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# Applications of thermodynamics in rare earth recycling research

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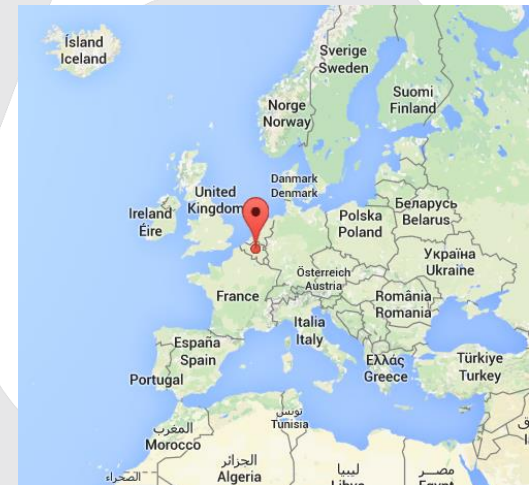
**InsPyro**

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# Introduction: InsPyro

B2B consultancy company  
KU Leuven spin-off (2009)  
Founded and run by PhD's

- Process development & improvement through:
  - Modelling and literature
  - Experiments
  - Characterization
  - Industrial experience
- Industries:
  - Recycling incl. batteries and residues
  - Non-ferrous metallurgy (lead-zinc)
  - Steel, cast iron and ferro-alloys
- [www.inspyro.be](http://www.inspyro.be)

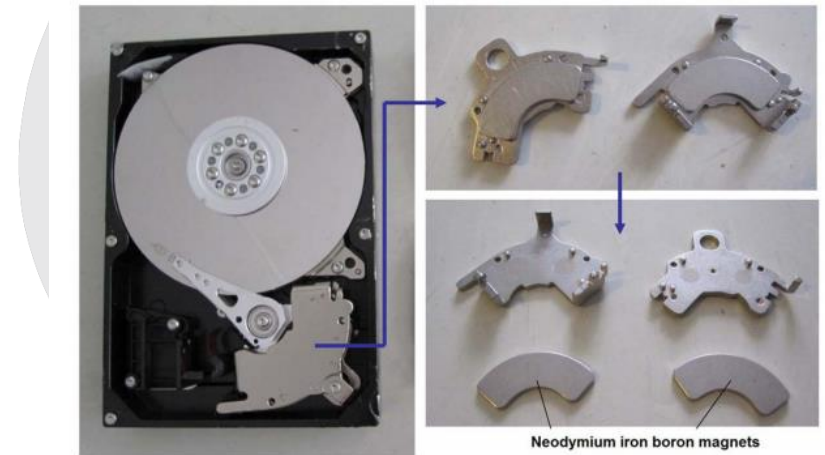


# Rare earth recycling and thermodynamics

- Thermodynamic approach highly successful in understanding and predicting high temperature processes
- Several high temperature processes under investigation for rare earths
- Requirement: databases of relevant phases (Gibbs free energy of solids, solutions,...)

# Example: EREAN project

- Focus on magnets
  - Electric motors
    - Windmills
    - Cars
  - Hard disk drives
- Balance problem
  - Nd and Dy highly wanted



# The balance problem

	REE	Bastnasite Mountain Pass, USA	Bastnasite Bayan Obo, China	Monazite Mt. Weld, Australia	Xenotime Lehat, Malaysia	High Y RE laterite Longnan, China	Low Y RE laterite Xunwu, China	Loparite Kola Peninsula Russia
Light REE	La	33.8	23.0	25.5	1.2	1.8	43.4	25.0
	Ce	49.6	50.0	46.7	3.1	0.4	2.4	50.5
	Pr	4.1	6.2	5.3	0.5	0.7	9.0	5.0
	Nd	11.2	18.5	18.5	1.6	3.0	31.7	15.0
	Sm	0.9	0.8	2.3	1.1	2.8	3.9	0.7
Heavy REE	Eu	0.1	0.2	0.4	Trace	0.1	0.5	0.1
	Gd	0.2	0.7	<0.1	3.5	6.9	3.0	0.6
	Tb	0.01	0.1	<0.1	0.9	1.3	Trace	Trace
	Dy	0.03	0.1	0.1	8.3	6.7	Trace	0.6
	Ho	0.01	Trace	Trace	2.0	1.6	Trace	0.7
	Er	0.01	Trace	Trace	6.4	4.9	Trace	0.8
	Tm	0.01	Trace	---	1.1	0.7	Trace	0.1
	Yb	0.01	Trace	---	6.8	2.5	0.3	0.2
	Lu	Trace	Trace	---	1.0	0.4	0.1	0.2
	Y	0.1	Trace	<0.1	61.0	65.0	8.0	1.3

# Rare earth alloys

- Application of rare earths in alloys
  - Database for aluminium alloys containing rare earths
  - Database for magnesium alloys containing rare earths

Al Alloys
Ag, <b>Al</b> , <u>As</u> , <u>Au</u> , <b>B</b> , <b>Ba</b> , <b>Be</b> , <b>Bi</b> , <b>C</b> , <b>Ca</b> , <b>Ce</b> , <u>Co</u> , <b>Cr</b> , <b>Cu</b> , <b>Dy</b> , <b>Er</b> , <b>Eu</b> , <b>Fe</b> , <u>Ga</u> , <b>Gd</b> , <b>Ge</b> , <b>H</b> , <u>Hf</u> , <u>Hg</u> , <b>Ho</b> , <b>In</b> , <b>K</b> , <b>La</b> , <b>Li</b> , <b>Lu</b> , <b>Mg</b> , <b>Mn</b> , <u>N</u> , <u>Na</u> , <u>Nb</u> , <b>Nd</b> , <b>Ni</b> , <u>O</u> , <u>P</u> , <b>Pb</b> , <b>Pr</b> , <u>S</u> , <b>Sb</b> , <b>Sc</b> , <b>Si</b> , <b>Sm</b> , <b>Sn</b> , <b>Sr</b> , <u>Ta</u> , <b>Tb</b> , <b>Ti</b> , <b>Tm</b> , <b>V</b> , <u>W</u> , <b>Y</b> , <b>Yb</b> , <b>Zn</b> , <b>Zr</b>
Mg Alloys
Ag, <b>Al</b> , <b>B</b> , <b>Ba</b> , <b>Be</b> , <b>Bi</b> , <b>C</b> , <b>Ca</b> , <b>Ce</b> , <b>Cr</b> , <b>Cu</b> , <b>Dy</b> , <b>Er</b> , <b>Eu</b> , <b>Fe</b> , <b>Gd</b> , <b>Ge</b> , <b>H</b> , <b>Ho</b> , <b>In</b> , <b>K</b> , <b>La</b> , <b>Li</b> , <b>Lu</b> , <b>Mg</b> , <b>Mn</b> , <b>Na</b> , <b>Nd</b> , <b>Ni</b> , <b>Pb</b> , <b>Pr</b> , <b>Sb</b> , <b>Sc</b> , <b>Si</b> , <b>Sm</b> , <b>Sn</b> , <b>Sr</b> , <b>Tb</b> , <b>Ti</b> , <b>Tm</b> , <b>V</b> , <b>Y</b> , <b>Yb</b> , <b>Zn</b> , <b>Zr</b>

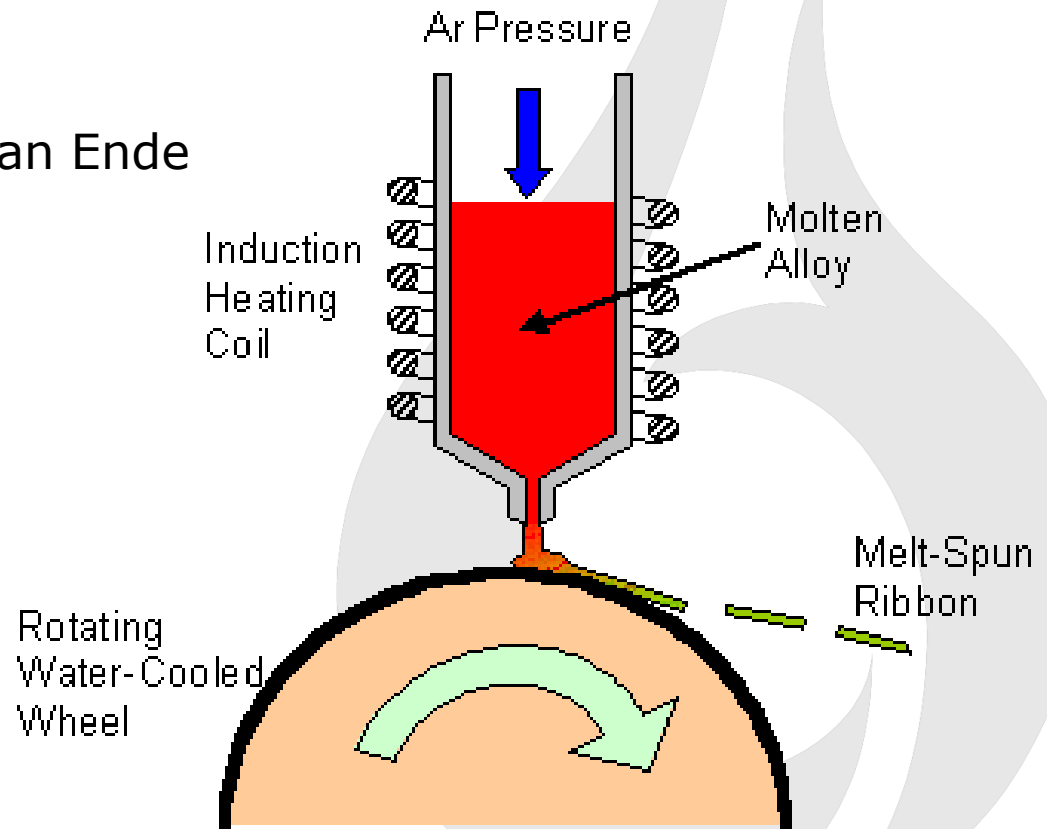
- Limited interactions in iron and zinc based systems
  - E.g. Fe-Dy-Tb
  - E.g. Fe-Nd-B

# Rare earth alloys

- Fe-Nd-B system relevant to magnets

E.g. Assessment by M.A. Van Ende

Solidification trajectory  
Scheil / equilibrium

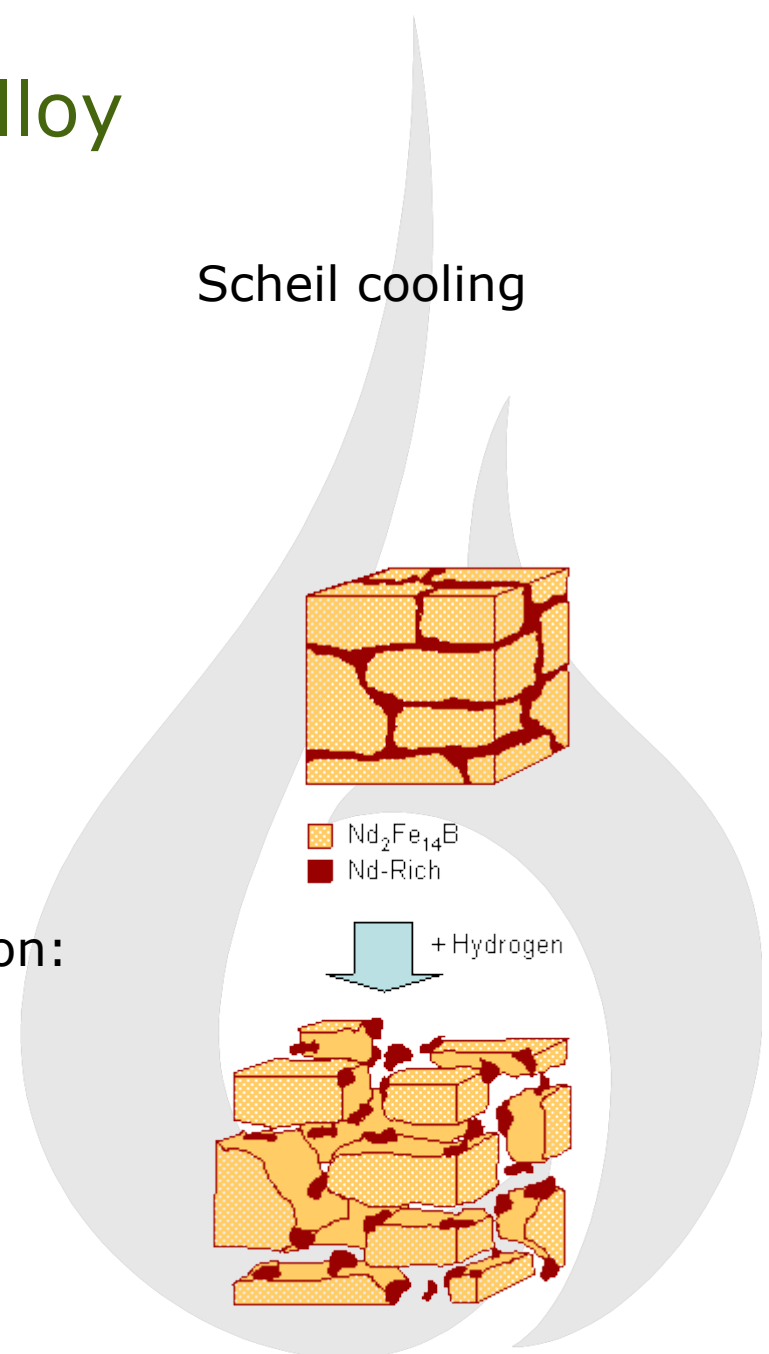


# Solidification of Fe-Nd-B alloy

Equilibrium cooling

Scheil cooling

Substitution, hydrogen deprecipitation:  
Database has no Ce, no H



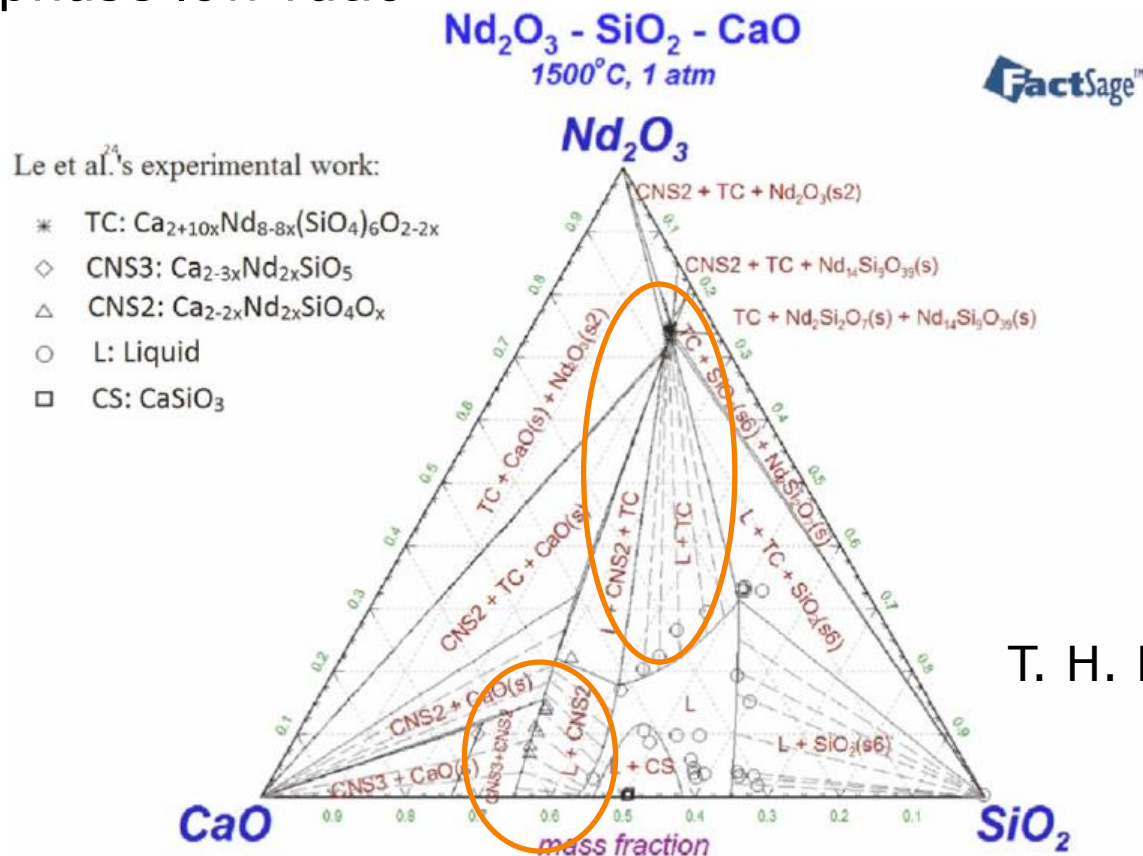


# Rare earths in slag

- Limited databases available
  - $\text{Al}_2\text{O}_3$ -REO
- Behaviour in silicate slags: focus on Nd
  - T.H. Le:
  - Phase Relations of the CaO-SiO<sub>2</sub>-Nd<sub>2</sub>O<sub>3</sub> System and the Implication for Rare Earths Recycling, Met Trans B
  - Thermodynamic assessment of the Nd<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> ternary system, Calphad

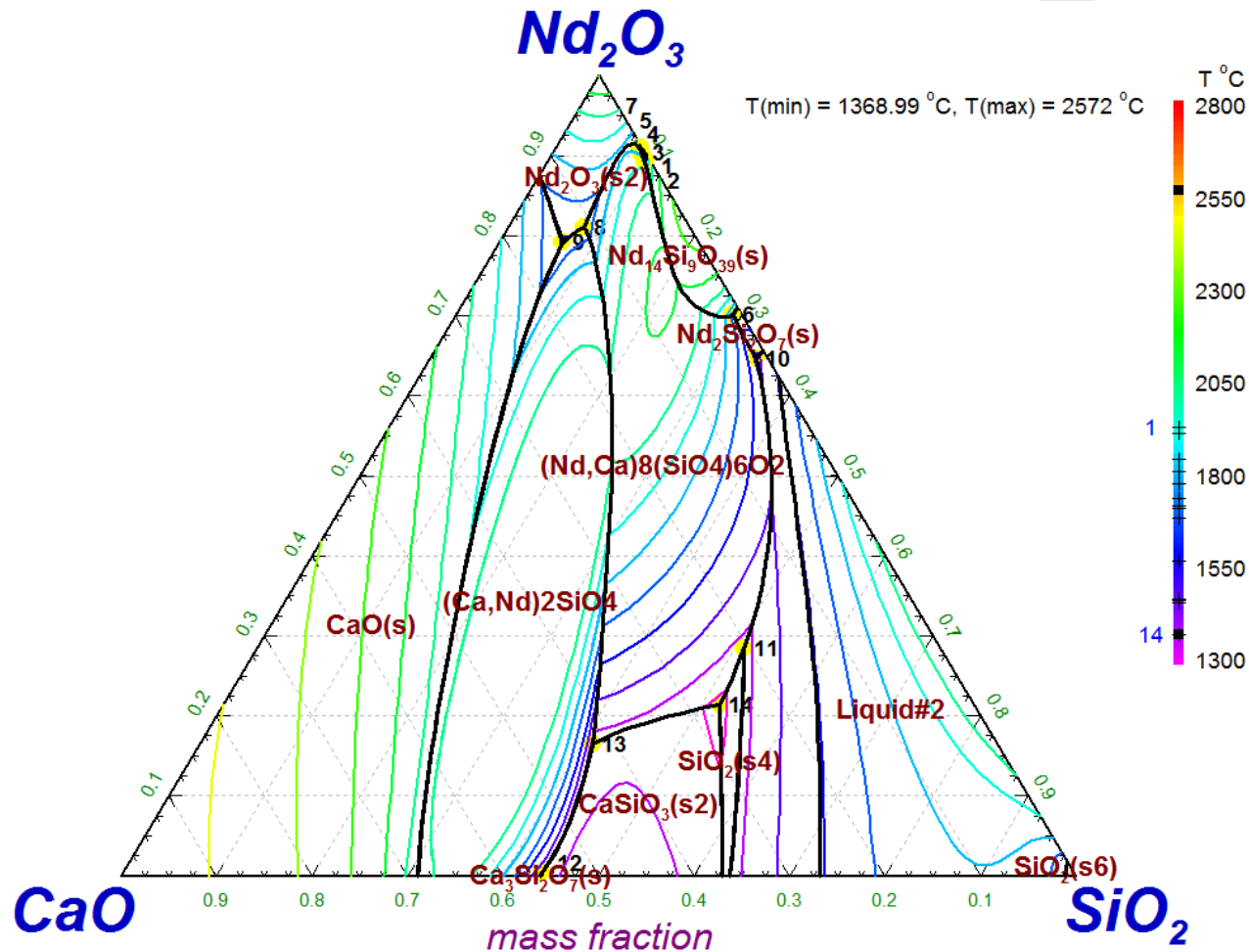
# Slag upgrading using solubility

- Ideal: L+S domain with large ratio of Nd
- Real:
  - High Nd phase, but high solubility
  - C<sub>2</sub>S phase low ratio



# Rare earths in slag

- Behaviour in silicate slags: focus on Nd (T.H. Le)

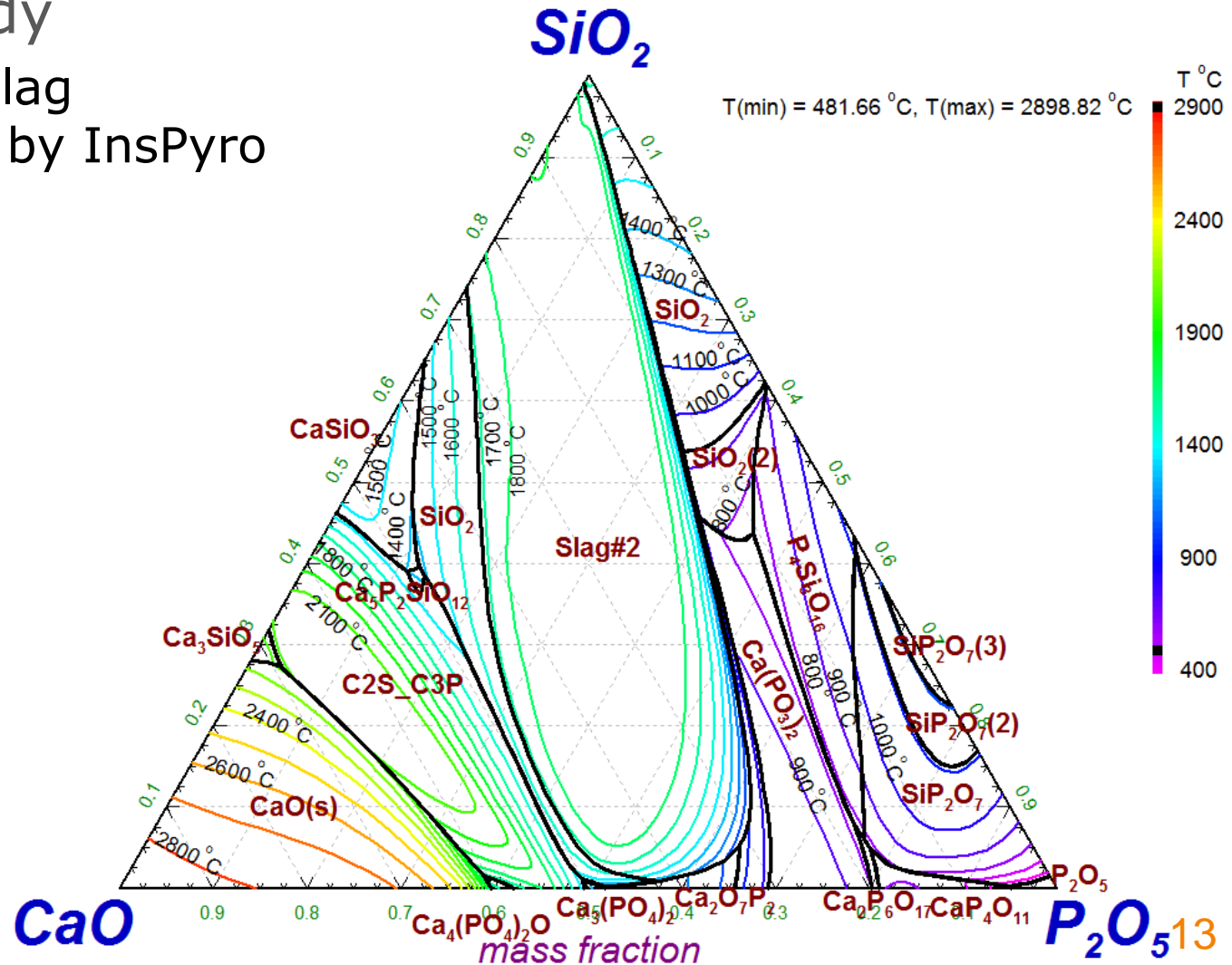


# NTNU work on apatite concentrate

- Apatite concentrate
- REE content not so large, but left in slag after removal of P, and possibly  $\text{CaC}_2$
- Thermodynamic estimation of process
- M.W. Kennedy et al. Pyrometallurgical Treatment of Apatite Concentrate with the Objective of Rare Earth Element Recover, J. Sustainable Metallurgy

# Rare earth concentration in slags

- Apatite smelting process proposed by T. Sun and M.W. Kennedy
  - Phosphate slag calculations by InsPyro



# Other processes

- Roasting + leaching processes (e.g. M.R. Onal):
  - Sulphates: some solids are available
  - Chlorides: some solids are available
  - Nitrates: ?
  - To be checked whether all is consistent
  - Aqueous database (Thereda) focus on actinides (heavy REE)
- High-temperature electrolysis
  - RE oxides and salts in liquid salt systems
  - System Li,Mg,Ca,La,Ce,Nd//F: mainly binary systems
  - System Li,Mg,Ca,La,Ce,Nd//Cl: mainly binary systems
  - $\text{ReCl}_3\text{-ReF}_3$  (Re = La,Ce,Nd): approximately optimized

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