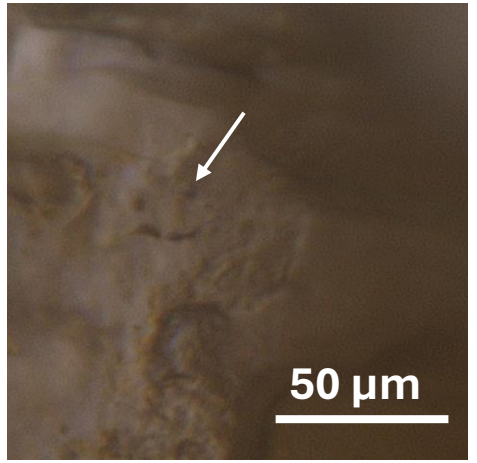
$PuCl_4$

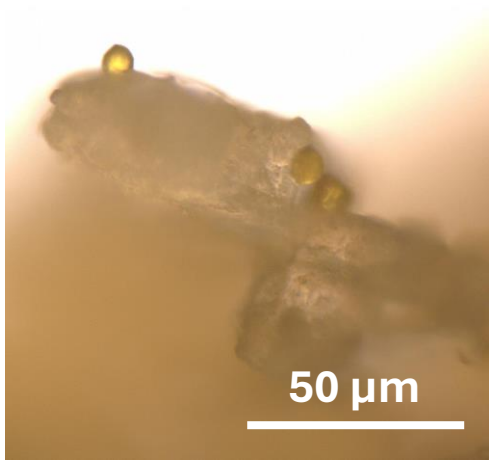
- Dissolution
  - HCl to dissolve starting material
  - KOH to convert to $Pu(OH)_4$
  - HCl added with KCl to dissolve
  - Distillation set up to boil off remaining solutions.
  - Salt left to dry
- Many assumed single phase inclusions
- <5 µm in surface area two-phase were found











Conclusions

- Fluid inclusions are preserved in commercial salts.

- Assuming all fluid inclusions are water, the water content in these inclusions can be up to 2%. Considering hydroscopic nature of salts, the total water content in these salts can exceed 2%.
  - Depending on the salt compositions being studied inclusions will impact overall properties.

- Fluid inclusions likely to contain high concentrations of water (synthesized media) or gaseous impurities.

Future Work

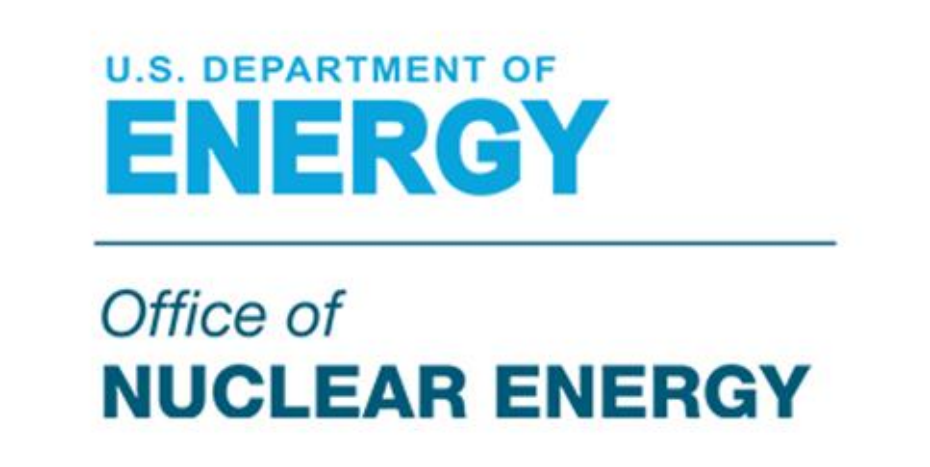
Continue taking images of fluid inclusions in various salts

Salt and inclusion characterization

- Micro Raman
- Laser Induced Breakdown Spectroscopy (LIBS)
- Cryo-Scanning Electron Microscopy (SEM)

Acknowledgments

- DOE-NE MSR Campaign
- The thermal team at PNNL
  - Kyle Makovsky
  - Michaella Harris
  - Kent Detrick
- Patricia Paviet for continued support



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Thank you

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