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Molten Salt Reactor PROGRAM

Density by gravitational displacement method and the issue of fluid inclusions

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PNNL

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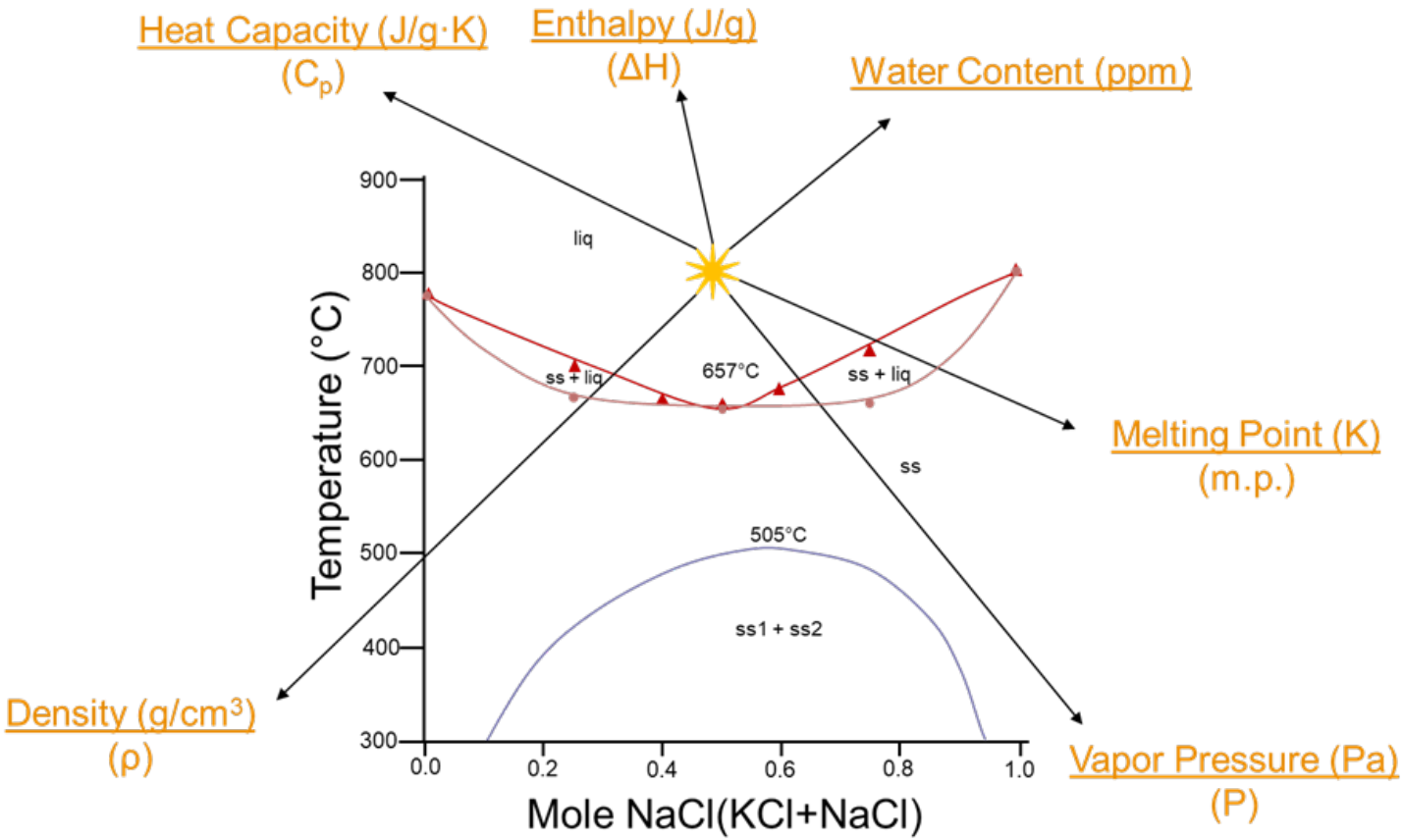
Outline

- Introduction
- Density by gravitational method
- Density by thermomechanical analysis
- Fluid inclusions

Introduction

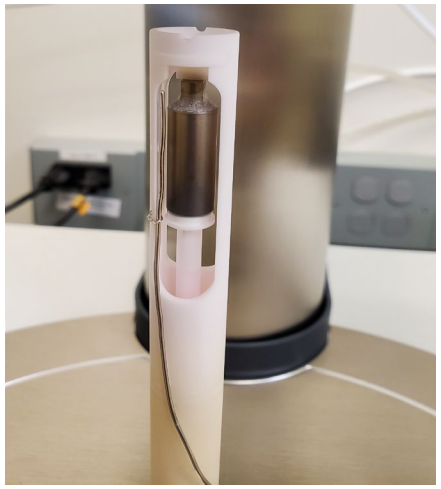
- Use PNNL and CSU expertise to perform thermophysical property measurements
  - Density via TMA
  - Heat Capacity via Drop Calorimetry
  - Volatility via XRD and EGA

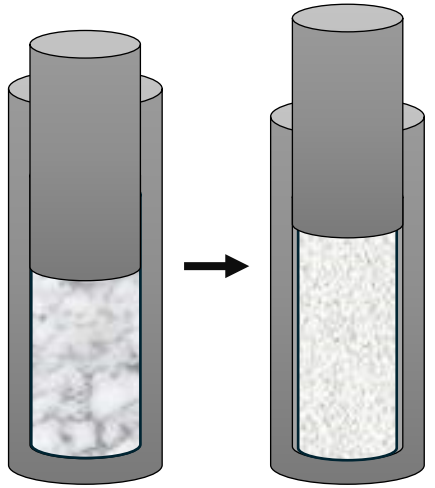
- FY24 Achievements to date:
  1. Improved sample preparation methodology
  2. Density and volatility method development
  3. Thermophysical property data collection on the KCl-$MgCl_2$ binary system
  4. Error analysis for drop calorimetry using principles of the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM 100:2008)



Density by gravitational method

- Pellet is pressed and weighed
- Initial height measured by calipers
- Analytical conditions
  - Heating rate of 10 K/min
  - Isothermal hold at target temp
  - Final height measured by calipers
  - The change in height of the plunger results in the final volume of the salt
    - $V_f = \pi r^2 \Delta h$, $\rho = m_f / V_f$

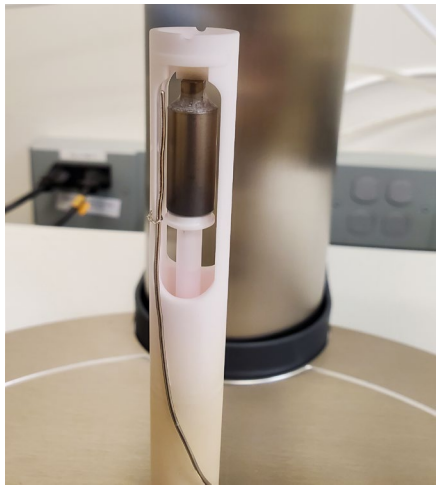




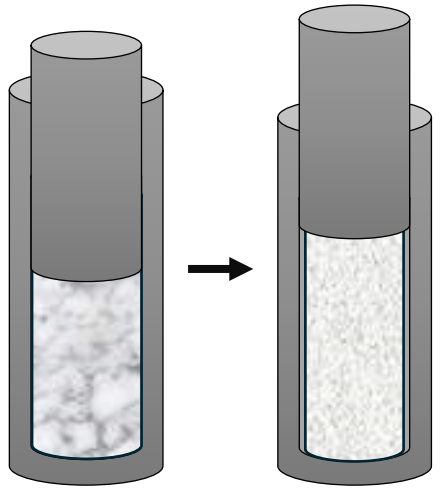
Ni Empty (g)	Ni + Pellet (g)	Height (cm)	Total Mass (g)	Final Mass of Salt (g)	Height Final (cm)	Density of 67 mol% KCl at 1050 K (g/cm³)
15.8516	16.1521	1.0100	15.9116	0.0599	0.6210	1.57
15.8520	16.1514	1.0120	15.9117	0.0600	0.6190	1.64
15.8515	16.1520	1.0270	15.9116	0.0599	0.6160	1.56
15.8517	16.1518	1.0310	15.9117	0.0600	0.6120	1.59
15.8517	16.1515	1.0230	15.9117	0.0600	0.6090	±0.08
15.8517	16.1518	1.0206	15.9116	0.0600	0.6154	

Density by gravitational method

- Sources of uncertainty:
  - Purity of salt(s)
  - Homogeneity of batched ratios
  - Reproducibility of mass measurements
    - Pellet mass, pre- and post-measurement pellet/crucible mass
      - E.g., salt loss during measurement
  - Temperature calibration of the TMA instrument
  - Reproducibility of height measurement



- Accuracy:
  - Overall change in height is very small, do digital calipers have the sensitivity to measure small height (i.e., volume changes)?
  - Prior to melt, the pressed pellet does not completely occupy the volume under the plunger
  - Thermal expansion of the crucible/plunger is not considered

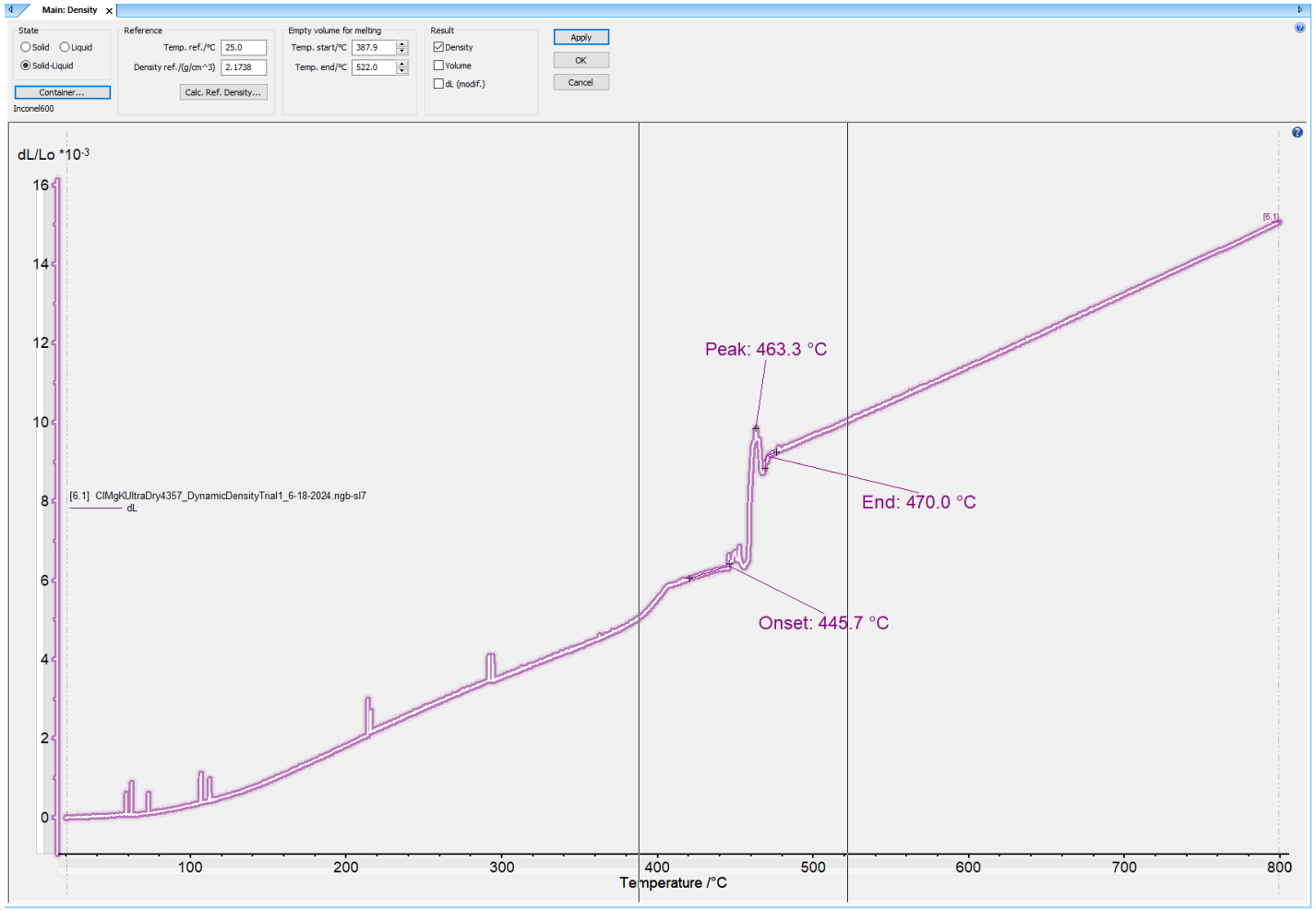


Density by thermomechanical analysis

- Pellet is pressed and weighed
- Analytical conditions
  - Heating rate of 5 K/min up to target temperature (1073 K)
  - Negligible force of 0.001 N applied
  - The change in height with temperature is measured by the instrument
  - Density calculated by:

$$\rho(T) = \rho(r)T(r)\frac{\left(1+\frac{\Delta L(T_r)}{L_0}\right)\cdot\left(1+\alpha_C(T_r)\right)^2}{\left(1+\frac{\Delta L(T)}{L_0}\right)\cdot\left(1+\alpha_C(T)\right)^2}$$

  - Where ρ(r) is reference density, T(r) is reference temperature, $\frac{\Delta L(T_r)}{L_0}$ is initial displacement at T(r), $\frac{\Delta L(T)}{L_0}$ is displacement measured at temperature, and α_C is the linear thermal expansion coefficient for the crucible material



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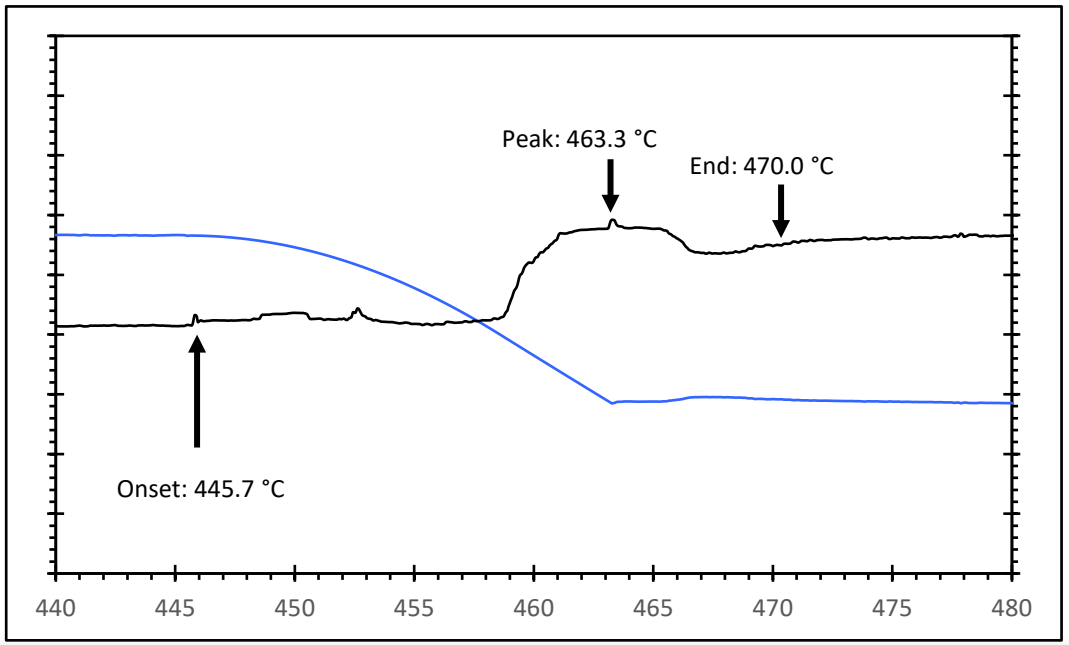
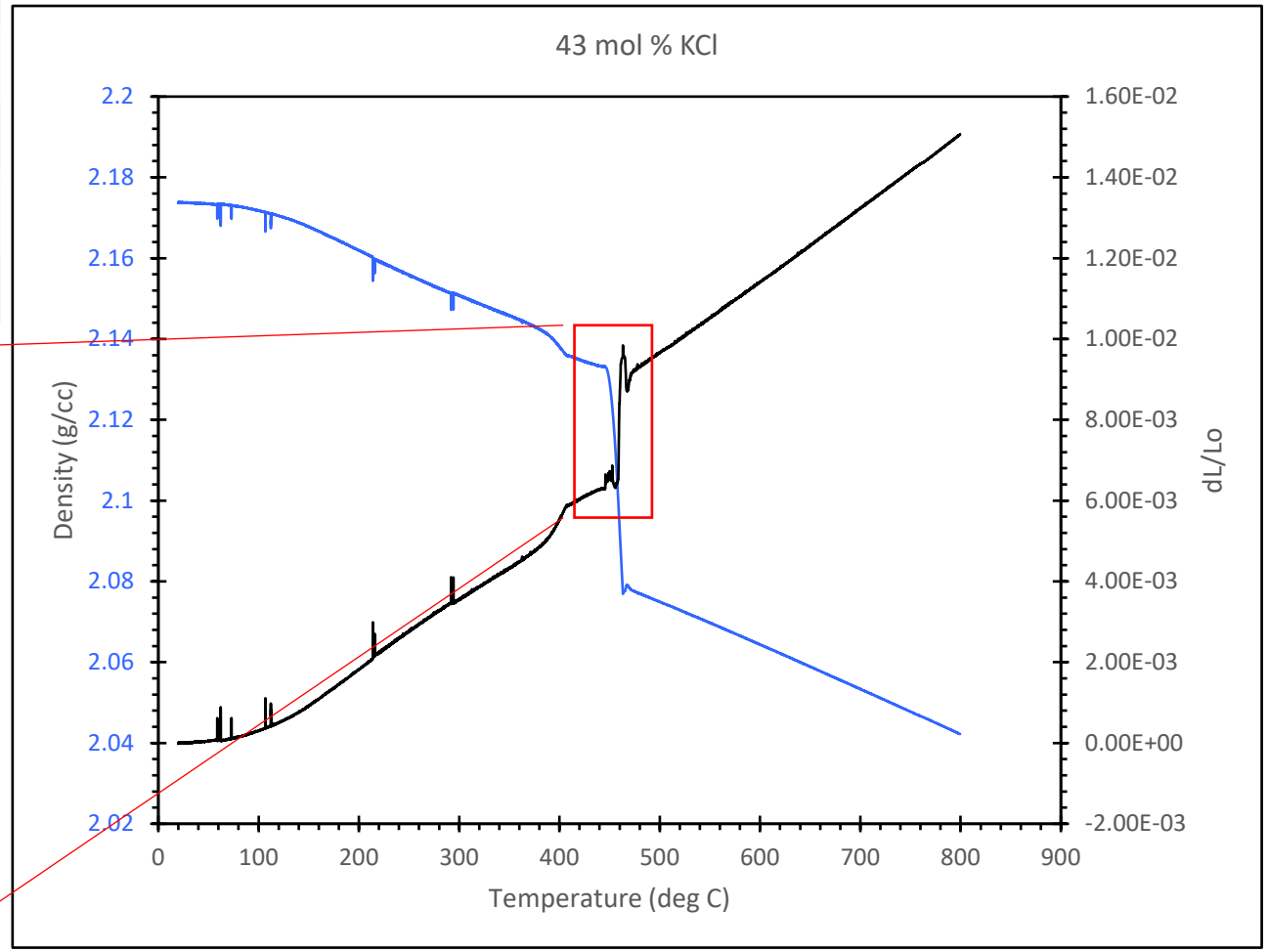
Density by thermomechanical analysis

Temp C	TMA	CMD*	AIMD*
445	2.13		
500	2.07		
600	2.06	1.90	1.69
700	2.05	1.87	1.67
800	2.04	1.85	1.62





*pers. comm. Nguyen (2024)

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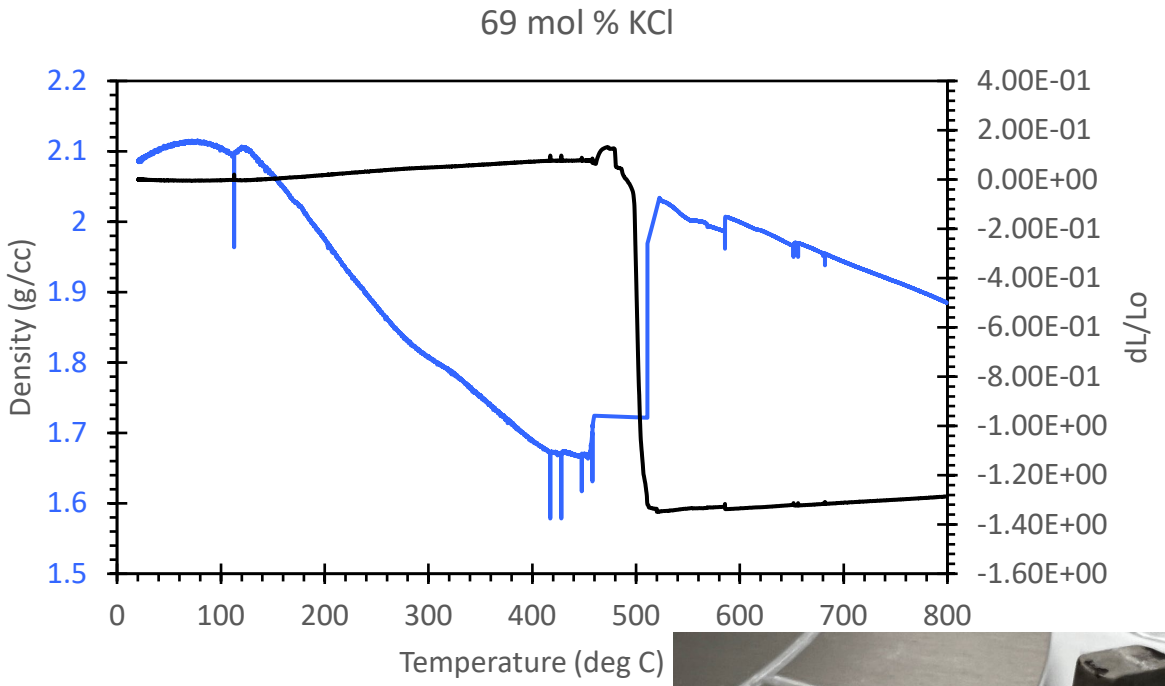
Density by thermomechanical analysis

- Sources of uncertainty:
  - Purity of salt(s)
  - Homogeneity of batched ratios
  - Reproducibility of mass measurements
  - Temperature calibration of the TMA instrument
  - Reproducibility of height measurement
    - Significantly improved by use of TMA
  - Subjective evaluation of cursor placement
- Improved accuracy:
  - Prior to melt, the pressed pellet does not completely occupy the volume under the plunger
    - However, placing cursors at appropriate location allows for the compensation of the melt filling the void space and its affect on the measured height change
  - Thermal expansion of the crucible/plunger ***is*** considered
- Main challenge is to prevent salt escape from crucible



Uncertainty analysis of density via TMA method

Using JCGM 100:2008 Guide to the Expression of Uncertainty in Measurement (GUM)

- Define Measurement Function
- Compute uncertainty for each input variable
- Compute uc(y)- the combined uncertainty
- Determine degrees of freedom for each variable
- Determine effective degrees of freedom for each variable
- Determine coverage factor, k
- Multiply k-factor by the combined uncertainty, result is the expanded uncertainty, U = k*uc(y)
- The measurand is then expressed as Y = y ± U

The measurement function:

$$\rho(T) = \rho(r)T(r)\frac{\left(1+\frac{\Delta L(T_r)}{L_0}\right)\cdot\left(1+\alpha_C(T_r)\right)^2}{\left(1+\frac{\Delta L(T)}{L_0}\right)\cdot\left(1+\alpha_C(T)\right)^2}\cdot B_e\cdot P_s\cdot V_c$$

Sources of Uncertainty for Propagation	Units	Assigned Error Type	Term	Value	std dev	n obs	deg freedom
Reference density	g/cm^3	type A or B	P(r)	actual			
Reference temperature	degrees C	type A	T(r)	actual			
Temperature calibration	degrees C	type A	T	actual			
Height calibration	mm	type A	dL/L$_o$	actual			
Subsampling from batched compositions	unitless	type A	B$_e$	1			
Salt purity	unitless	type B	P$_s$	1			
Manual picking of void volume correction	unitless	type B	V$_c$	1			

On the issue of Fluid Inclusions

- 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

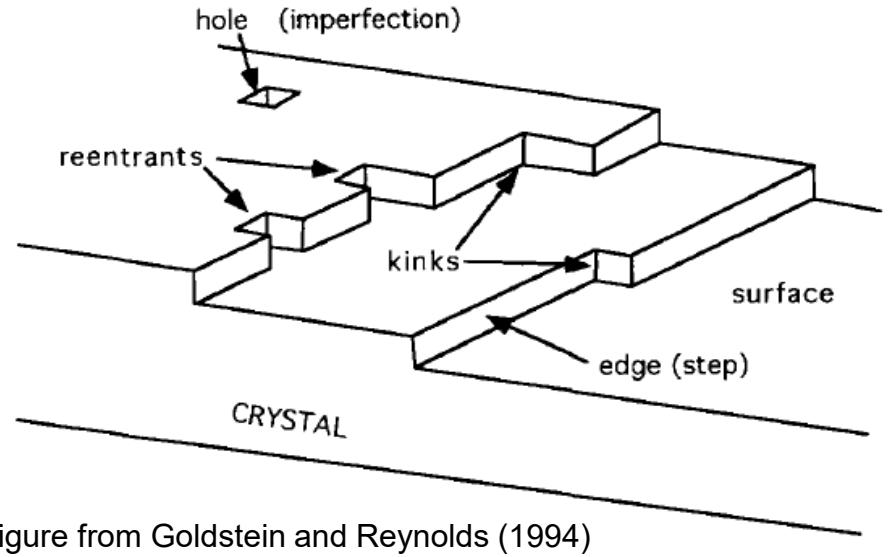
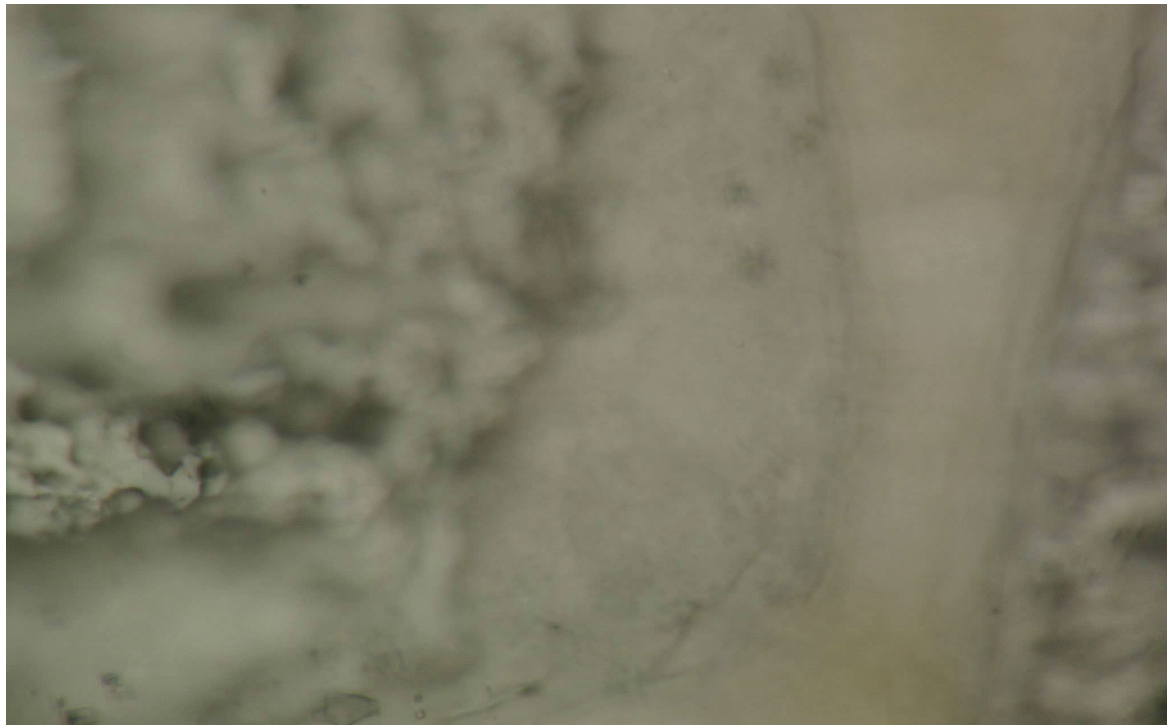


Figure from Goldstein and Reynolds (1994)

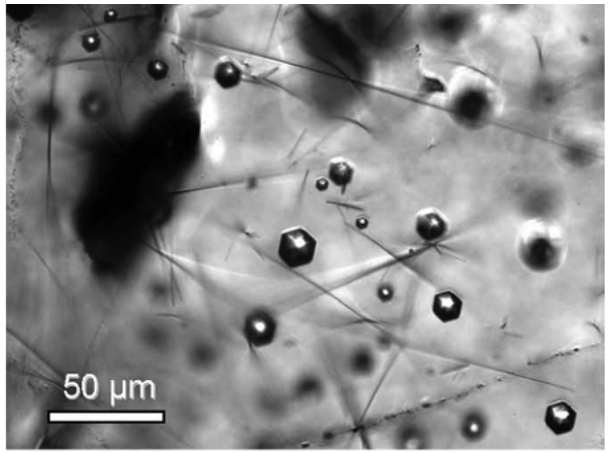
American Elements KCl 99.999% pure (metals basis)

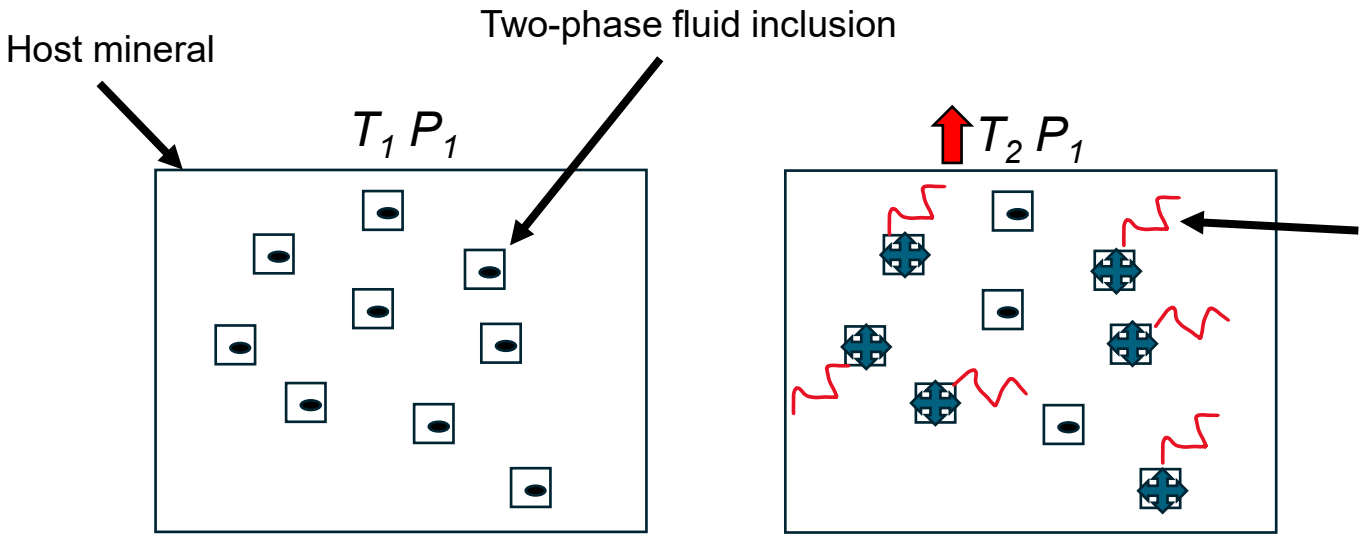


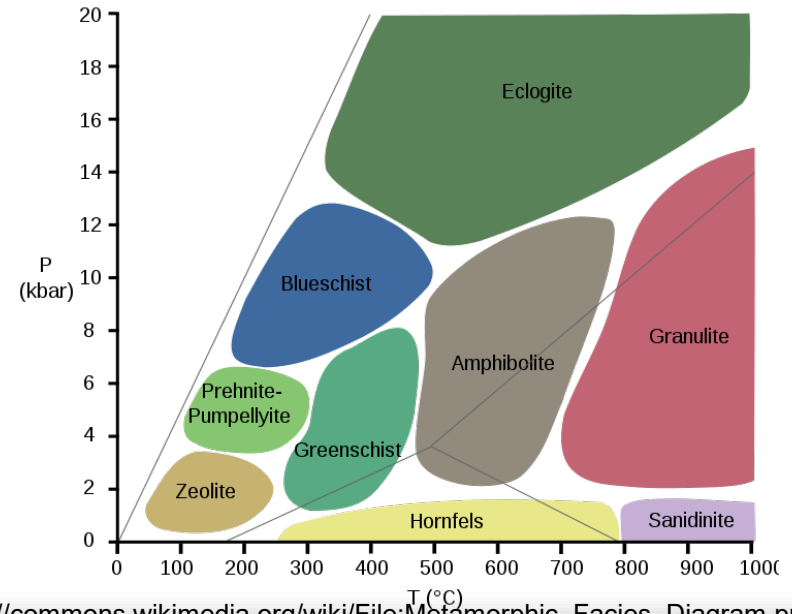
On the issue of Fluid Inclusions

- Preservation of fluid inclusions 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)



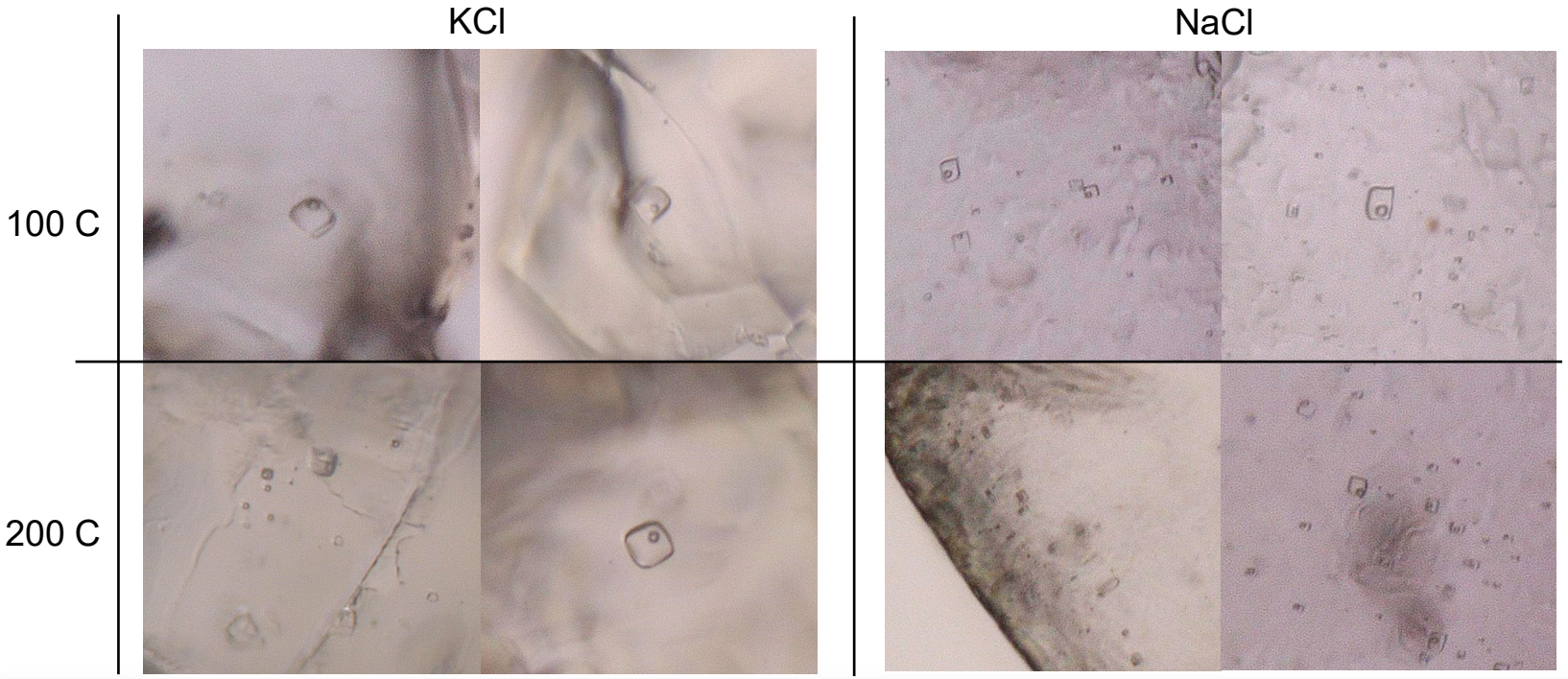




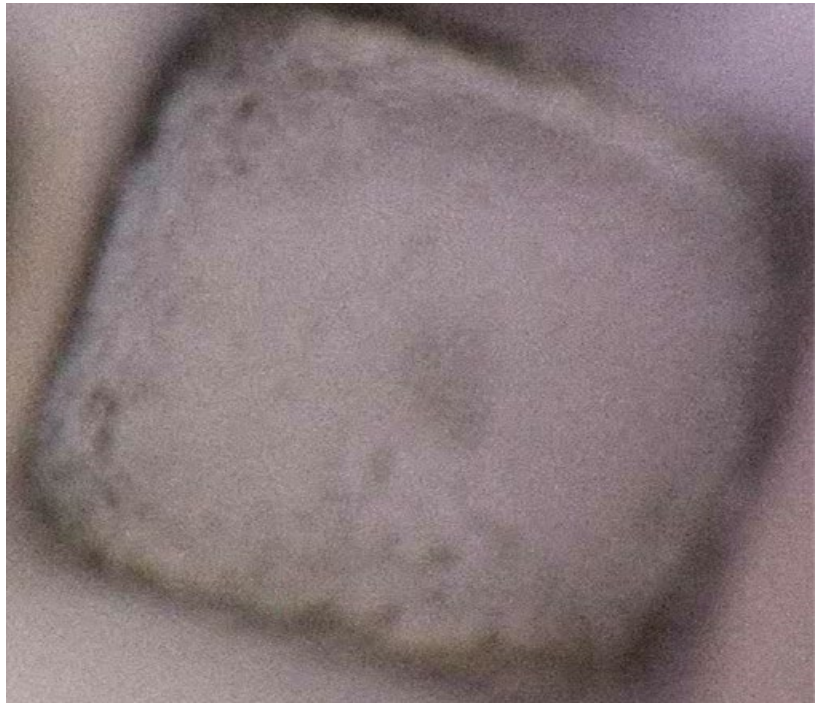
https://commons.wikimedia.org/wiki/File:Metamorphic_Facies_Diagram.png

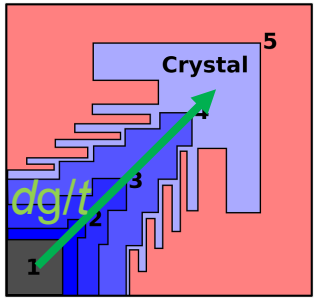
On the issue of Fluid Inclusions

- Preliminary Vacuum Oven Experiment
  - American Elements 99.999% pure (metals basis) KCl and NaCl
  - 1 g weighed and loaded into 20 mL scintillation vial
  - Experiment 1- hold for 8 hrs at 100 C; image inclusions
  - Experiment 2- using same salt, hold for 8 hrs at 200 C; image inclusions



NaCl Post 200 C





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

On the issue of Fluid Inclusions

- Existence of fluid inclusions 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 that need answering:
  - What salt species originate from aqueous precipitation?
    - Process driven? Manufacturer specific?
  - Can the process of manufacture be tailored towards conditions unfavorable for the creation of fluid inclusions?
  - Alternatively, for the end-user of the salts, is post-processing of salts to remove fluid inclusions:
    - Possible
    - More economical
  - 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?

Thank you

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