

Zircon/fluid trace element
partition coefficients
measured by recrystallization
of Mud Tank zircon at 1.5 GPa
and 800-1000°C

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Introduction: Zircon/Fluid Trace Element Partitioning

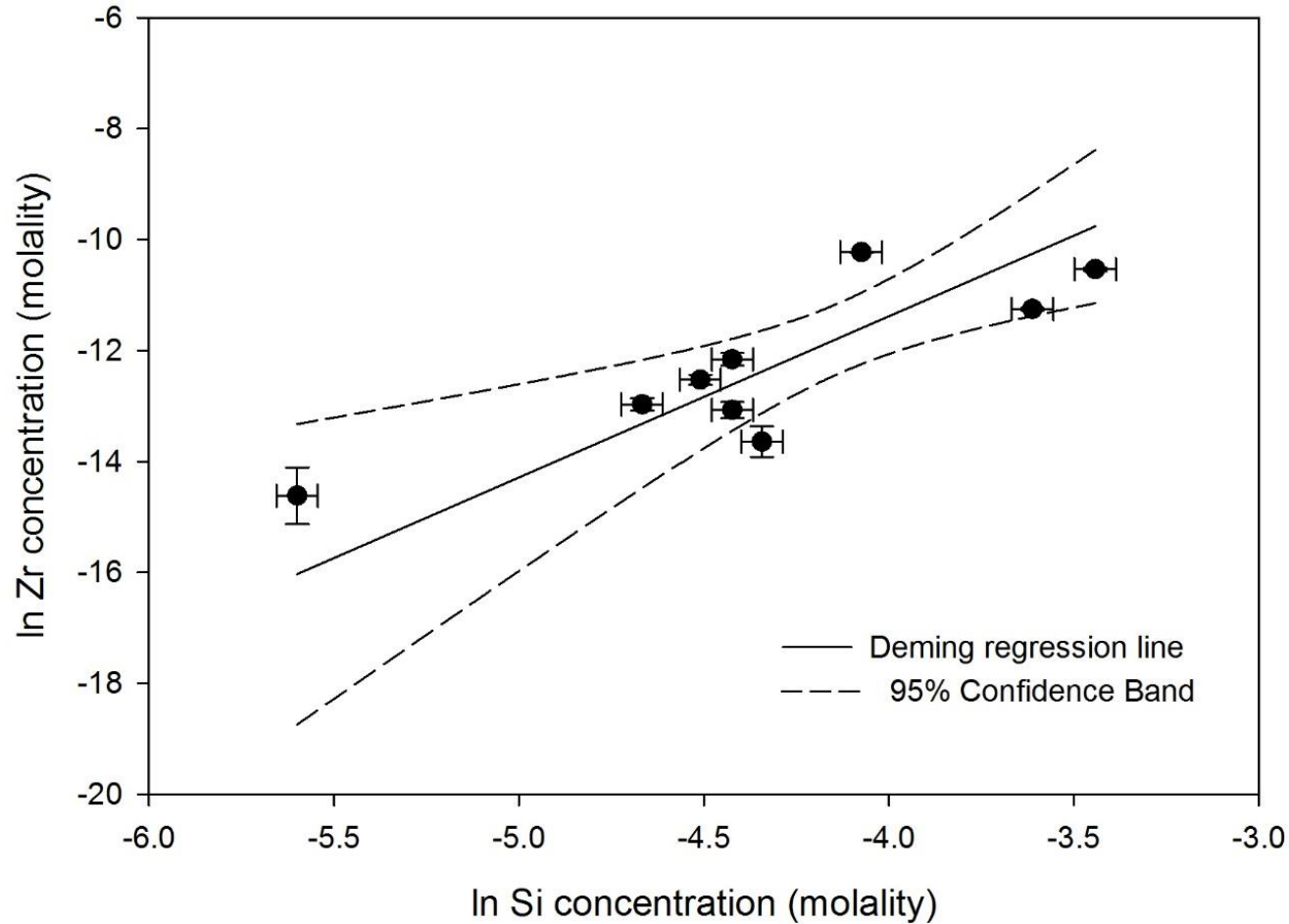
- For trace elements (that obey Henry's Law) the trace element partition coefficient

$$D = C_s/C_{fl}$$

where C_s = concentration in the solid and C_{fl} = concentration in fluid.

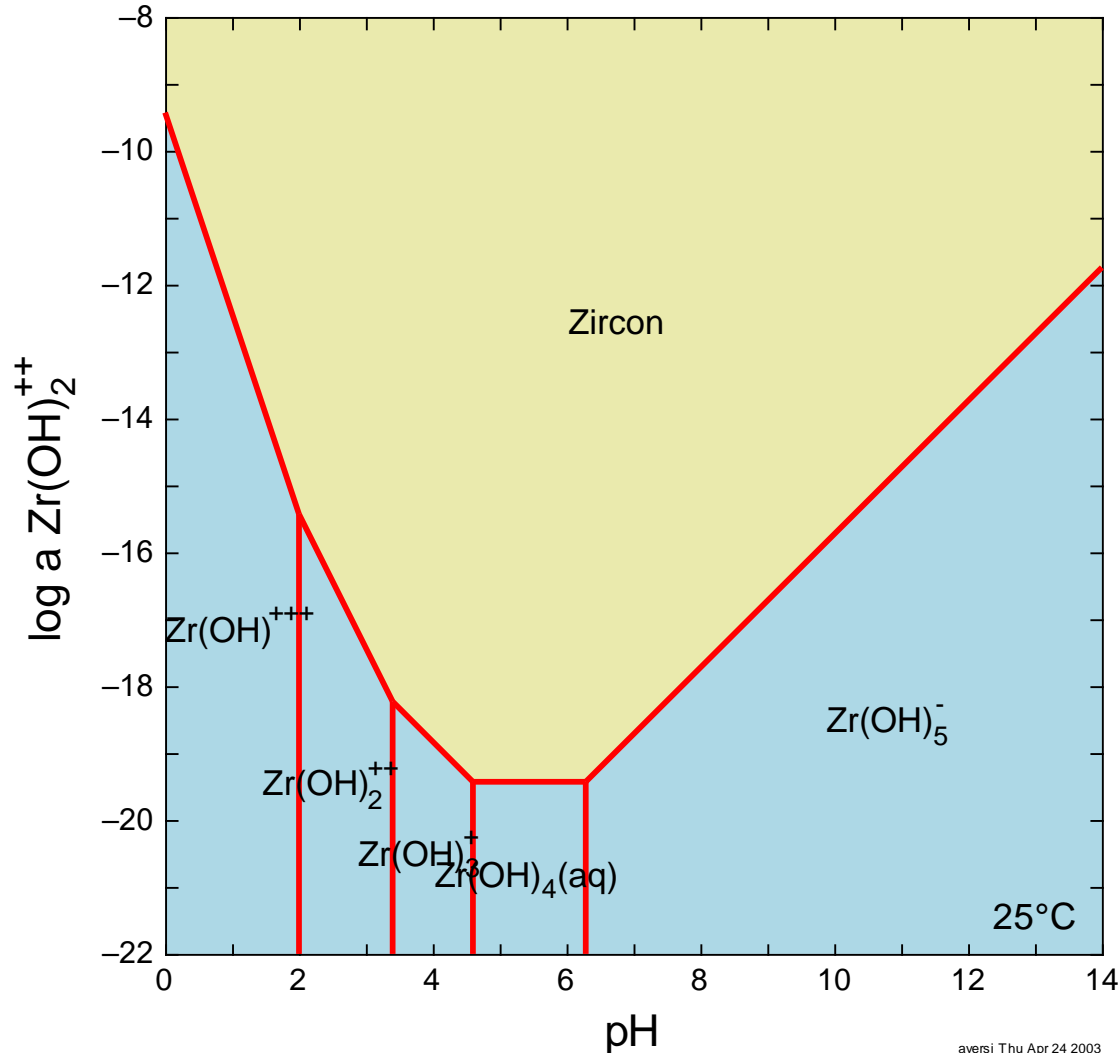
- If we measure the concentration of a trace element in a zircon crystal, we can estimate the concentration that was in the fluid that the zircon crystal grew from: $C_{fl} = C_s/D$
- Can trace element compositions of zircons be used to distinguish:
 - magmatic, metamorphic, and hydrothermal zircons?
 - different fluid compositions?
- Trace element partitioning equilibrium more likely in:
 - fluids than melts
 - fluids in which zircon is soluble: quartz-saturated acidic or alkaline fluids.

Zircon solubility \uparrow with \uparrow Si concentration



At 0.2 GPa and 600°C. From Ayers et al. (2012), GCA v. 96 pp. 18-28.

Zircon Solubility In Quartz-saturated Fluid



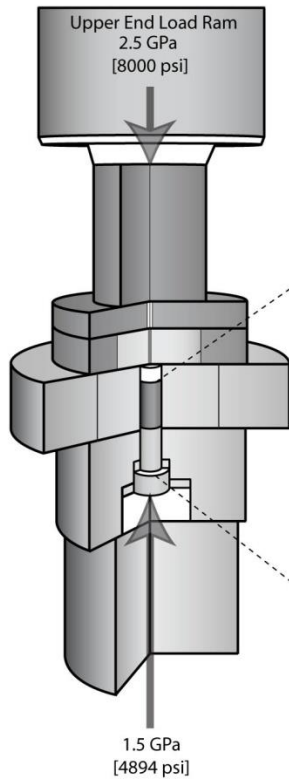
25°C and 1 bar pressure,
thermodynamic data from Adair et al. (1997)

Experimental Approach: Starting Materials

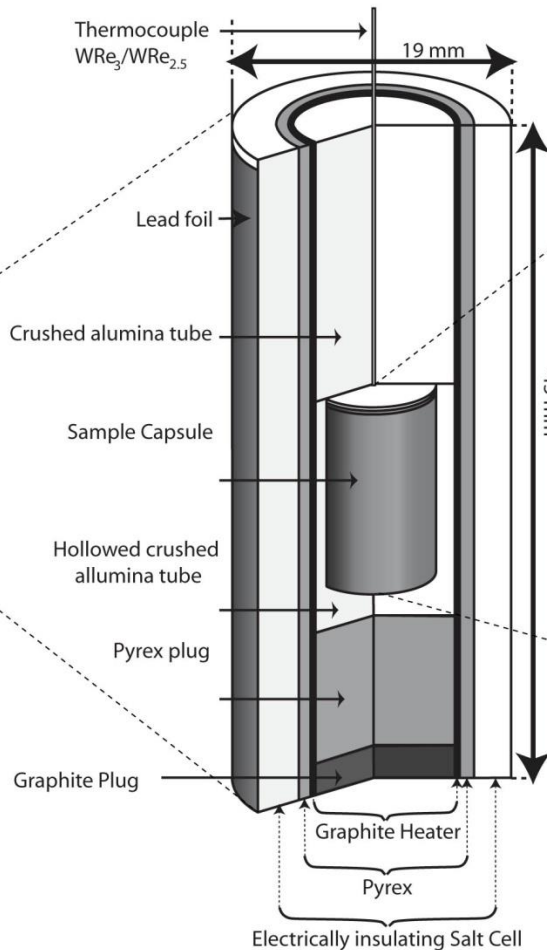
- Finely powdered Mud Tank zircon with low trace element concentrations.
- Fluid quartz-saturated $\text{H}_2\text{O} \pm \text{HCl}$ or NaOH doped with ~ 1000 ppm of trace elements.
- Small zircon crystals should recrystallize due to Kelvin effect and exchange trace elements with the fluid.
- Should be easy to distinguish recrystallized (high TE content) from unrecrystallized (low TE content).

Experiment setup

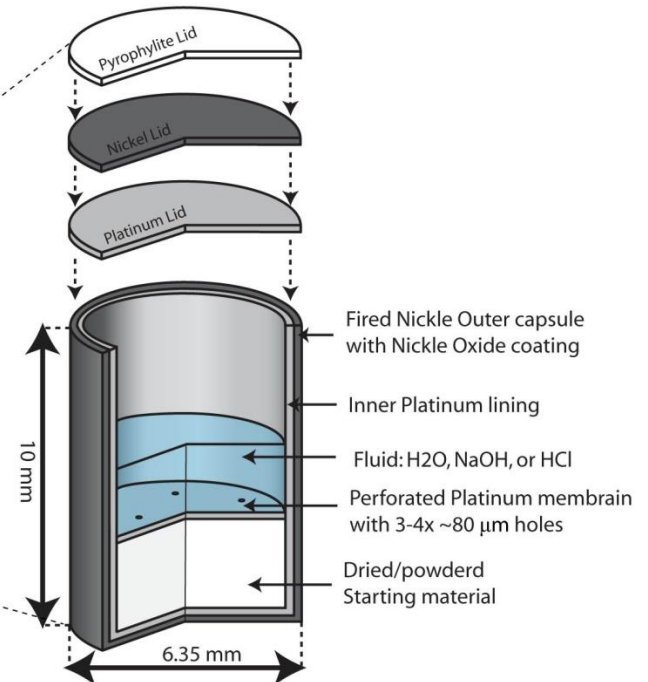
Piston-Cylinder Assembly



Sample Assembly



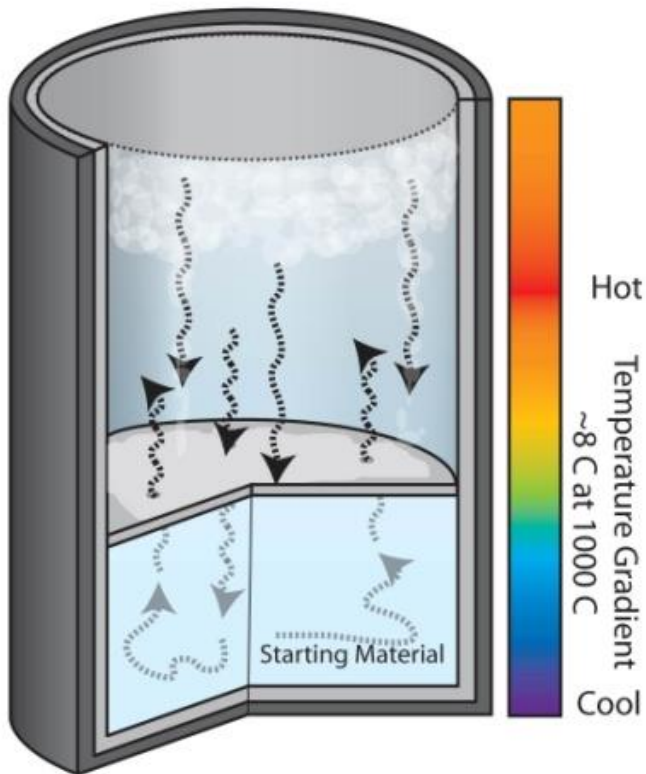
Sample Capsule



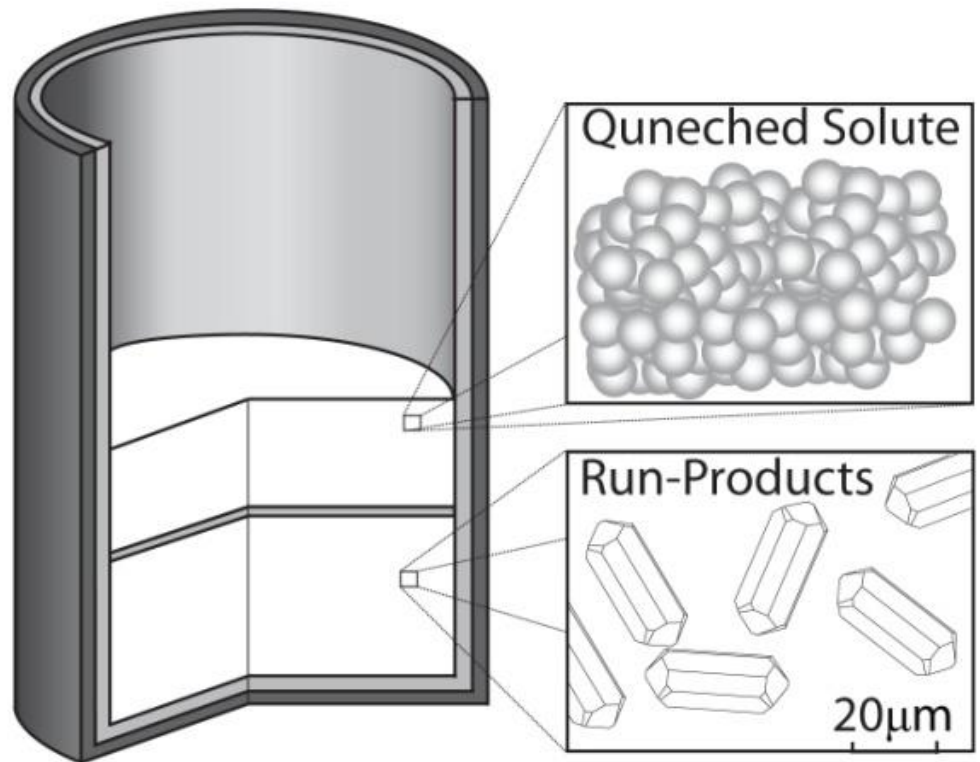
fO_2 buffered to NNO

Experiment capsule

During the run.



After the run.



After experiment

- Collect quenched solutes, fuse and analyze to estimate fluid composition.
- Analyze solutes and run product zircon grains using LA-ICP-MS (ThermoFisher iCAP Qc quadrupole ICP-MS and Photon Machine Excite 193nm excimer laser ablation system)
- If solutes can't be collected, calculate fluid composition from mass balance using total concentration C_t and run product zircon concentrations C_s :

$$C_t = X_{fli}C_{fli} + X_{si}C_{si} \text{ where } X_{si} = M_s/(M_s + M_{fli})$$

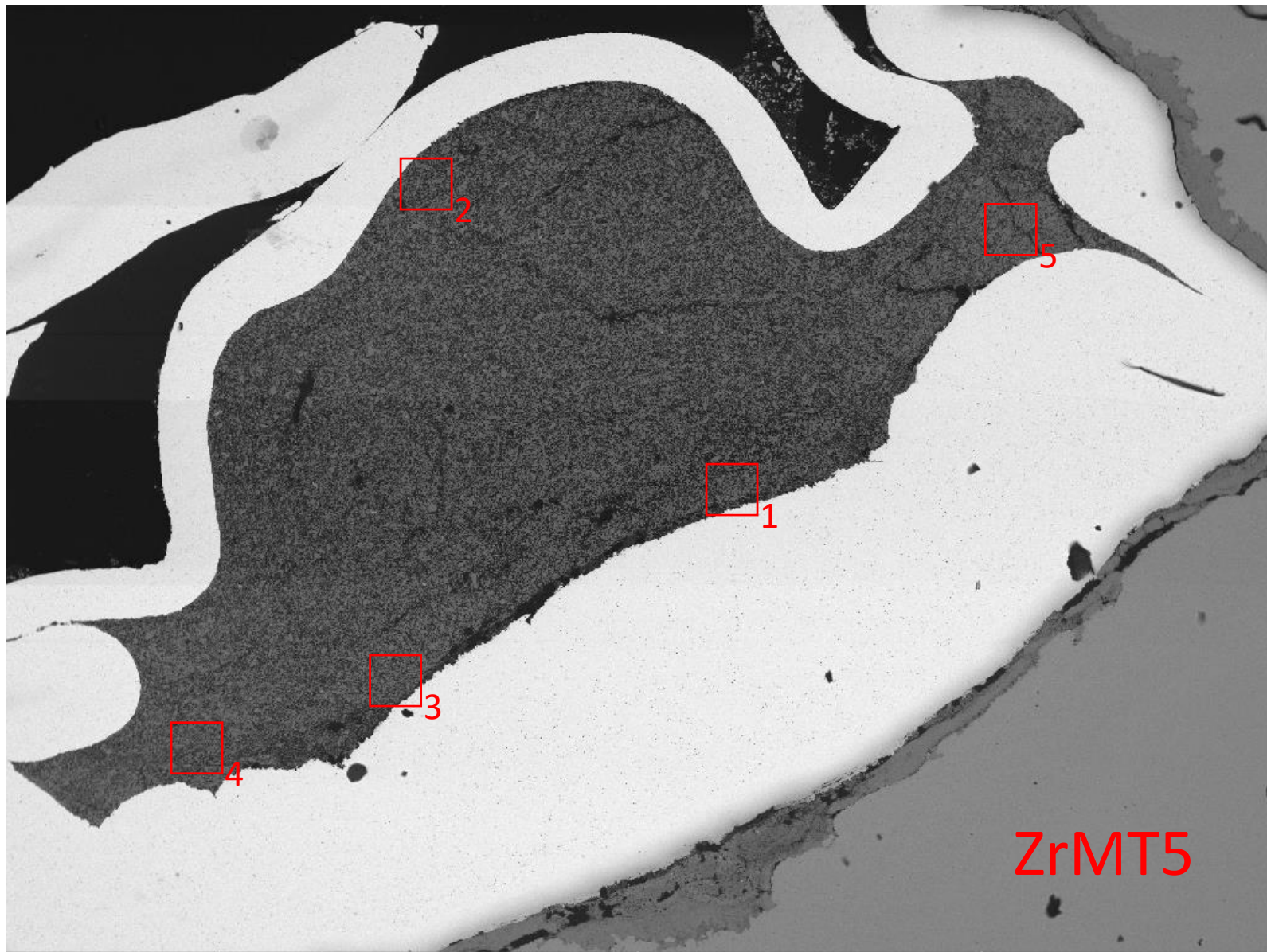
$$C_{fl} = (C_t - X_s * C_s)/X_{fl}$$

$$D = C_s/C_{fl}$$

Recrystallization Experiments

Experiment	Fluid	Temp (°C)
ZrMT02	H ₂ O	900
ZrMT03	H ₂ O	800
ZrMT05	H ₂ O	1000
ZrMT07	1m NaOH	900
ZrMT08	1m HCl	900

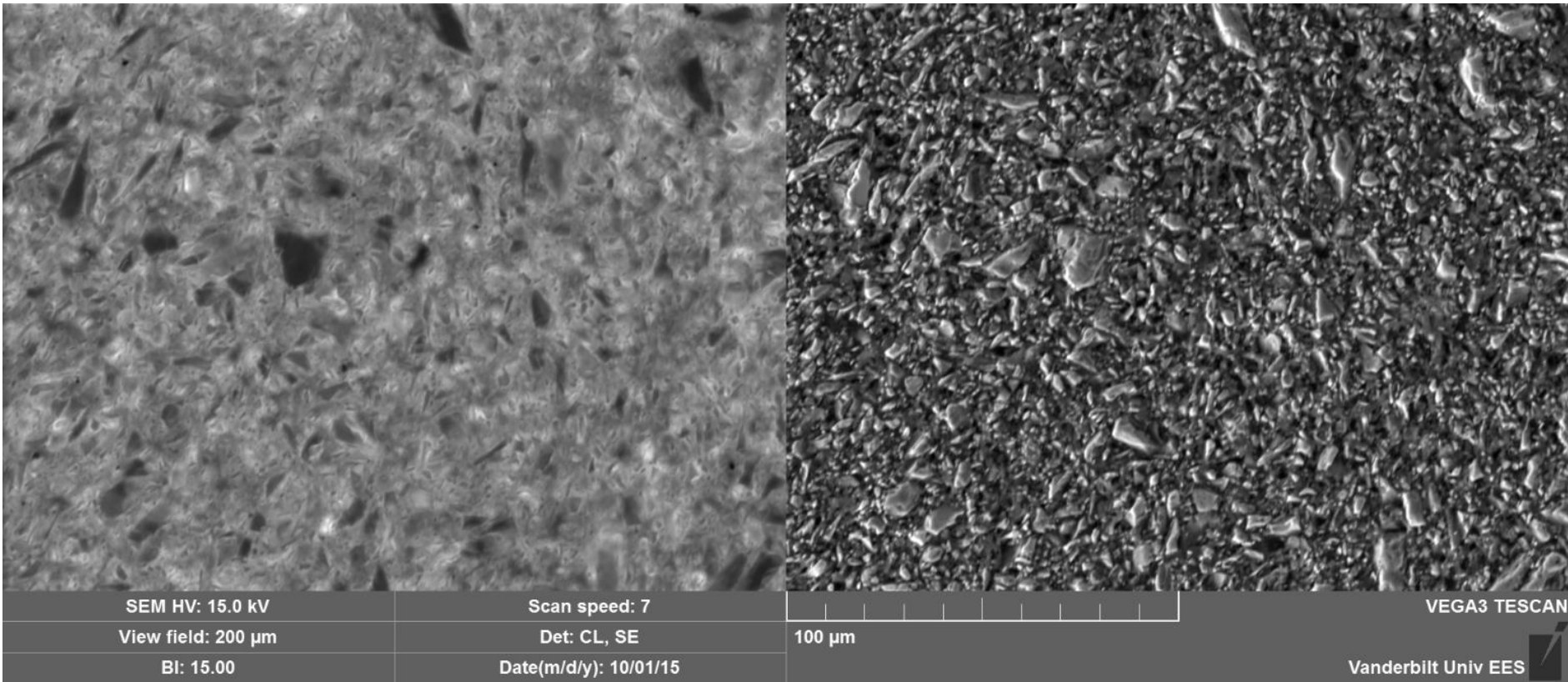
All fluids quartz-saturated. Experiment pressure = 1.5 GPa, duration = 168 h, $fO_2 = NNO$.



ZrMT5

SEM HV: 15.0 kV	Scan speed: 5	1 mm	VEGA3 TESCAN
View field: 3.68 mm	Det: BSE		
BI: 15.00	Date(m/d/y): 10/01/15	Vanderbilt Univ EES	

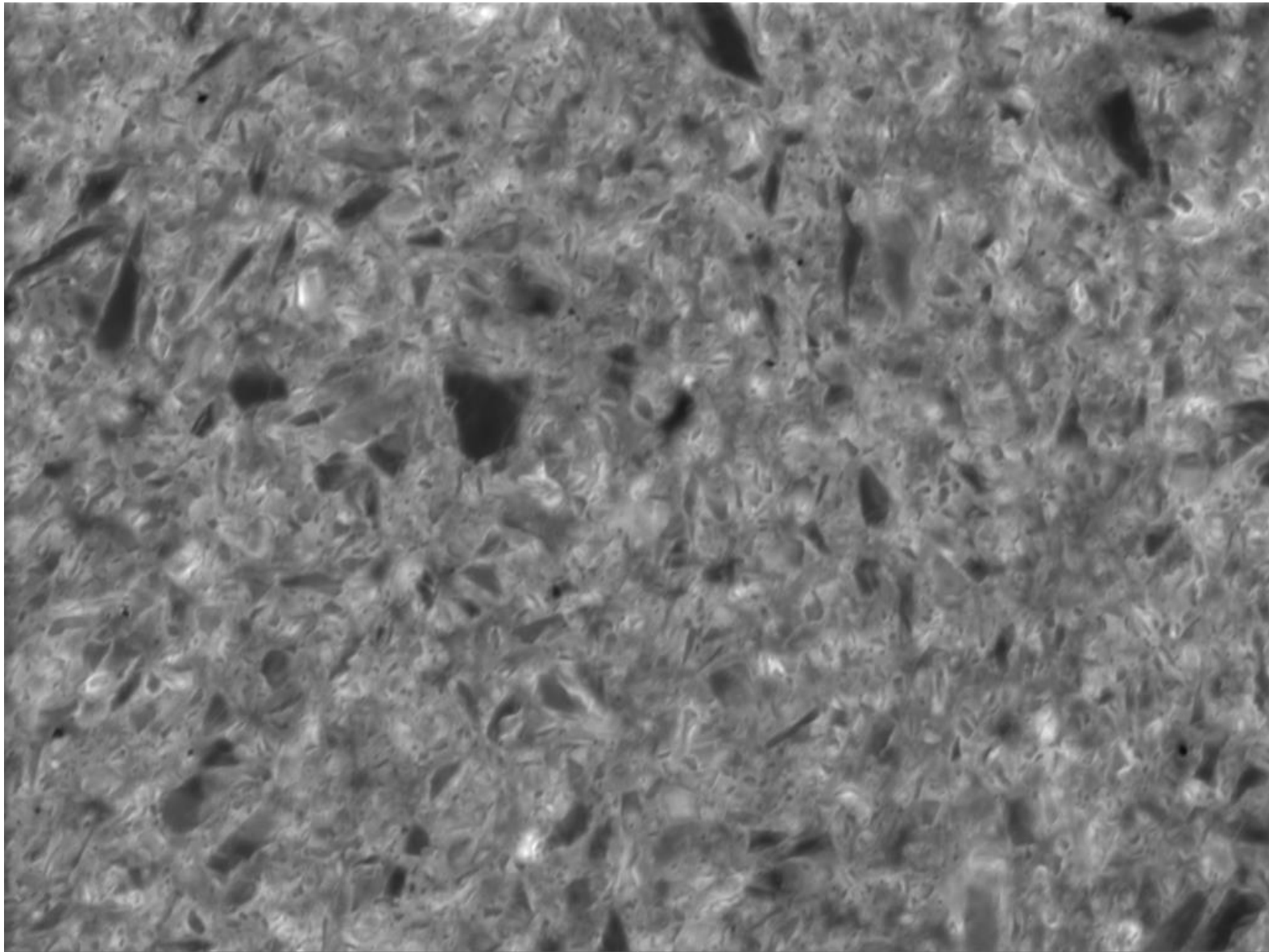
ZrMT05 run product zircon



Cl image

BSE image

ZrMT5 Zircon



SEM HV: 15.0 kV

Scan speed: 7

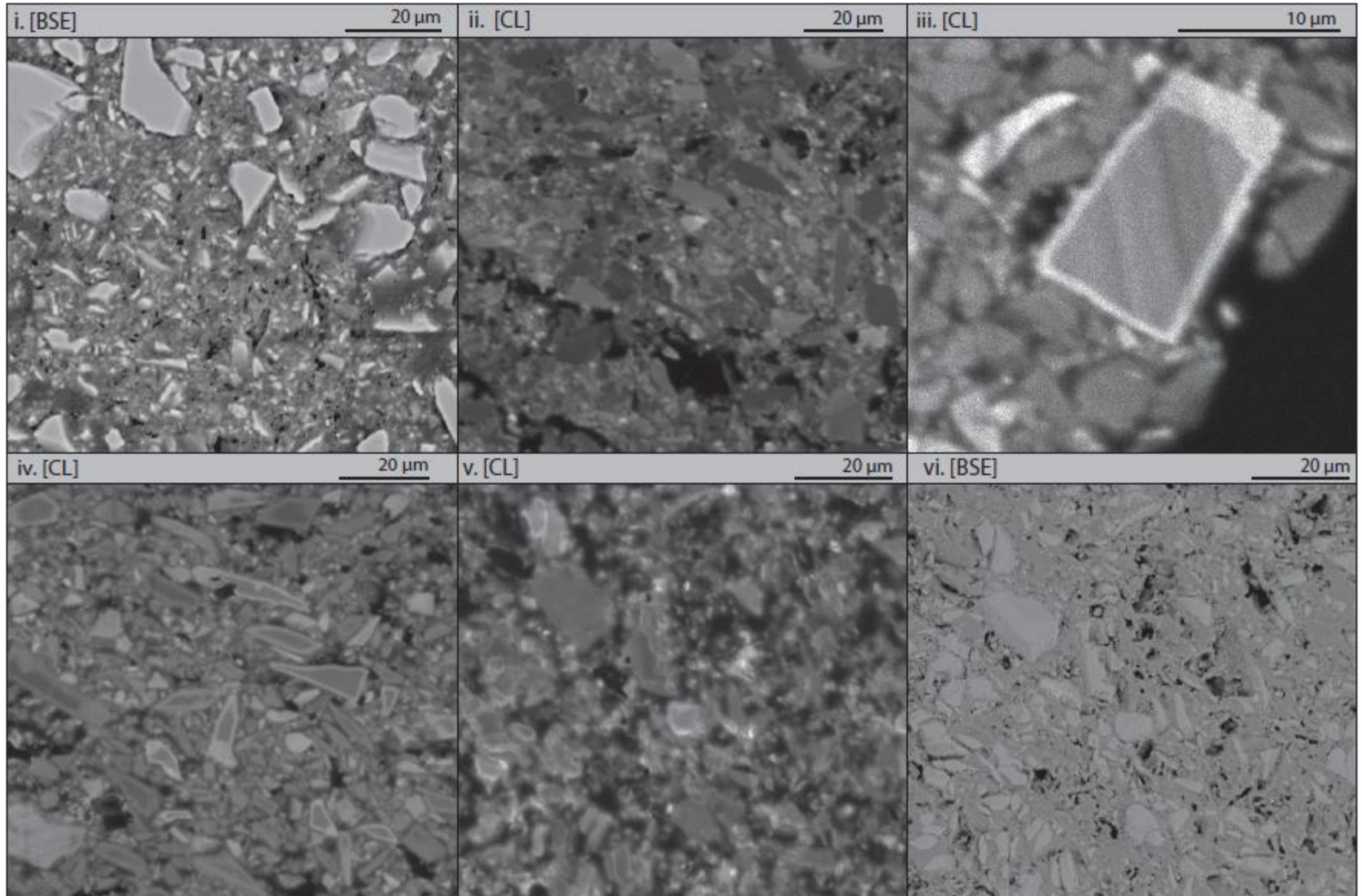
View field: 200 μ m

Det: CL, SE

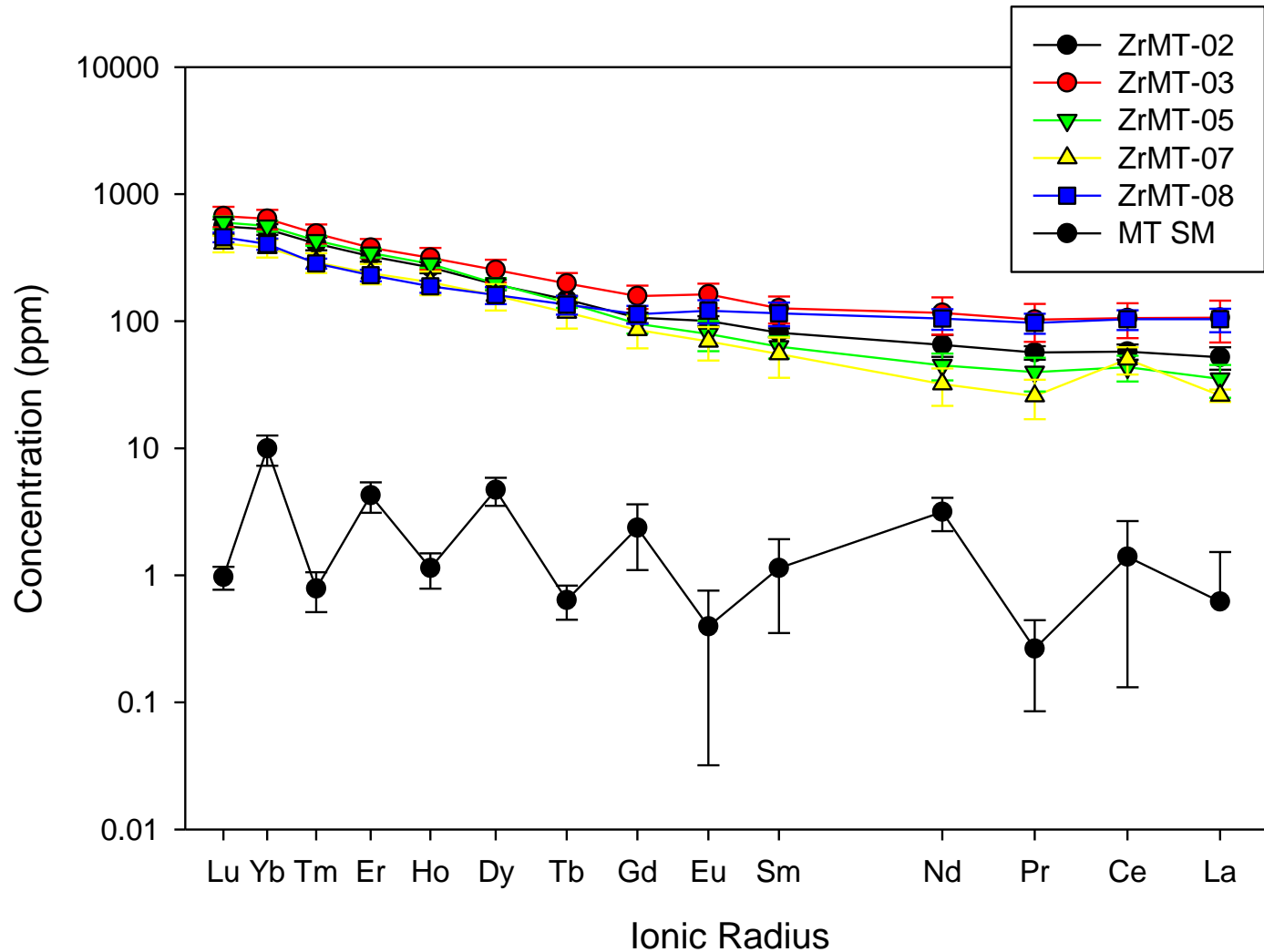
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Date(m/d/y): 10/01/15

Recrystallization Experiment Run Products

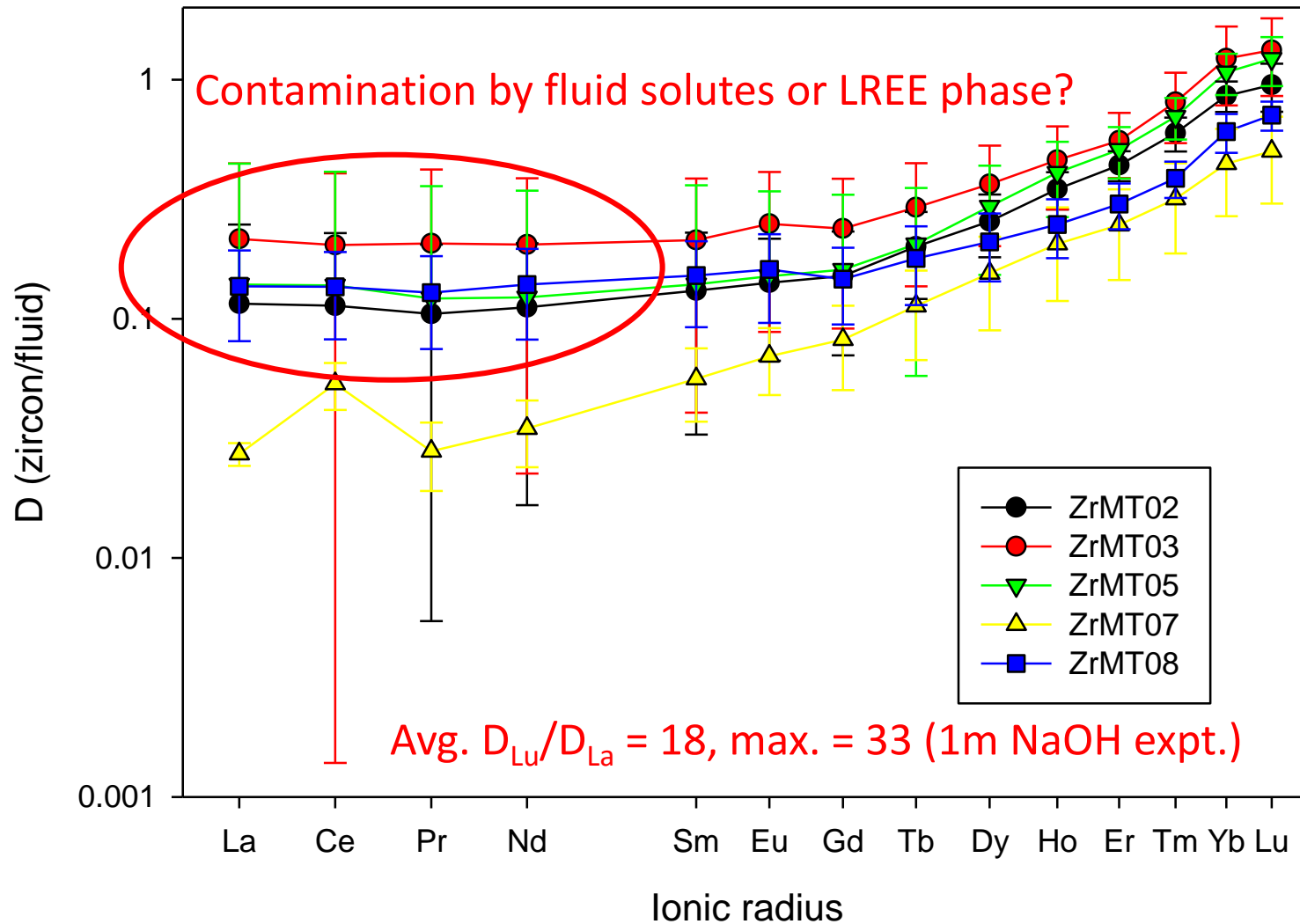


Zircon Trace Element Concentrations



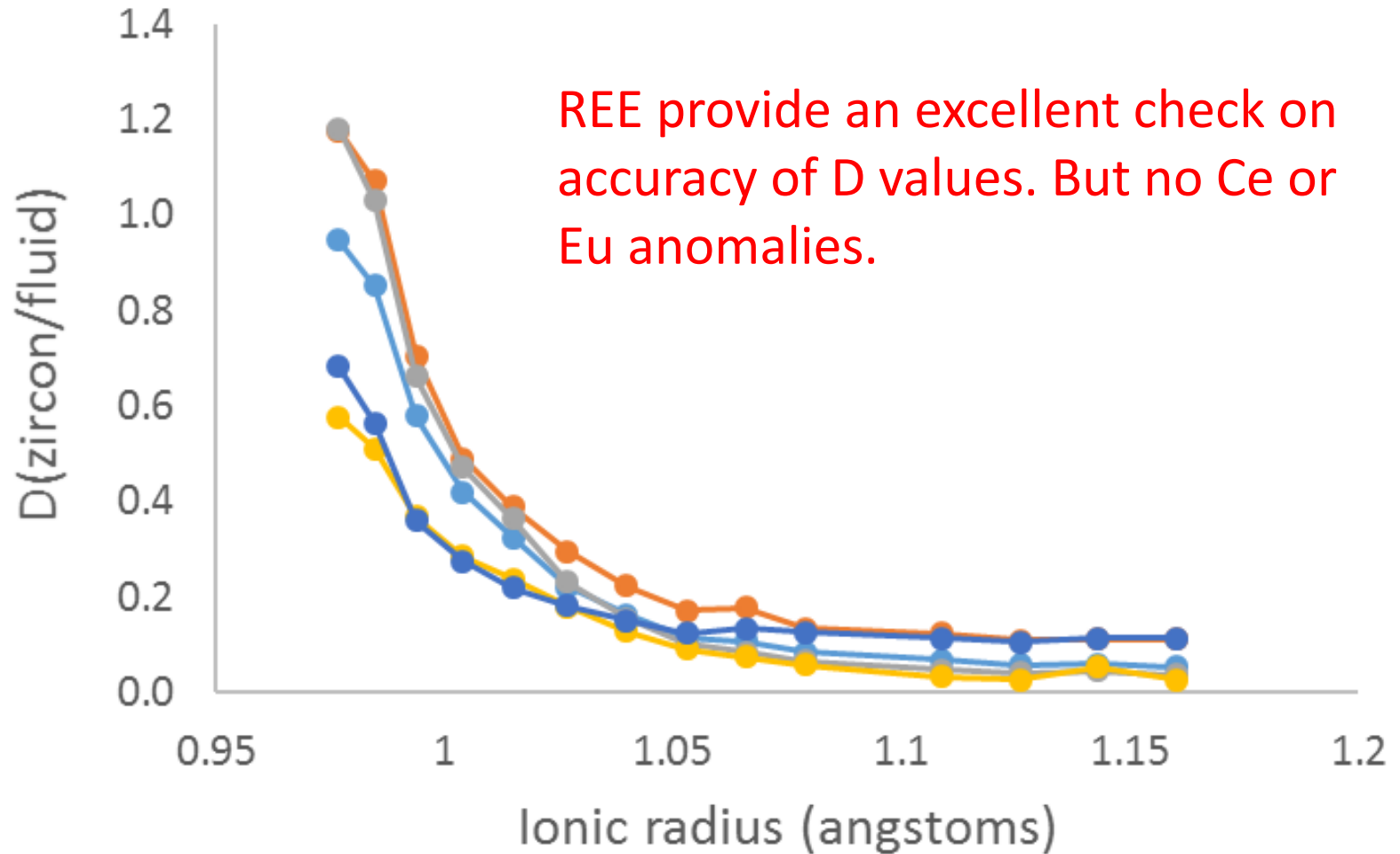
Processed LA-ICP-MS data in Glitter, used “MDL unfiltered” values to calculate average concentrations in zircon. Ten analyses per sample, error bars ± 1 sigma.

D(zircon/fluid) values



Calculated by mass balance from bulk starting composition and concentrations in run product zircon crystals. Error bars ± 1 st. dev..

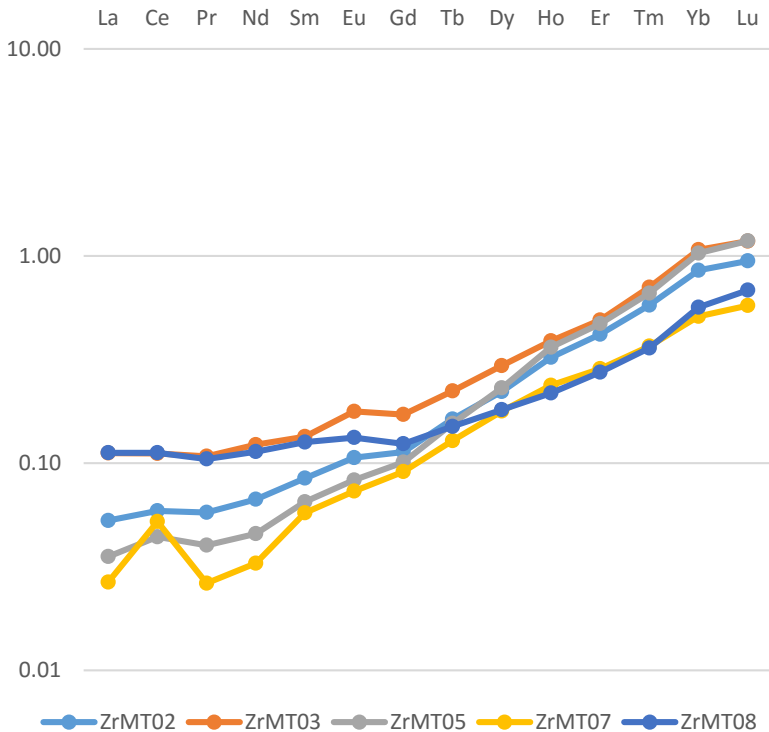
Onuma diagram: D_{REE} values



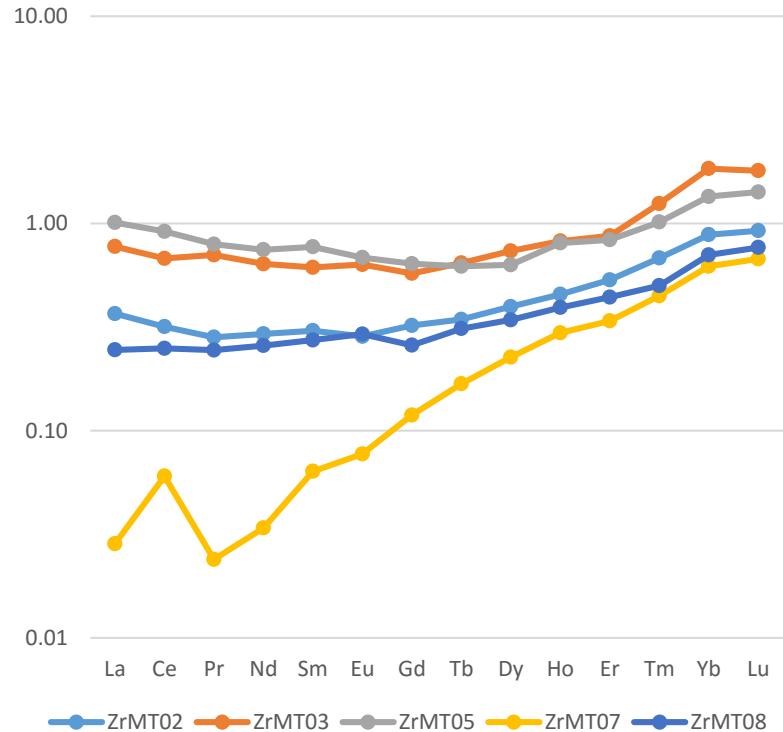
—●— ZrMT02 —●— ZrMT03 —●— ZrMT05 —●— ZrMT07 —●— ZrMT08

Are average C_s biased to low values and calculated C_{fl} to high values due to mixed analyses of recrystallized and unrecrystallized MT zircon, yielding minimum D values?

Average D values



Maximum Cs and D values

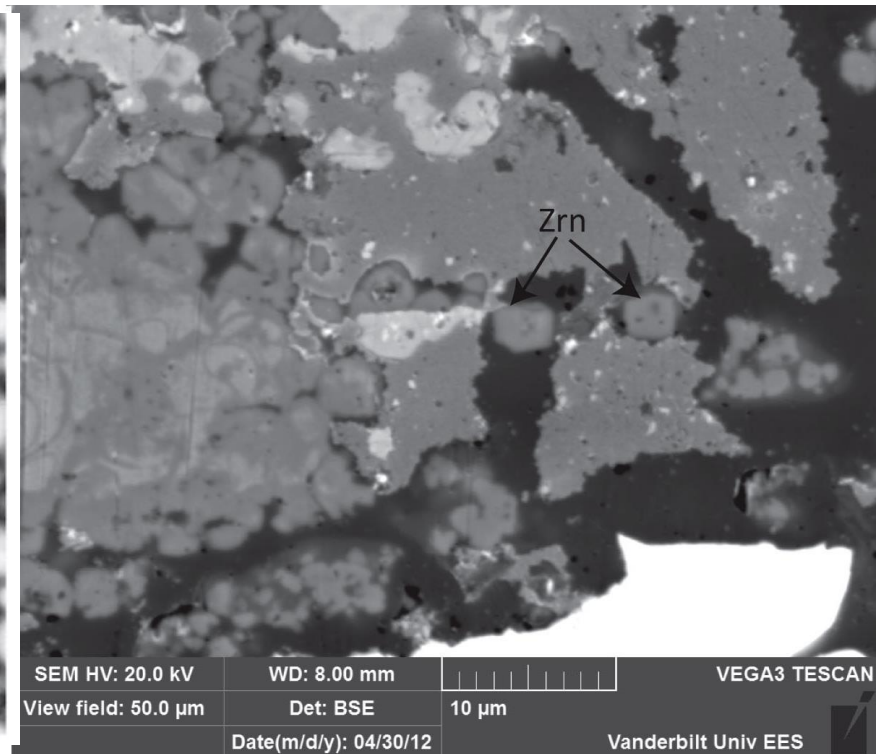
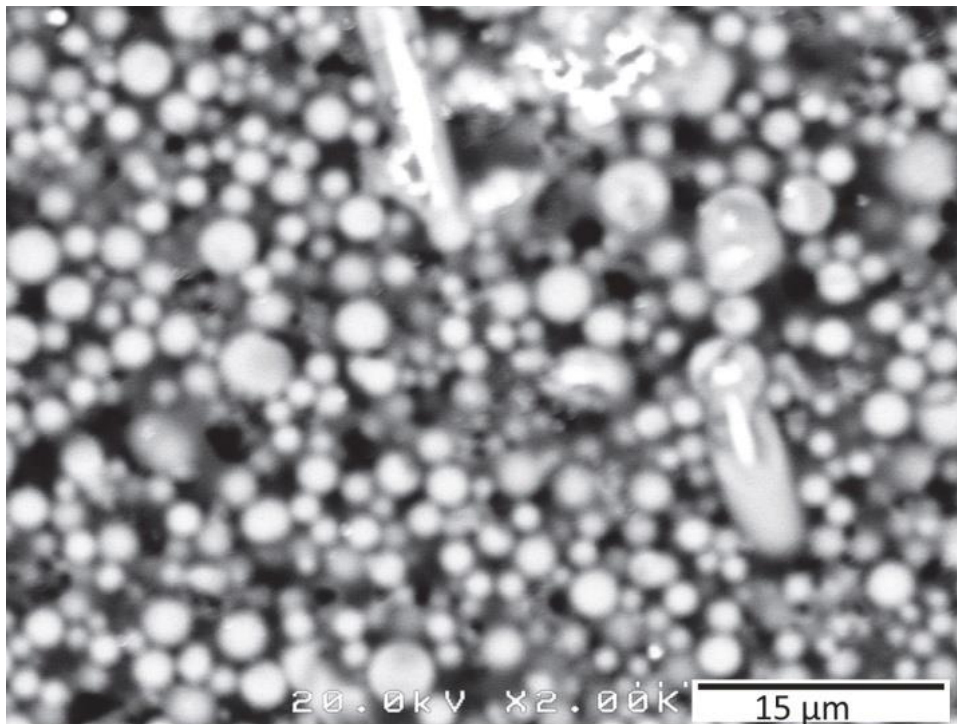
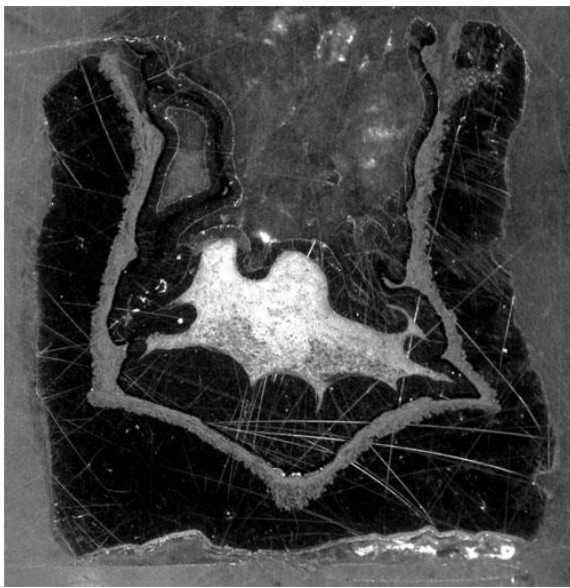


Synthesis Experiments: $\text{ZrO}_2 + \text{SiO}_2$

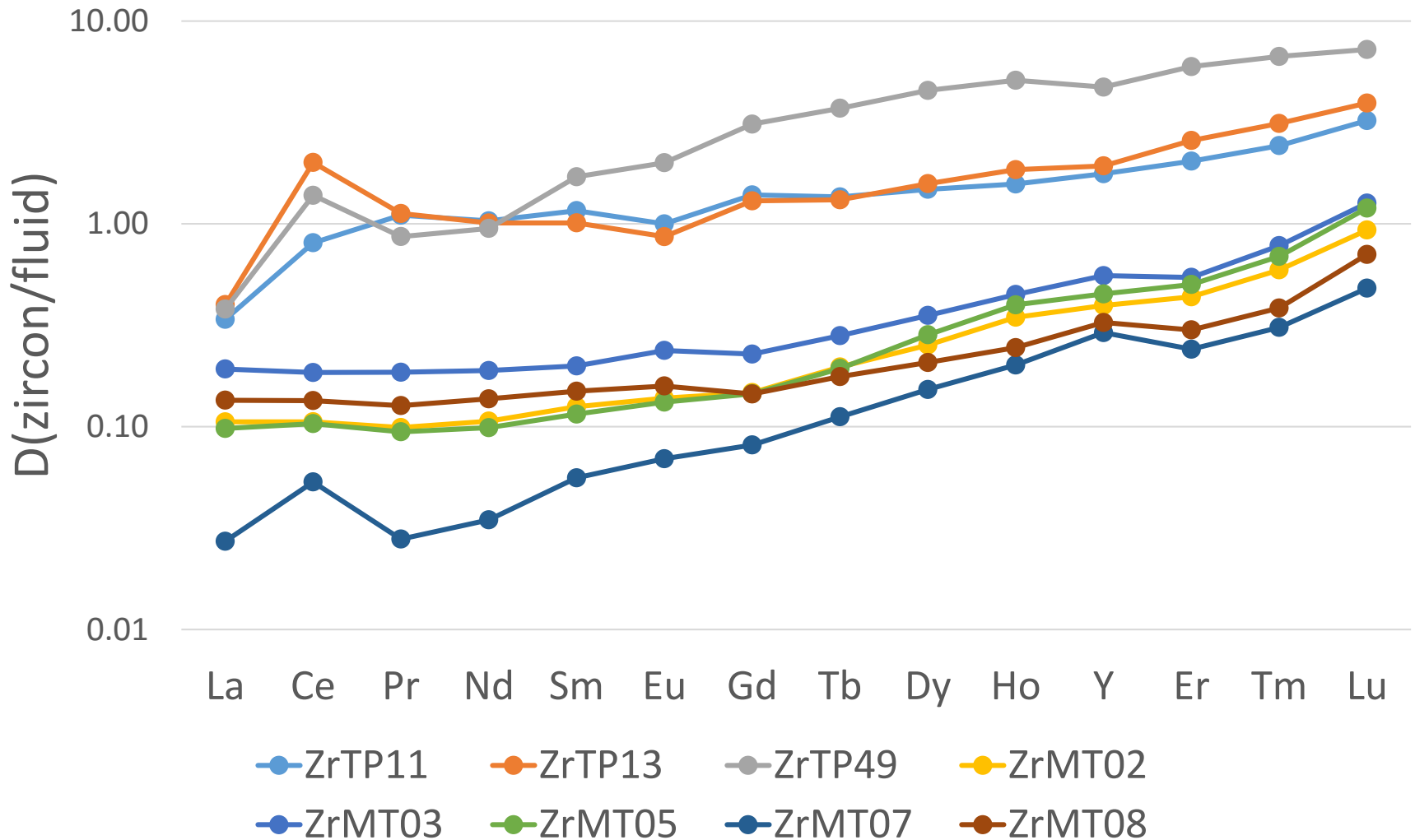
Experiment	Fluid	Time (h)	Temp ($^{\circ}\text{C}$)
ZrTP11	H_2O	168	800
ZrTP13	H_2O	72	800
ZrTP14	H_2O	24	800
ZrTP34	H_2O	96	900
ZrTP35	H_2O	96	900
ZrTP40	1m NaOH	168	800
ZrTP46	1m NaOH	72	800
ZrTP49	1m NaOH	96	900
ZrTP51	1m HCl	48	800
ZrTP52	1m HCl	48	800
ZrTP53	1m HCl	96	800
ZrTP54	1m HCl	72	900

Synthesis run products

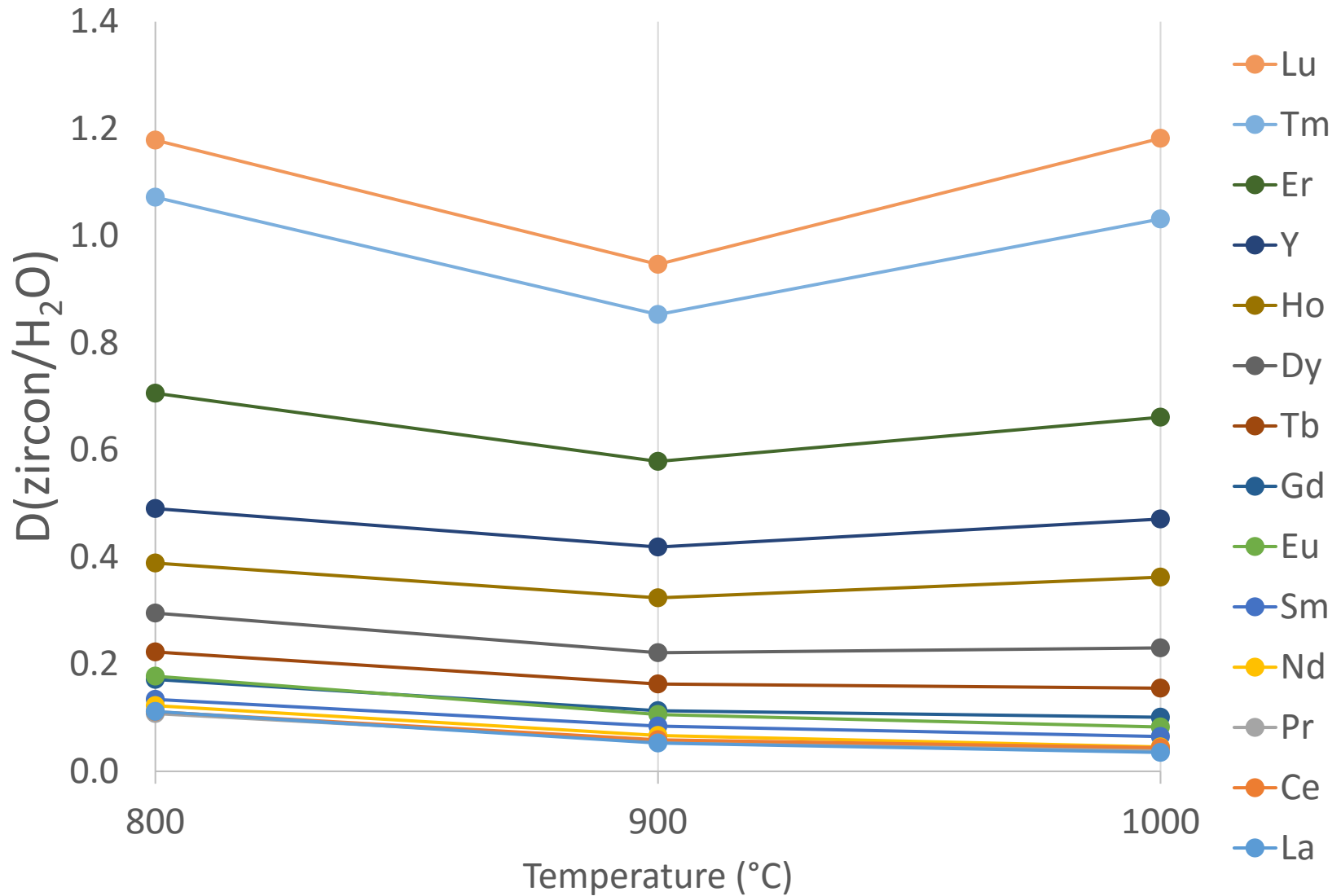
D(zircon/fluid) values calculated using C_{fl} and C_t since impossible to get clean analyses of run product zircon



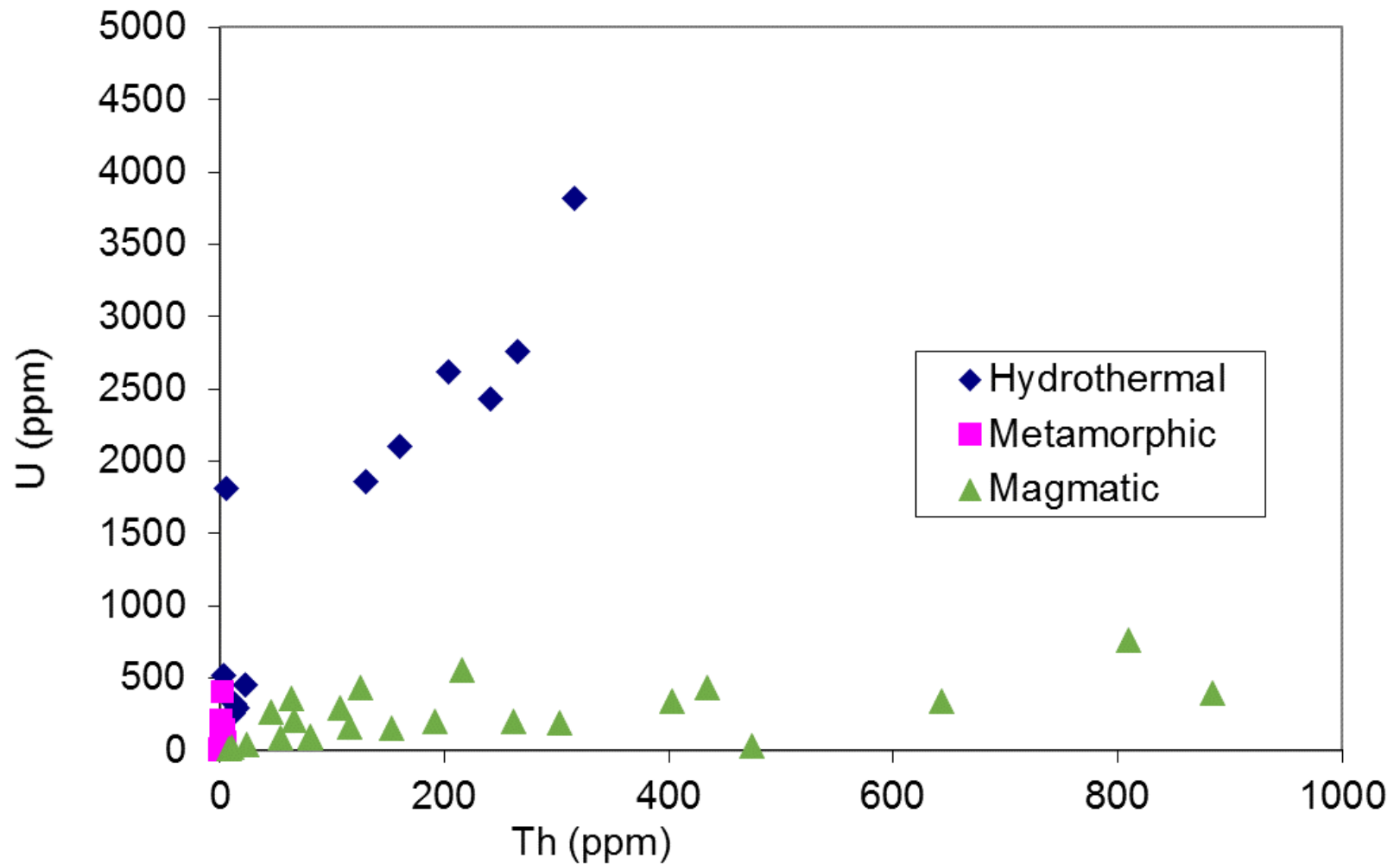
Comparison: Synthesis and Recrystallization Experiments



No systematic T dependence of D values in ZrMT experiments



Hydrothermal, magmatic or metamorphic?



Data from Rubatto (2000)

D(zircon/fluid) for HFSE in recrystallization experiments

Ion	Avg. D	Median D
Hf ⁴⁺	12	9
Th ⁴⁺	0.8	0.7
U ⁶⁺ (?)	8.3	1.3
Nb ⁵⁺	0.15	0.12
Ta ⁵⁺	0.28	0.25

D_U slightly higher than for HFSE other than Hf.

Not enough to explain why hydrothermal zircons have high U?

Conclusions

- Small zircon crystals recrystallize due to Kelvin effect. Large crystals form rims during coarsening.
- Zircon recrystallization promotes trace element partitioning equilibrium.
- Low trace element (REE) fractionation and lack of Ce and Eu anomalies likely due to contamination by fluid or LREE-rich phase, but may reflect disequilibrium.
- Analytical methods with spatial resolution higher than LA-ICP-MS needed to accurately measure zircon D values experimentally.
- Zircon is a tough nut to crack experimentally.