Harnessing High Temperature Materials for Extraction and Processing

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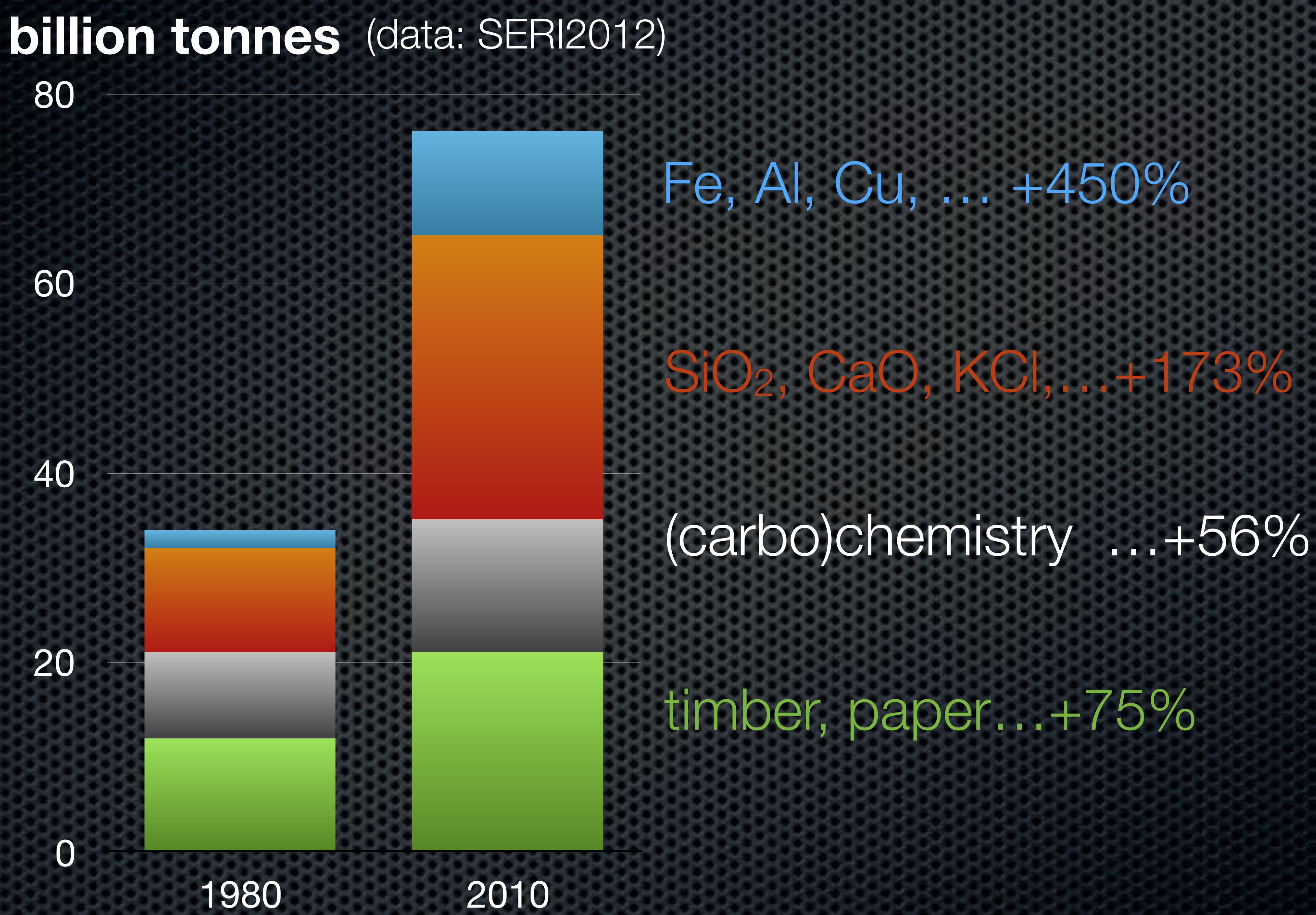
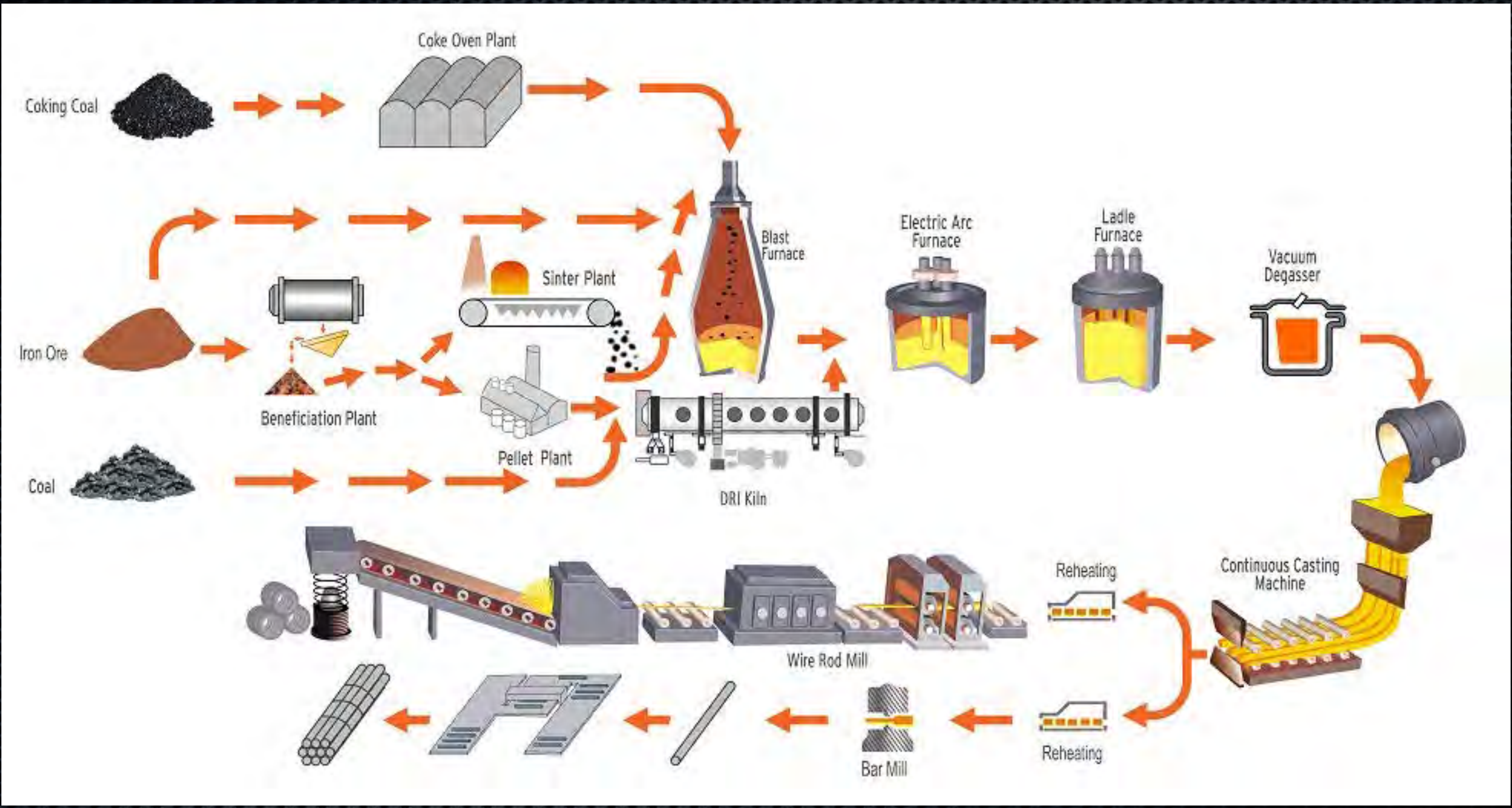
MIT ILP R&D Conference, November 15th, 2017
Cambridge, MA

Materials for 9 billion people?



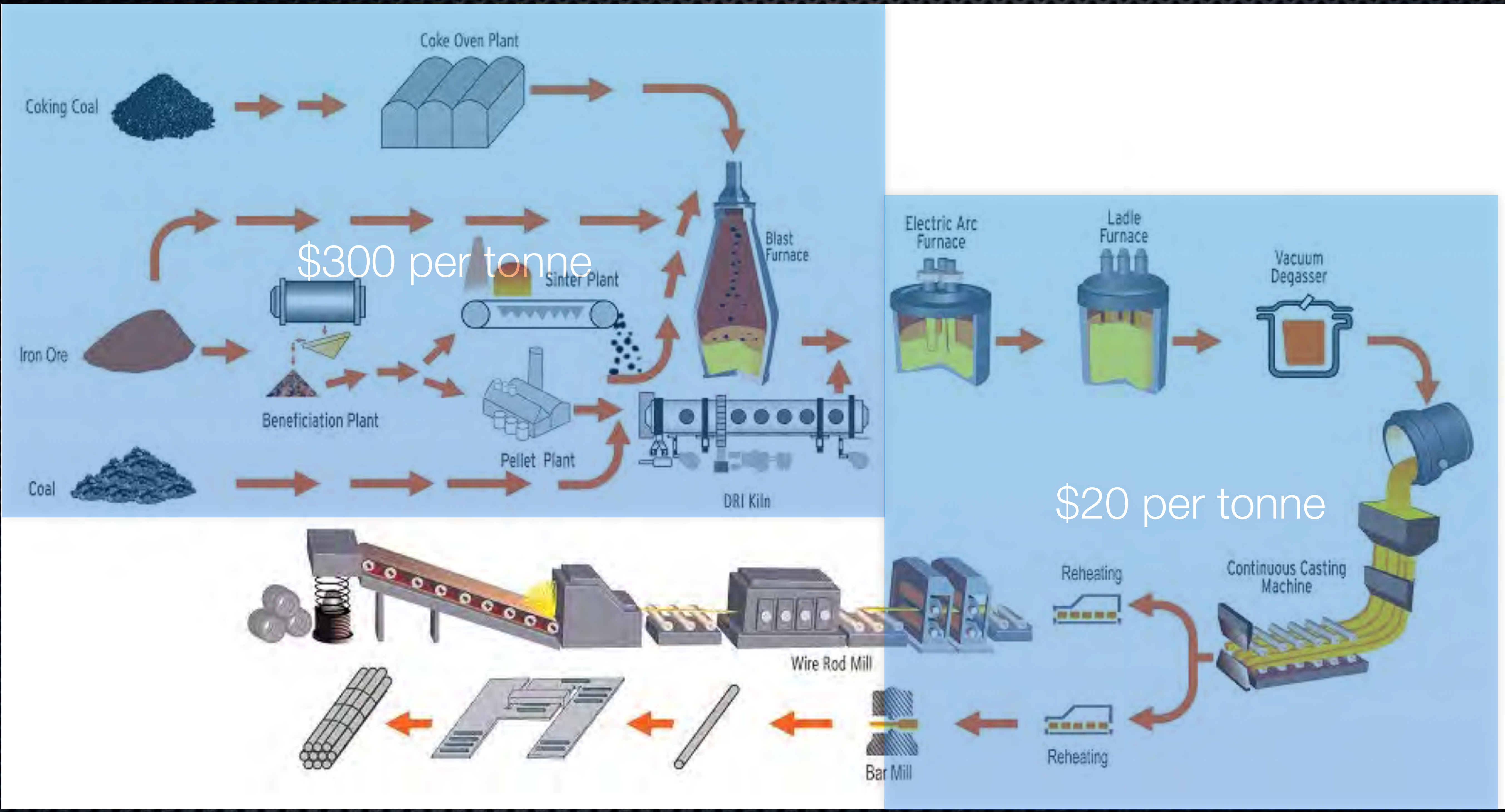
fastest growth is in minerals and metals

Metals processing: steel



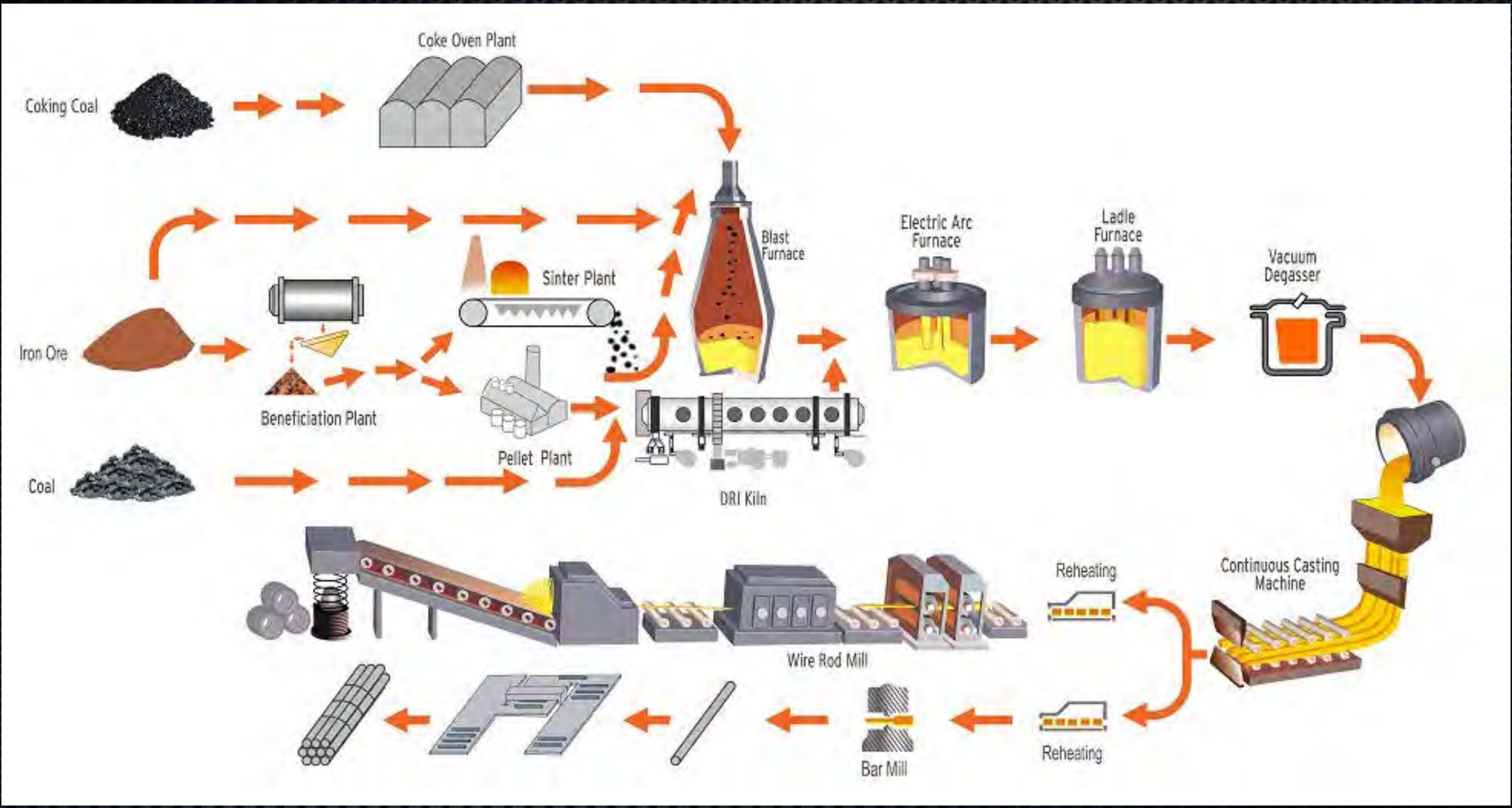
typical plant capacity: 114 tonnes each 1/2 hour

Metals processing: steel



cost < $0.32 per kg (less than retail price of flour)

Metals processing: steel



the liquid state and high temperature are ubiquitous

Metals extraction involves melts

Copper - 20 Mt per year
3600 kWh / t
from concentrate to
copper cathodes
conversion costs: $320/t

Aluminium - 60 Mt per year
electrolysis
conversion costs: $1000/t

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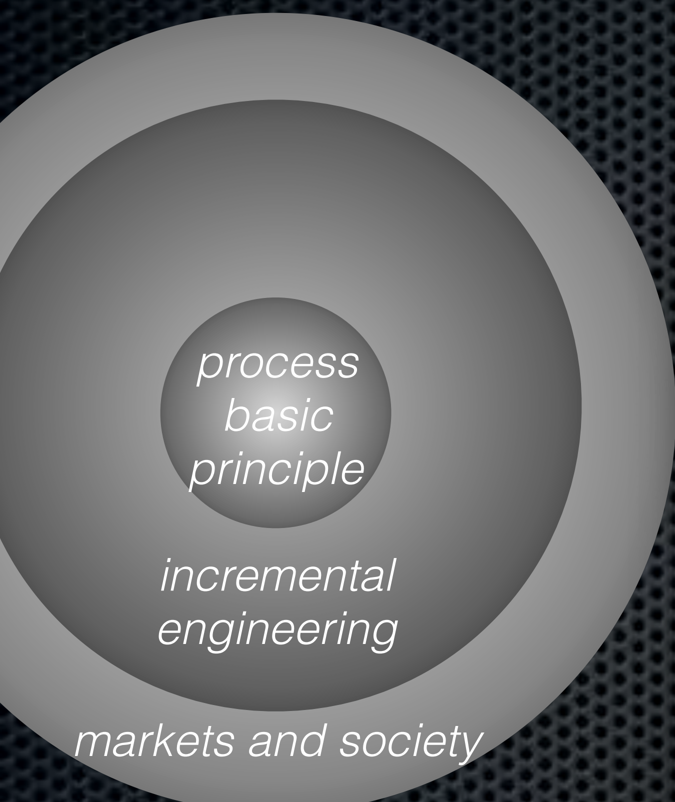
Sustainable Materials Processing

Existing processes



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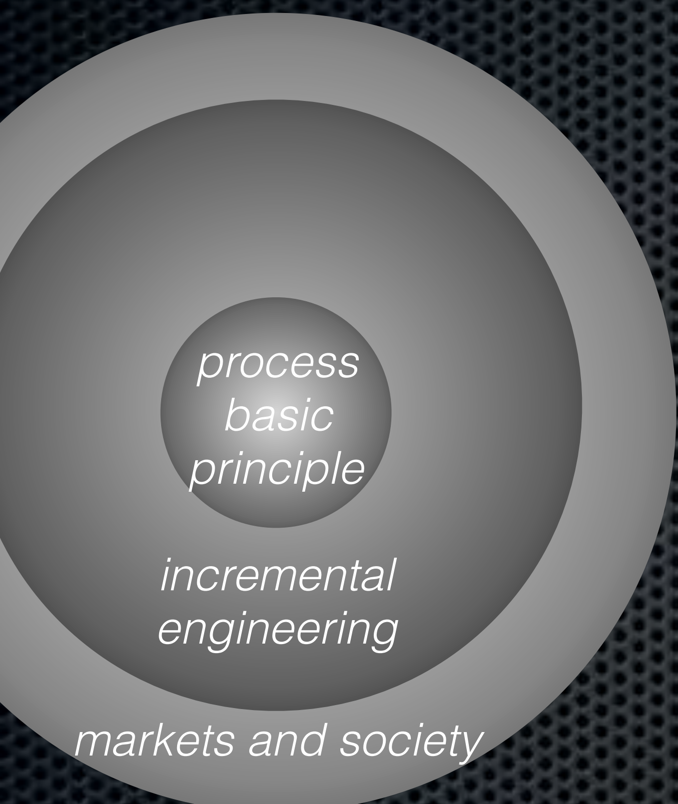
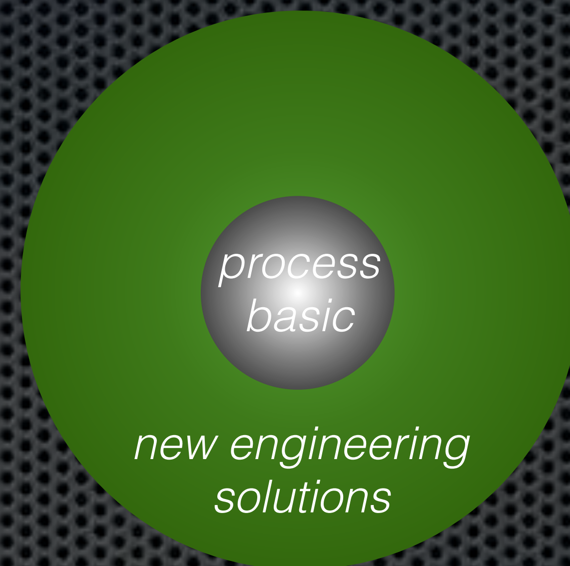
Sustainable Materials Processing

Existing processes

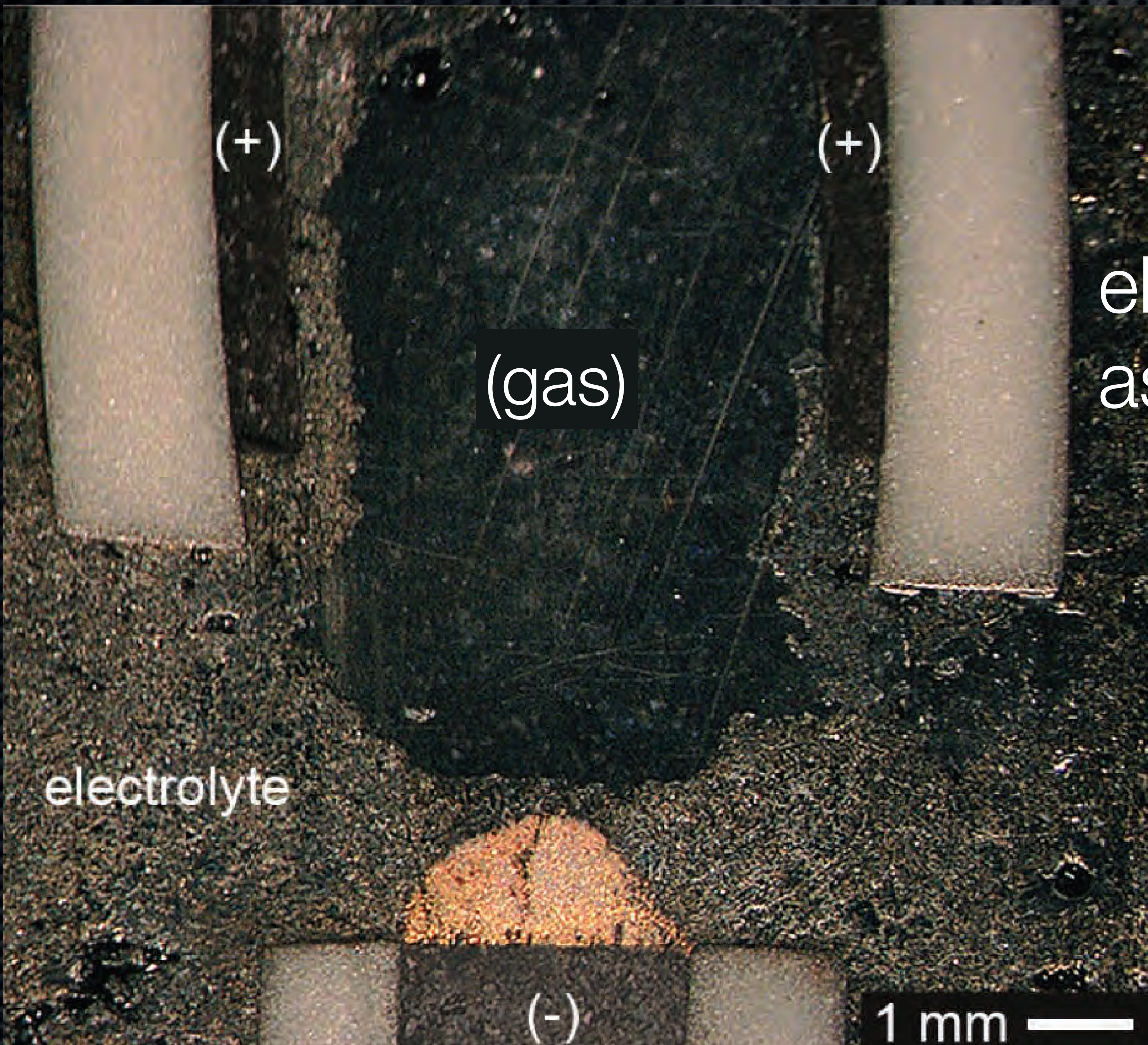




higher productivity

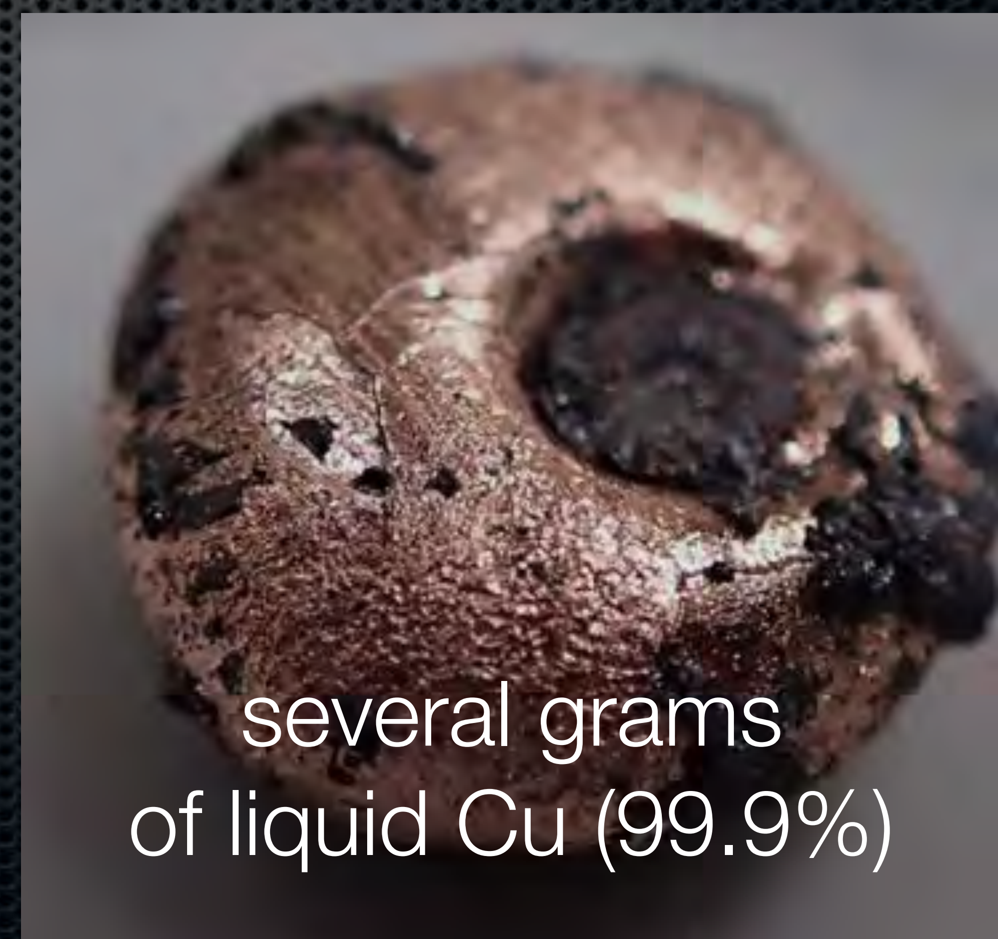
higher selectivity

Sulfides electrolysis



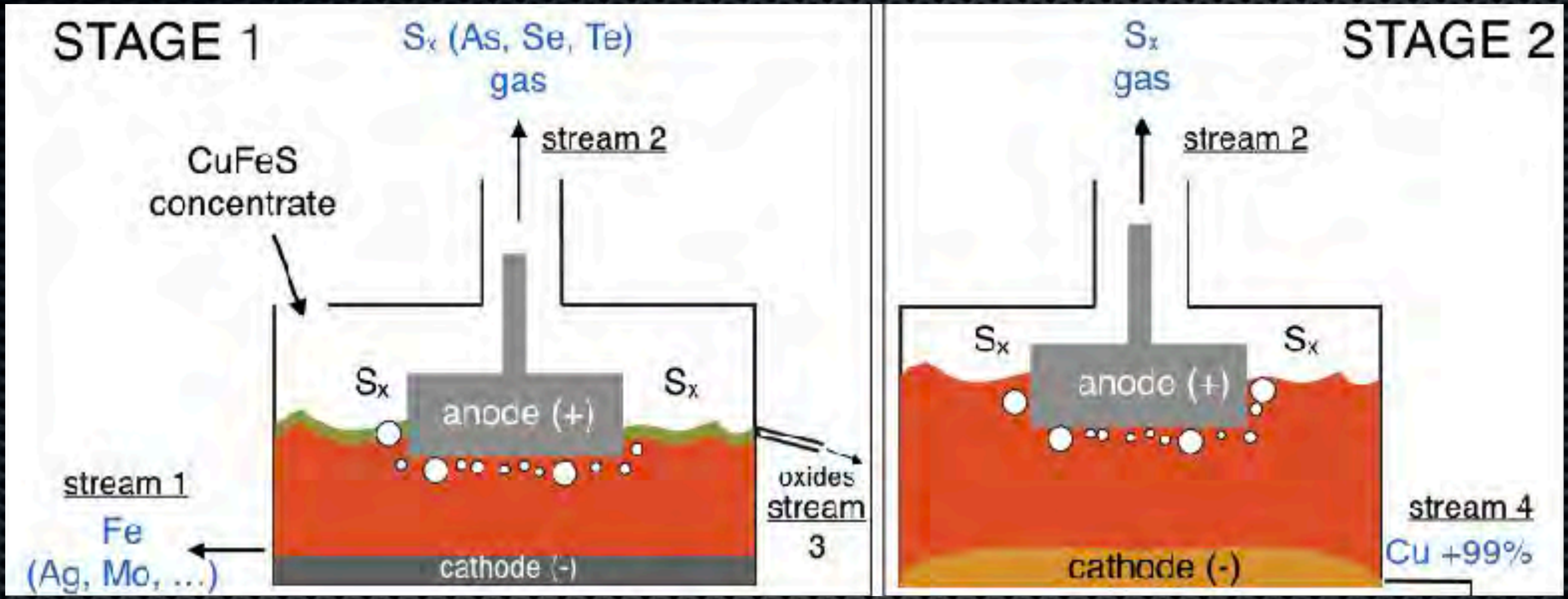
electrolytic decomposition of metal sulfides

elemental sulfur as anodic product



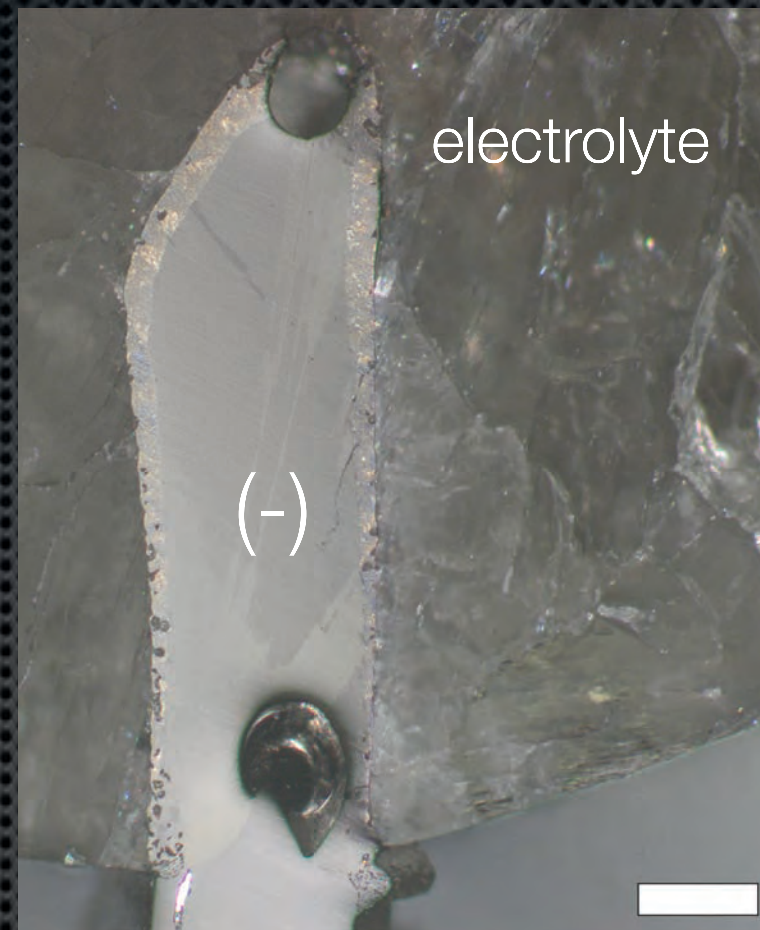
several grams of liquid Cu (99.9%)

Sulfides electrolysis



- productivity 6x the one of aluminium electrolysis
- electrical energy consumption around 3000kWh/t (-20%)
- sulfur as by-product with selective recovery of As, Se, Te
- principles transferable to Mo, Ag, Au, Zn, Co, Ni …

Molten rare-earth oxides electrolysis



- high selectivity for La vs Y (99 vs 1)
- compatible with rare-earth oxide concentrates
- enables to produce refractory alloys (e.g. Ir-La)
- production of oxygen as by-product

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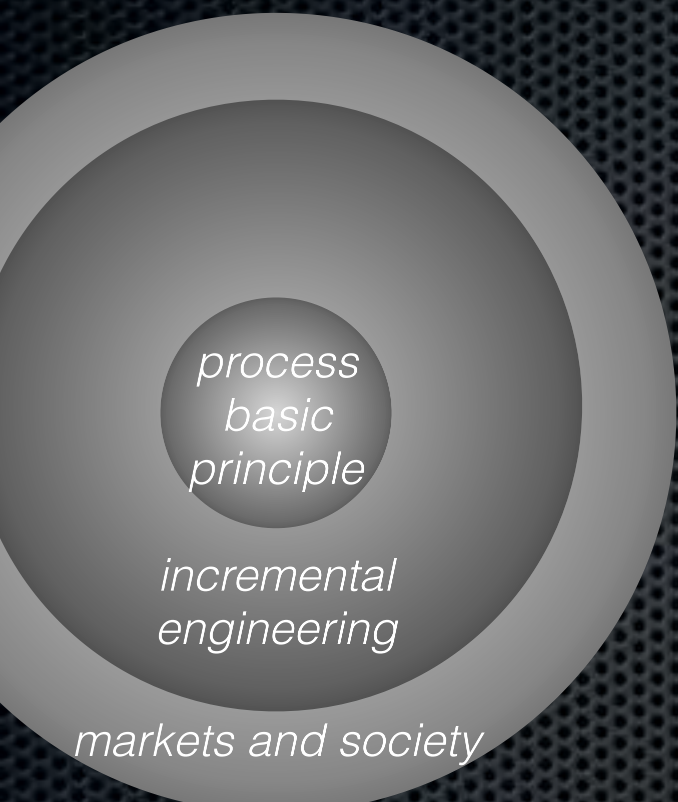
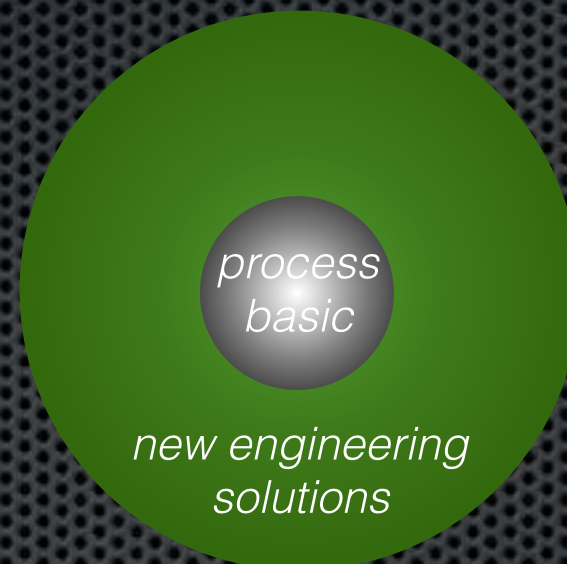
Sustainable Materials Processing

Existing processes





higher productivity

higher selectivity

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Multi-physics of aluminium casting for more recycling

Direct-chill casting of aluminium slabs

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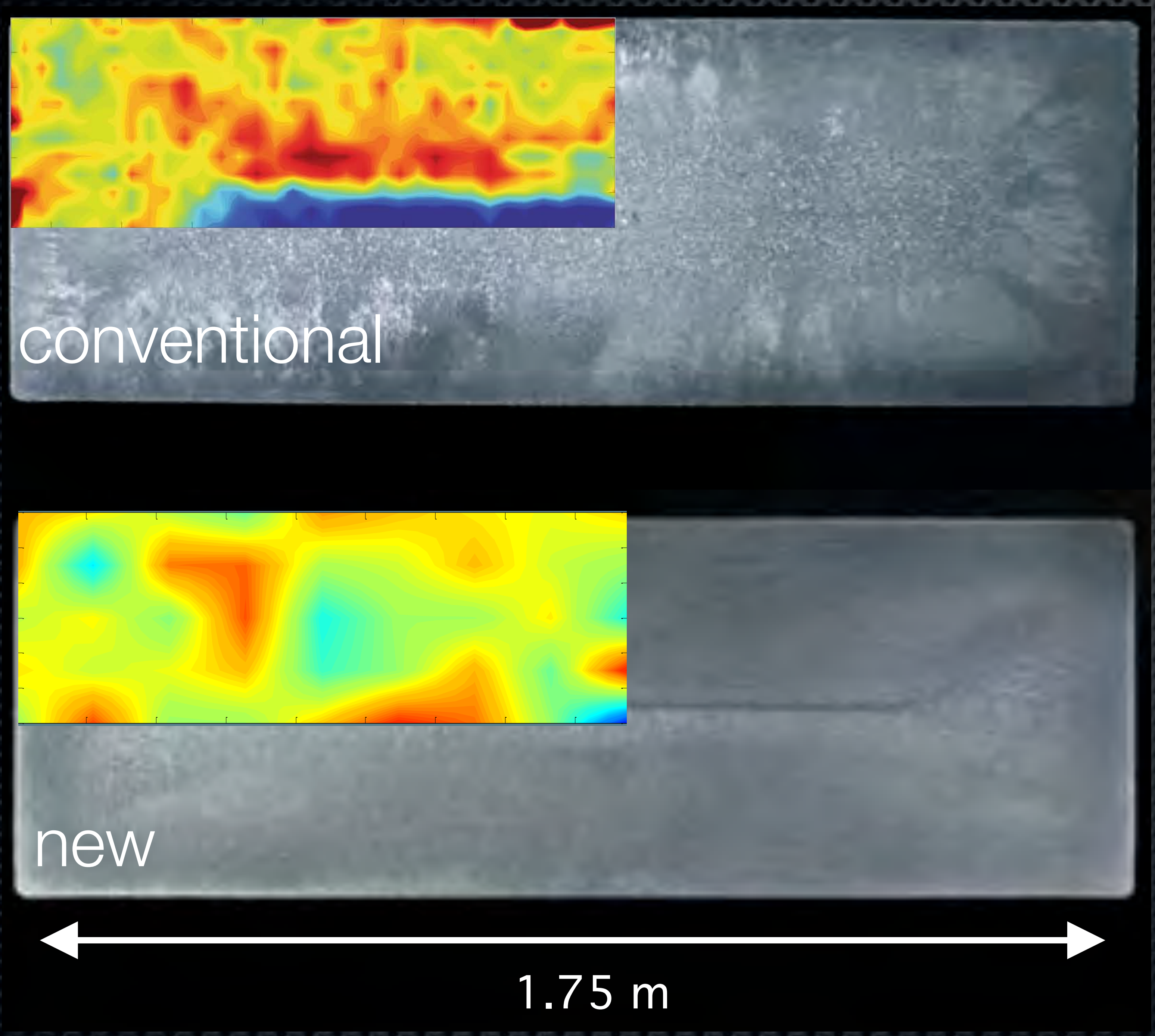
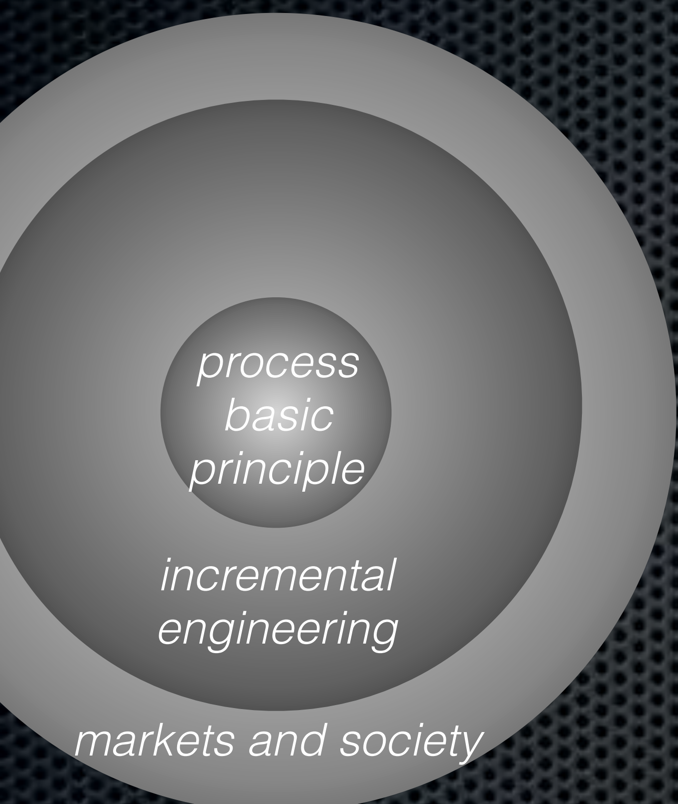
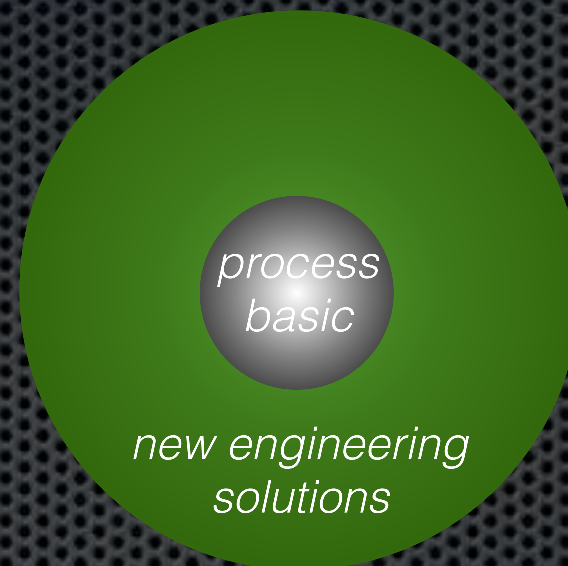


- demonstration of the role of 2-phase flow in DC casting
- novel, cost-effective method to improve alloy elements distribution
- 100 tonnes of Al products, rolled into +10 miles of sheet
- 20% increase in productivity at the plant

Sustainable Materials Processing

Existing processes

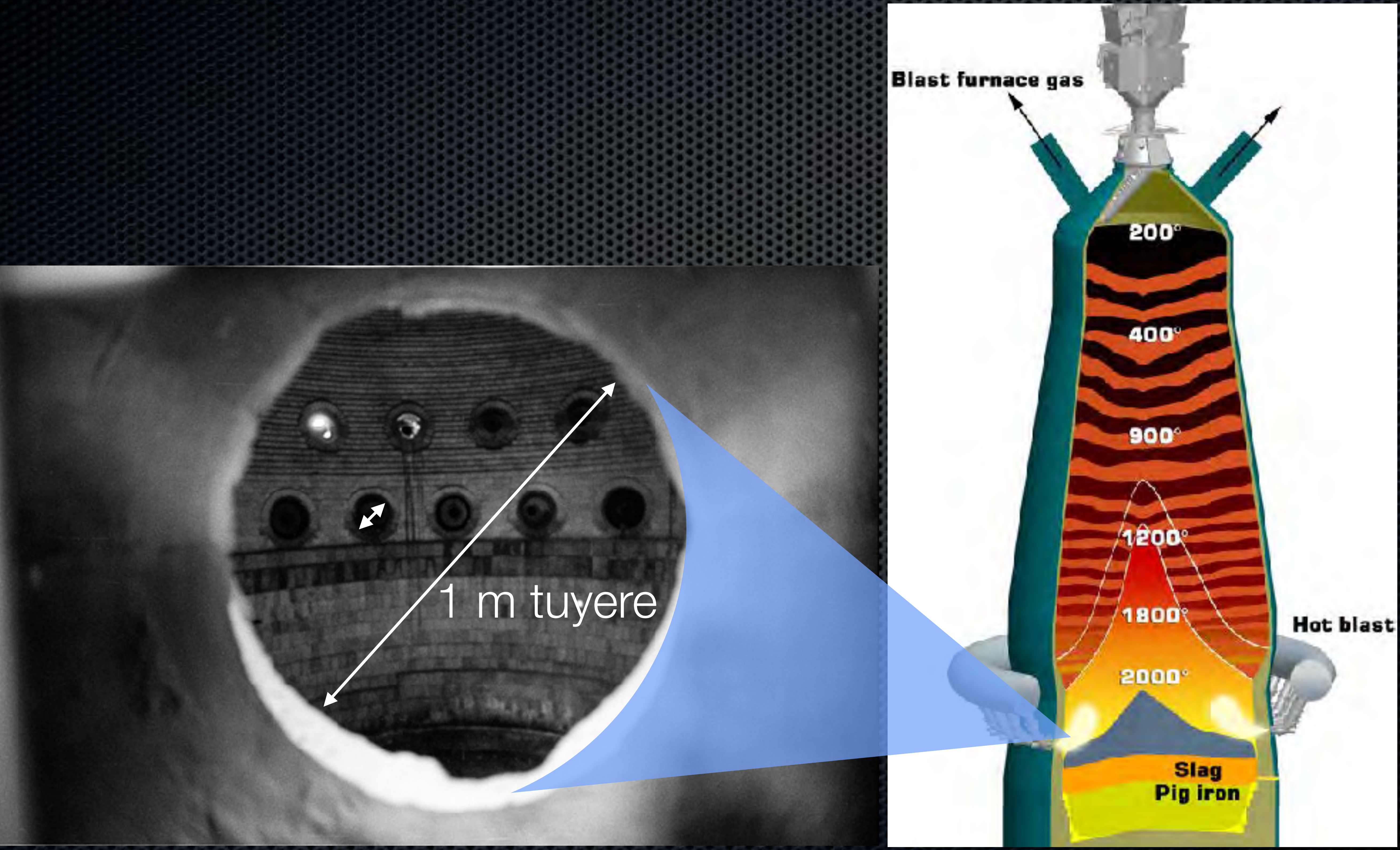




higher productivity

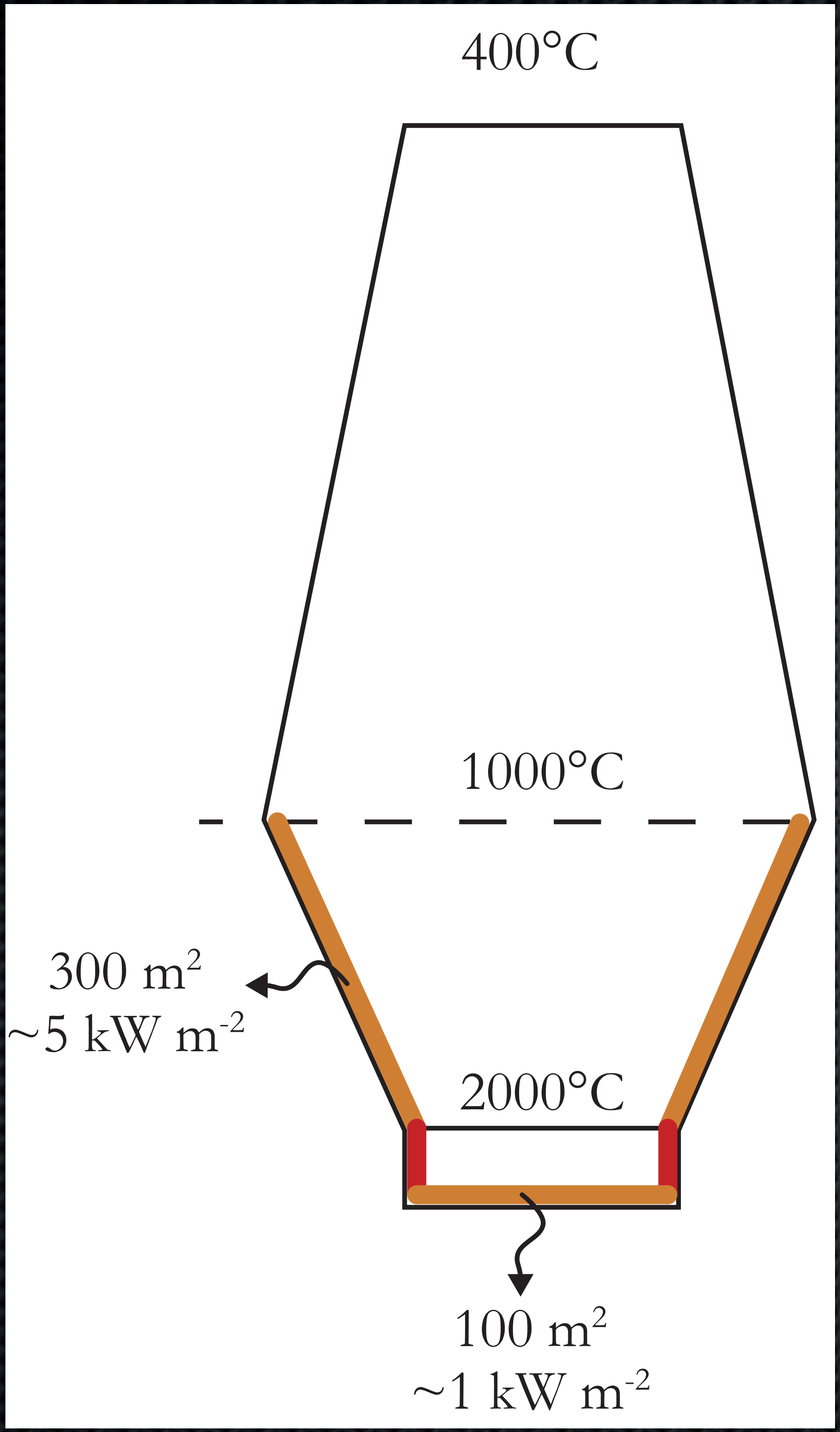
how about energy efficiency improvement?

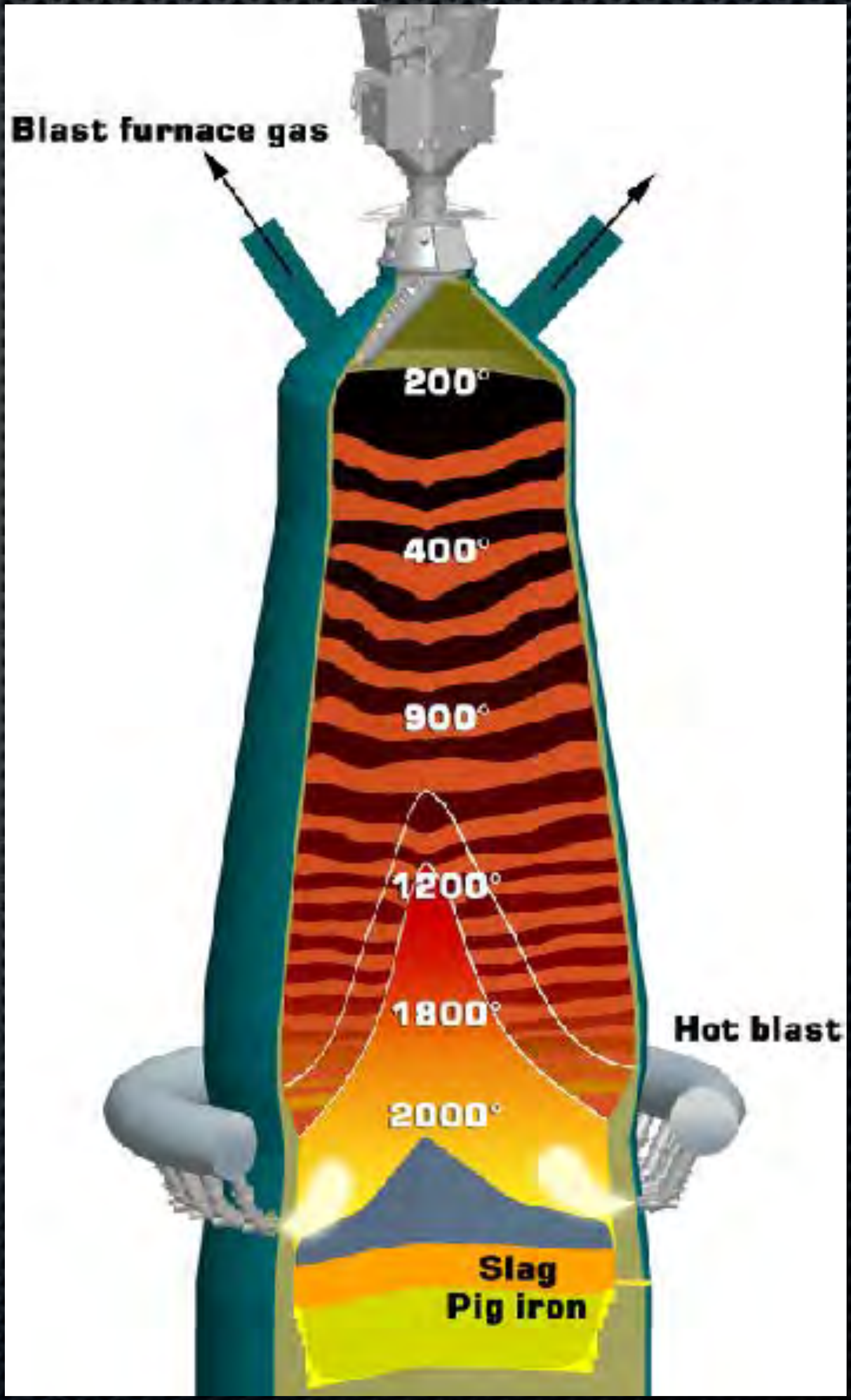
Heat management : steel



Blast furnace, H=30m, ⌀= 15m

Heat management : steel





Blast furnace, H=30m, ⌀= 15m

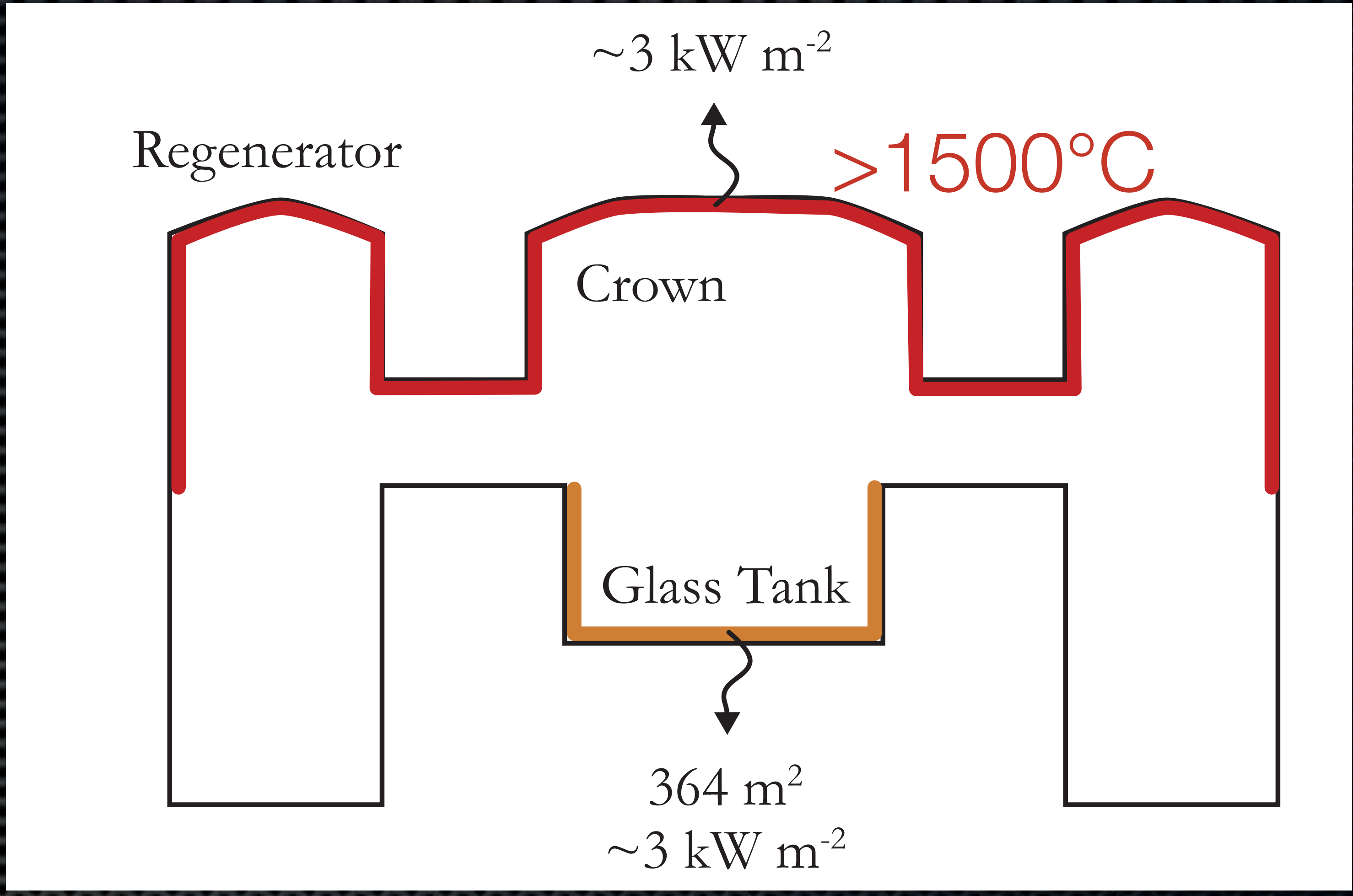
Heat management : glass

Glass melting, 12m x 20m

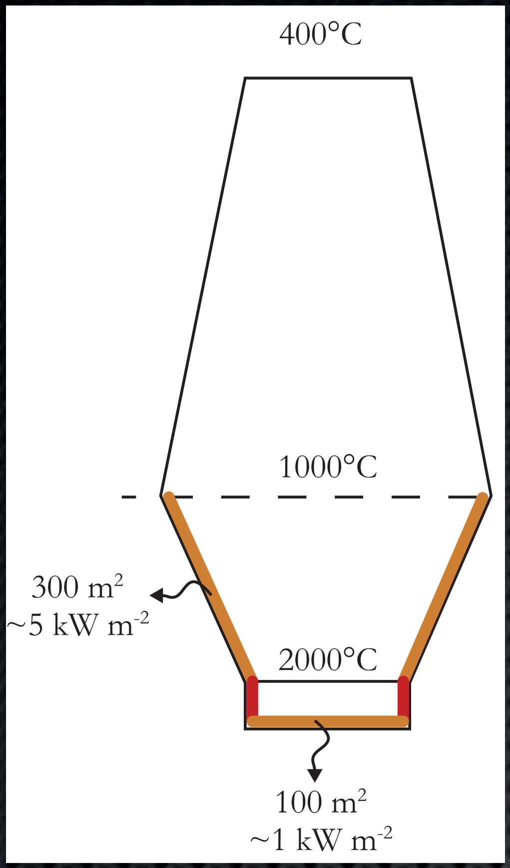
image: Sonilas Benelux

Heat management : glass

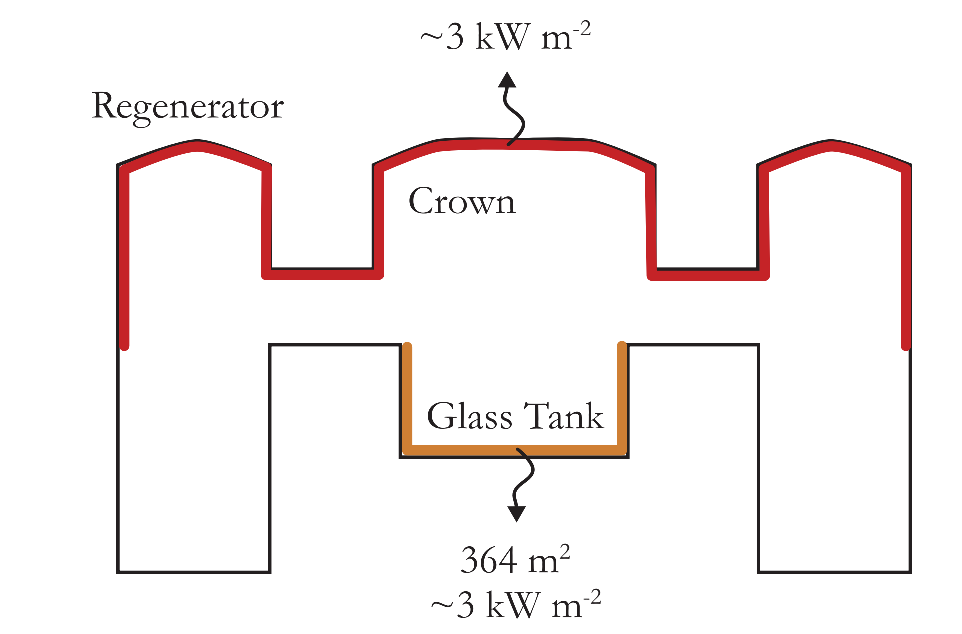

image: Sonilas Benelux



Heat management : high T !



- Temperature in excess of 1000°C
- Heat flux less than few kW/m^2
- Surfaces greater than 20,000 sq ft



Is it possible to harvest or manage such heat?

thermoelectric at temperature greater than 1000°C for low heat fluxes?

Zhao, Rinzler and Allanore, *ECS Journal of Solid State Science and Technology*, 6 (3) N3010-N3016 (2017)

Thermoelectricity for low heat fluxes

ΔT	thermal conductivity W/m/K	thickness material	heat flux
400	2	1 cm	80 kW/m^2
400	2	16 cm	5 kW/m^2

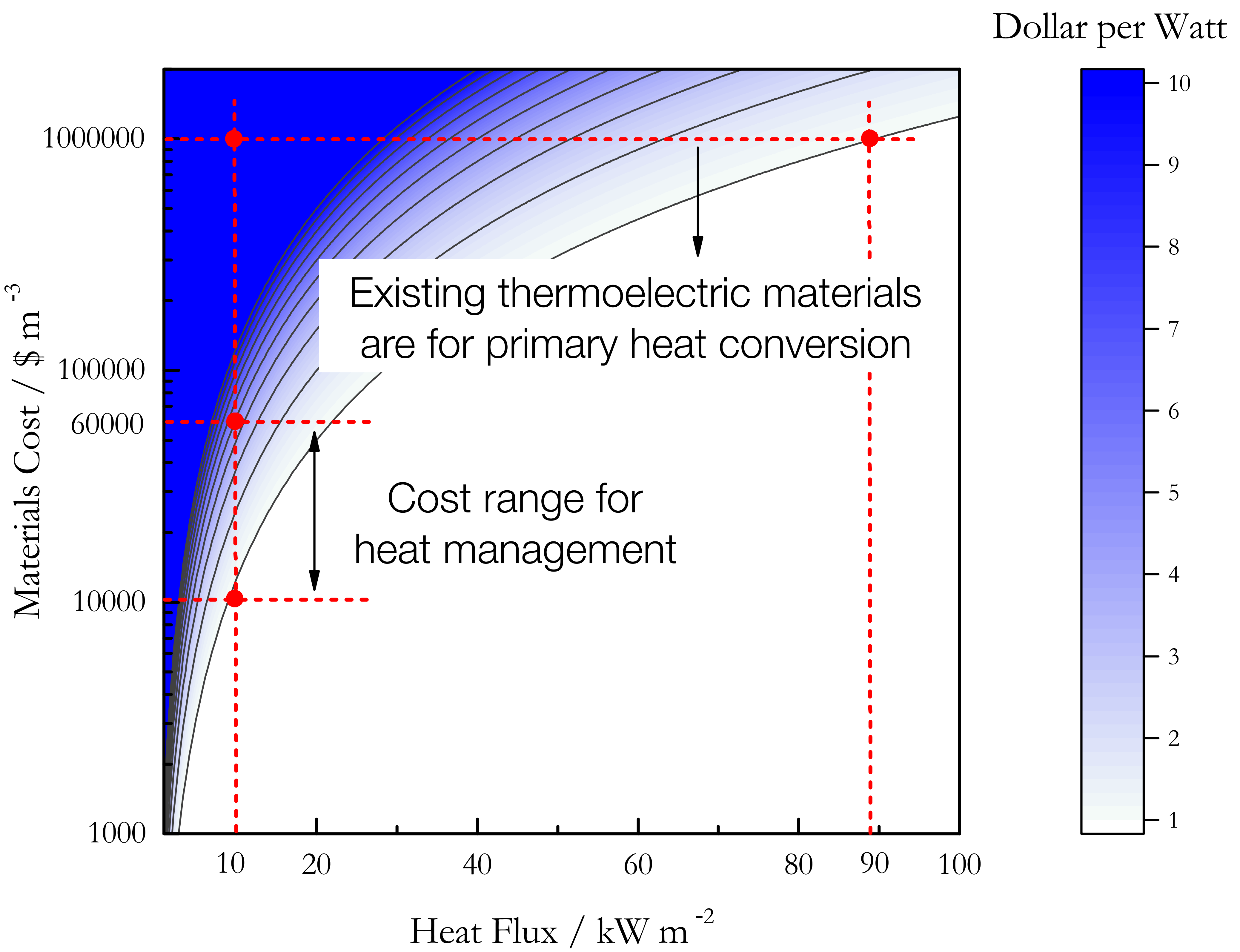
e.g. crystalline Bi_2Te_3
225°C
few cm thick?

Industrial reality: temperature in excess of 1000°C, few kW/m^2

call for different metrics and materials

Zhao, Rinzler and Allanore, *ECS Journal of Solid State Science and Technology*, 6 (3) N3010-N3016 (2017)

Thermoelectricity for low heat fluxes



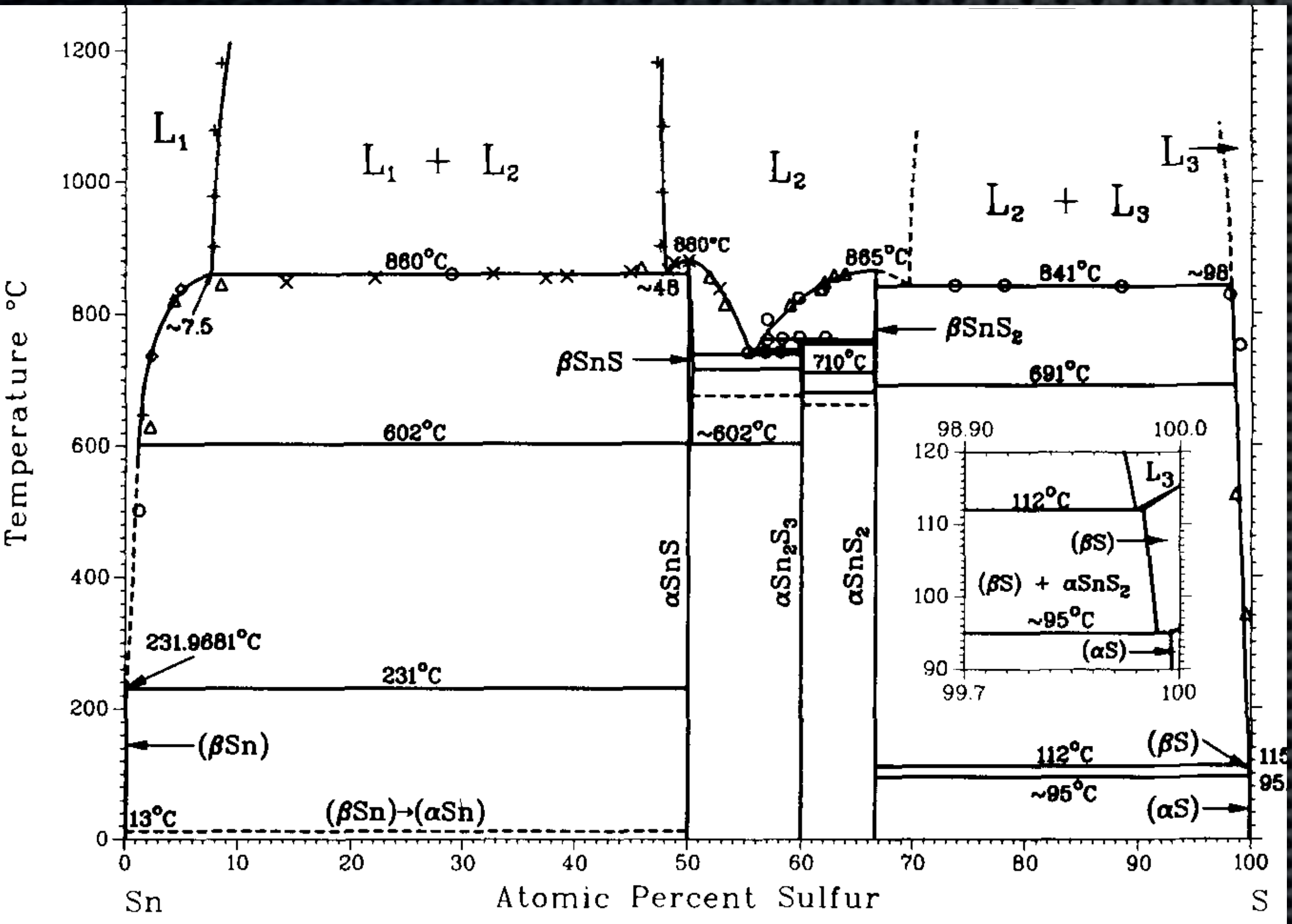
Molten semiconductor?

	Figure of Merit	Thermal conductivity	Melting point	Cost $\$/m^3$
Ni_3S_2	na	na	800°C	54,000
SnS	na	na	882°C	65,000
PbS	na	na	1120°C	13,500
Cu_2S	1 @1130°C	0.8 to 1.4	1130°C	27,400
FeS	na	na	1200°C	<5,000
FeO	na	na	1400°C	<3,000

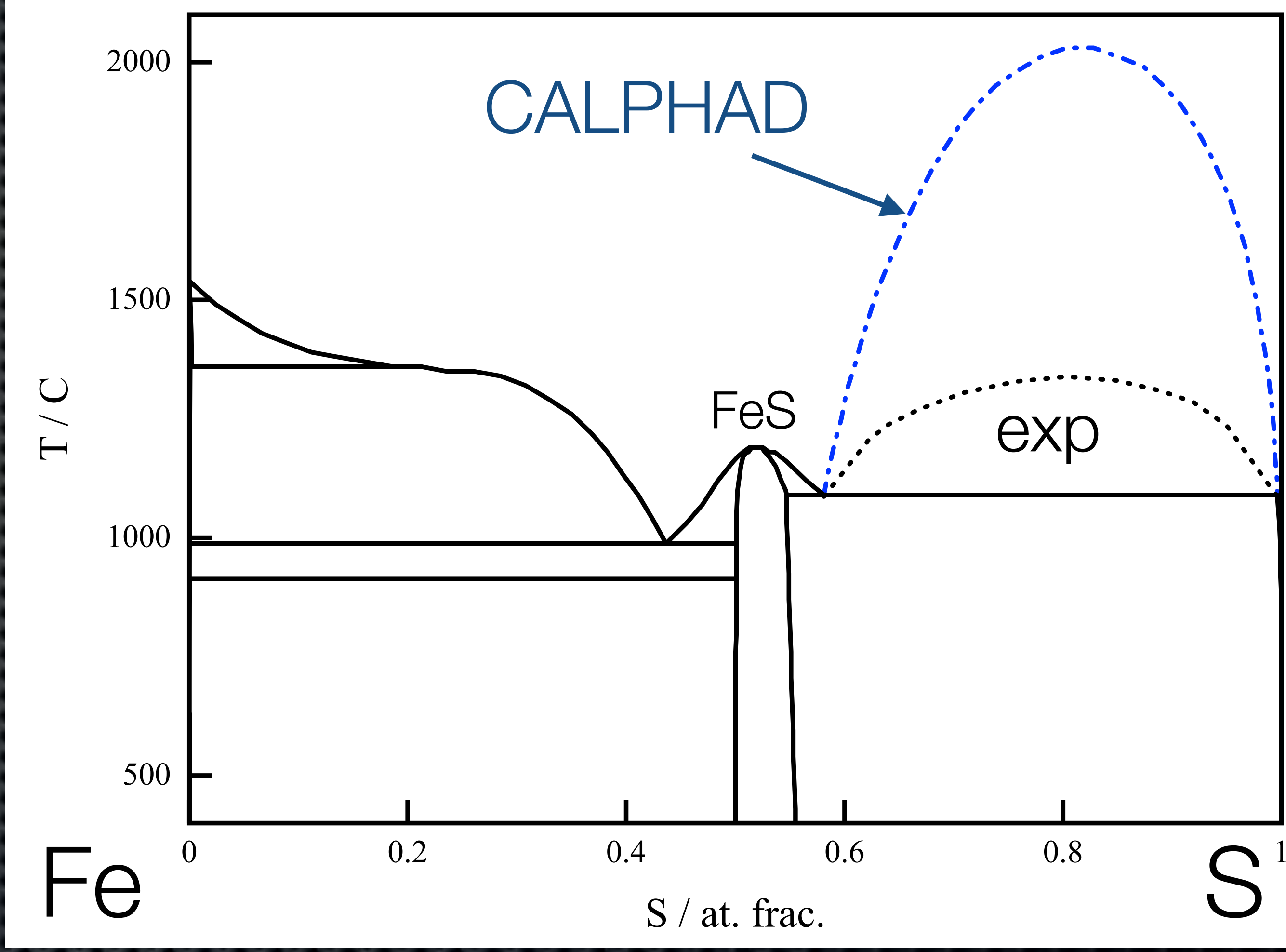
How do we know the range of temperature for semiconductivity?
Can we demonstrate power generation at T>1000°C?
What are the actual material performance limitations?

Materials science for high T?

- Handbook of phase diagrams…



Sharma and Chang, Bulletin of Alloy Phase Diagram, 1986



Materials science for high T?

- Need for transport properties: Handbook again?
  - density
  - viscosity
  - electronic properties (conductivity, Seebeck, mobility)
  - thermal conductivity:
    - electronic thermal conduction?
    - radiation? … optical properties

most useful database are trade secrets…
and unique for each field (!)

Acknowledgements

MITei
MIT Energy Initiative

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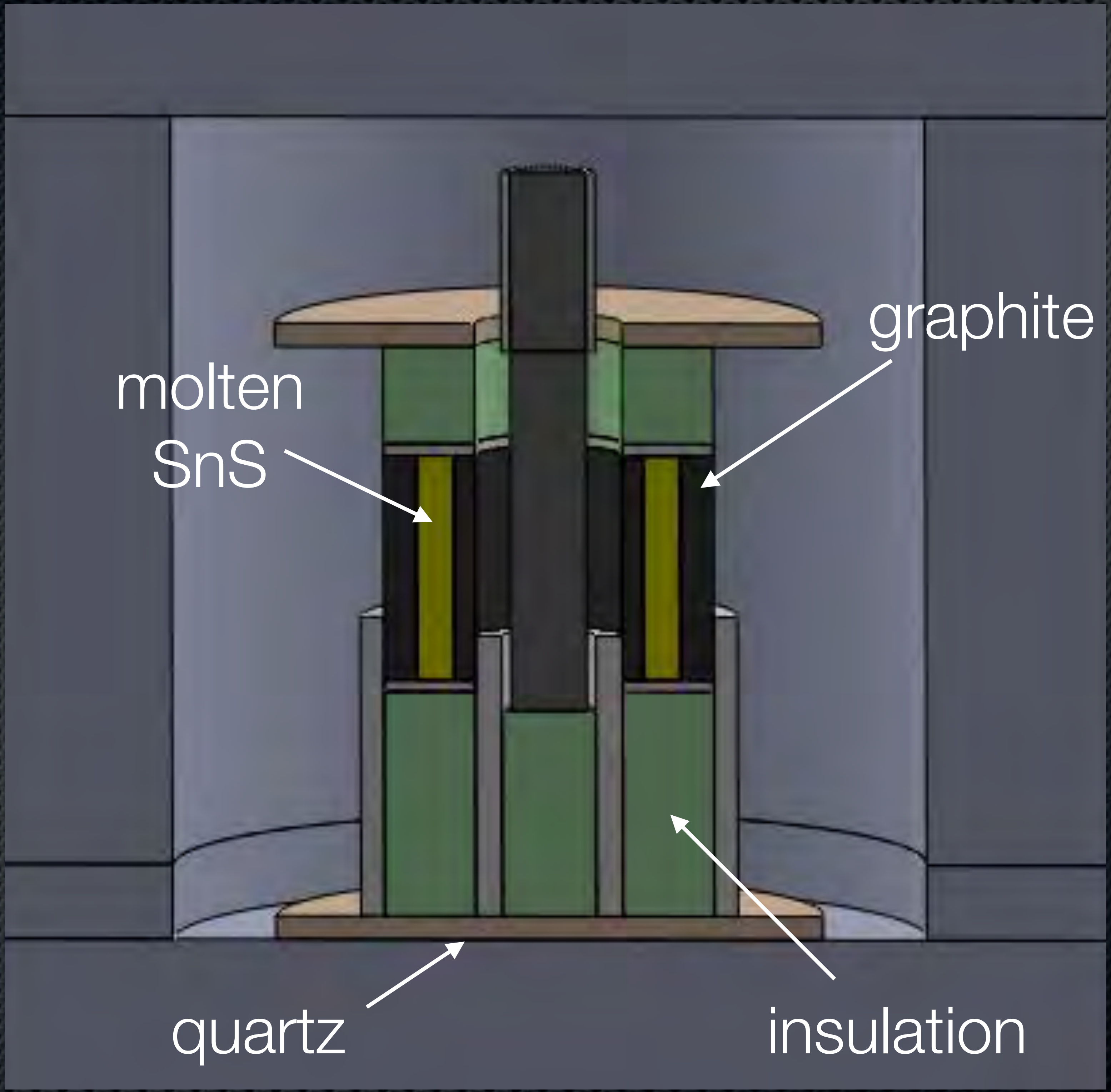
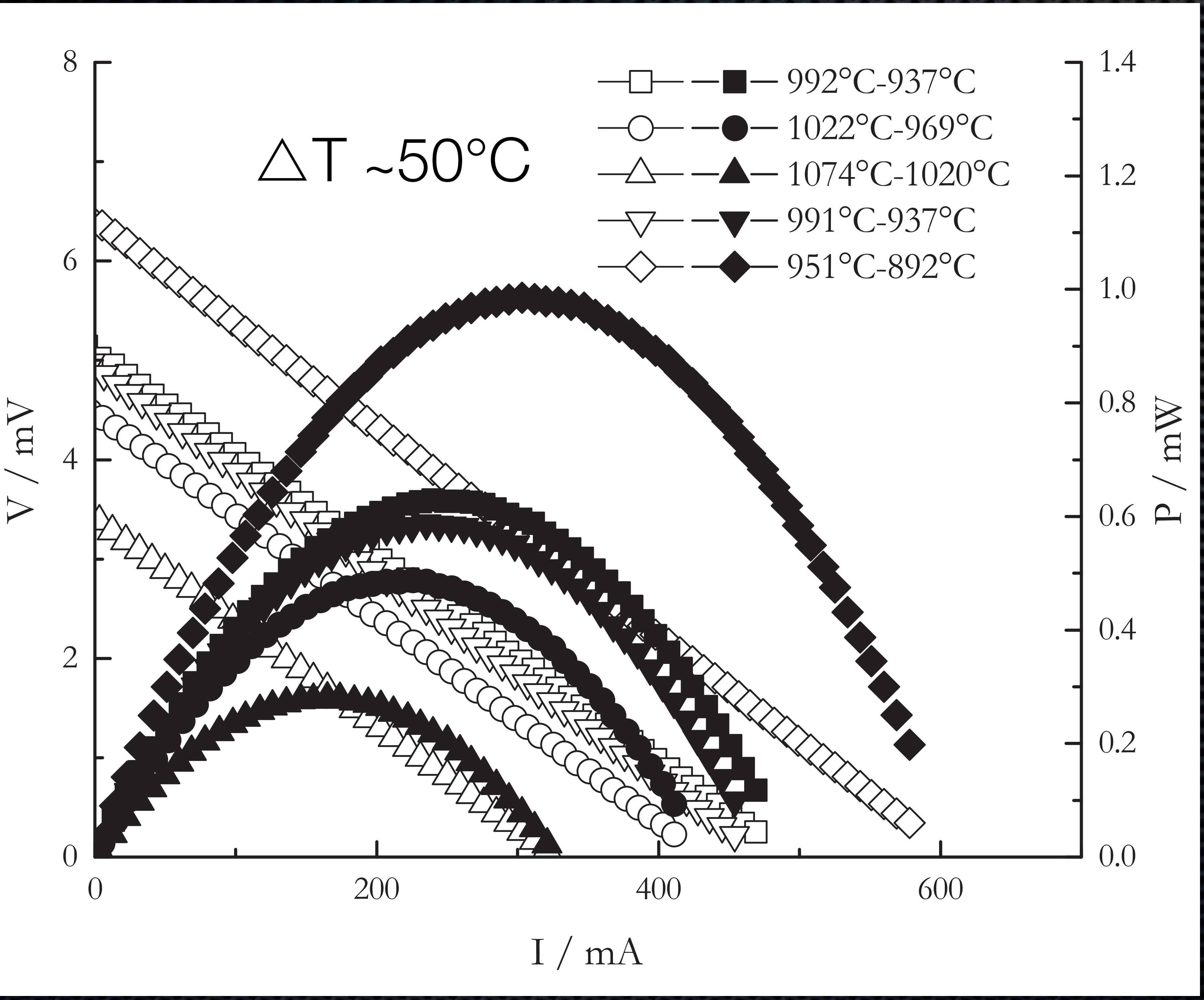
UNITED STATES AIR FORCE

Device tested with SnS



Device tested with SnS

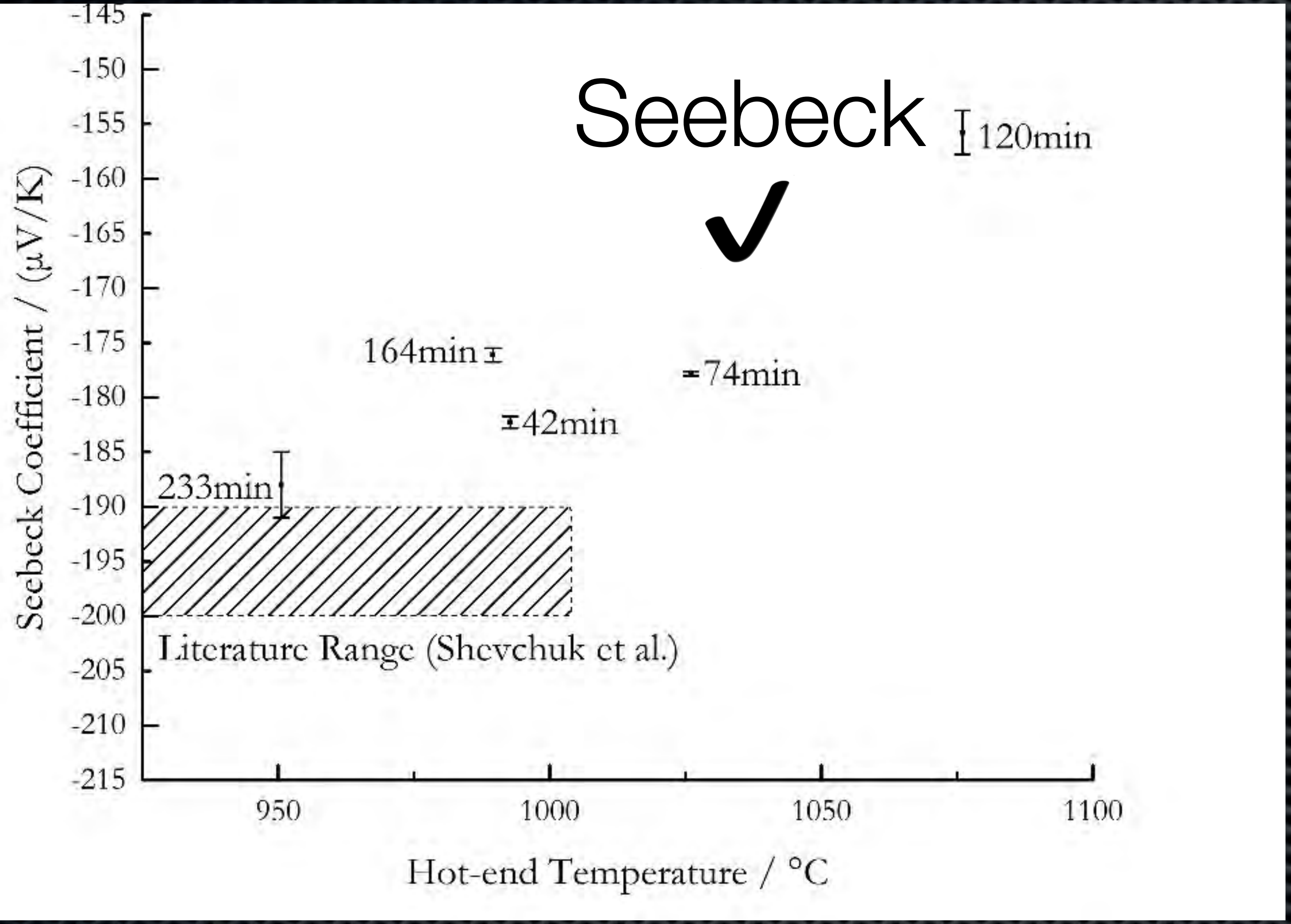


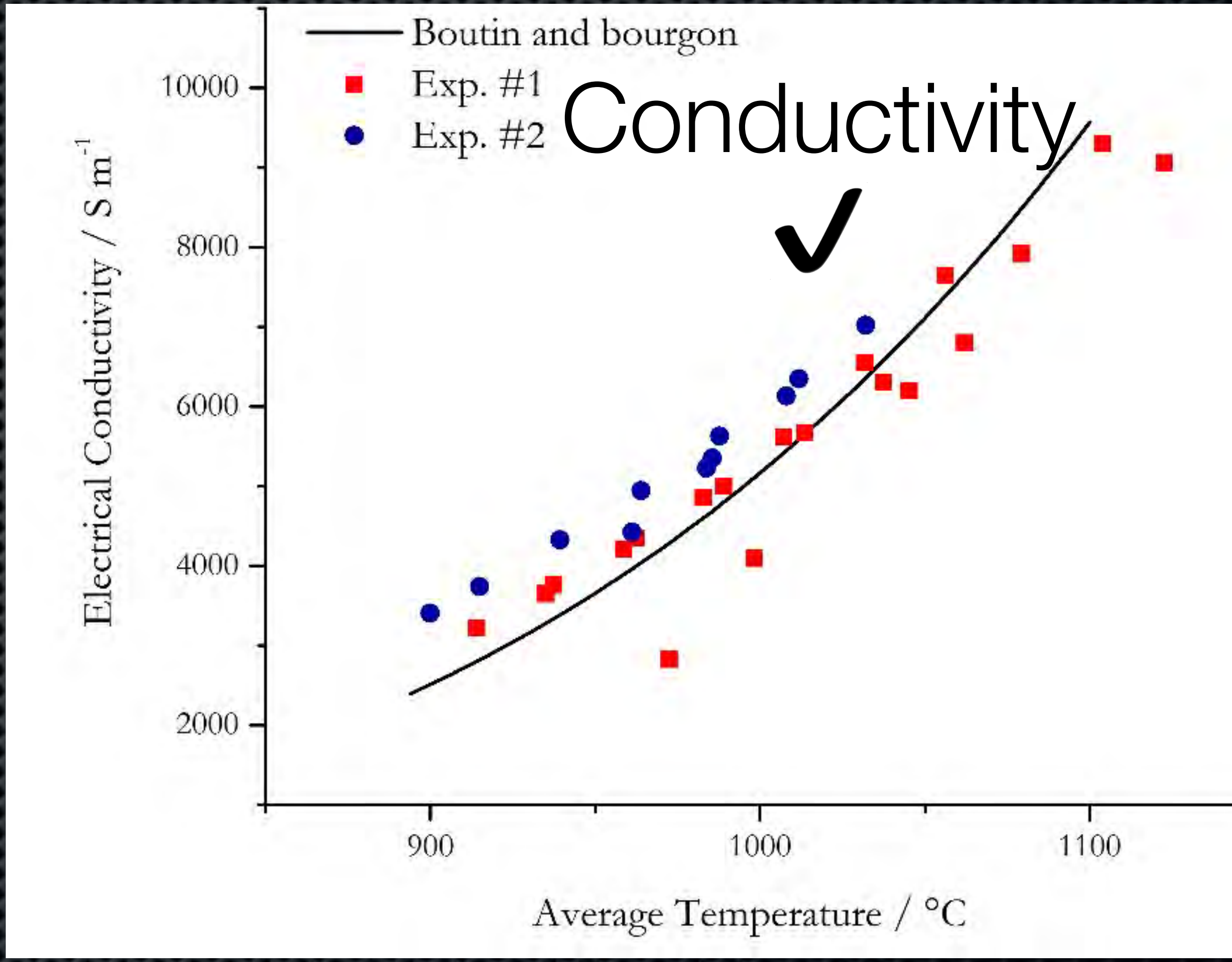
- successful power generation at T>1000°C
- very stable power
- >4h operation
- reusable

Zhao, Rinzler and Allanore, *ECS Journal of Solid State Science and Technology*, 6 (3) N3010-N3016 (2017)

Device and material

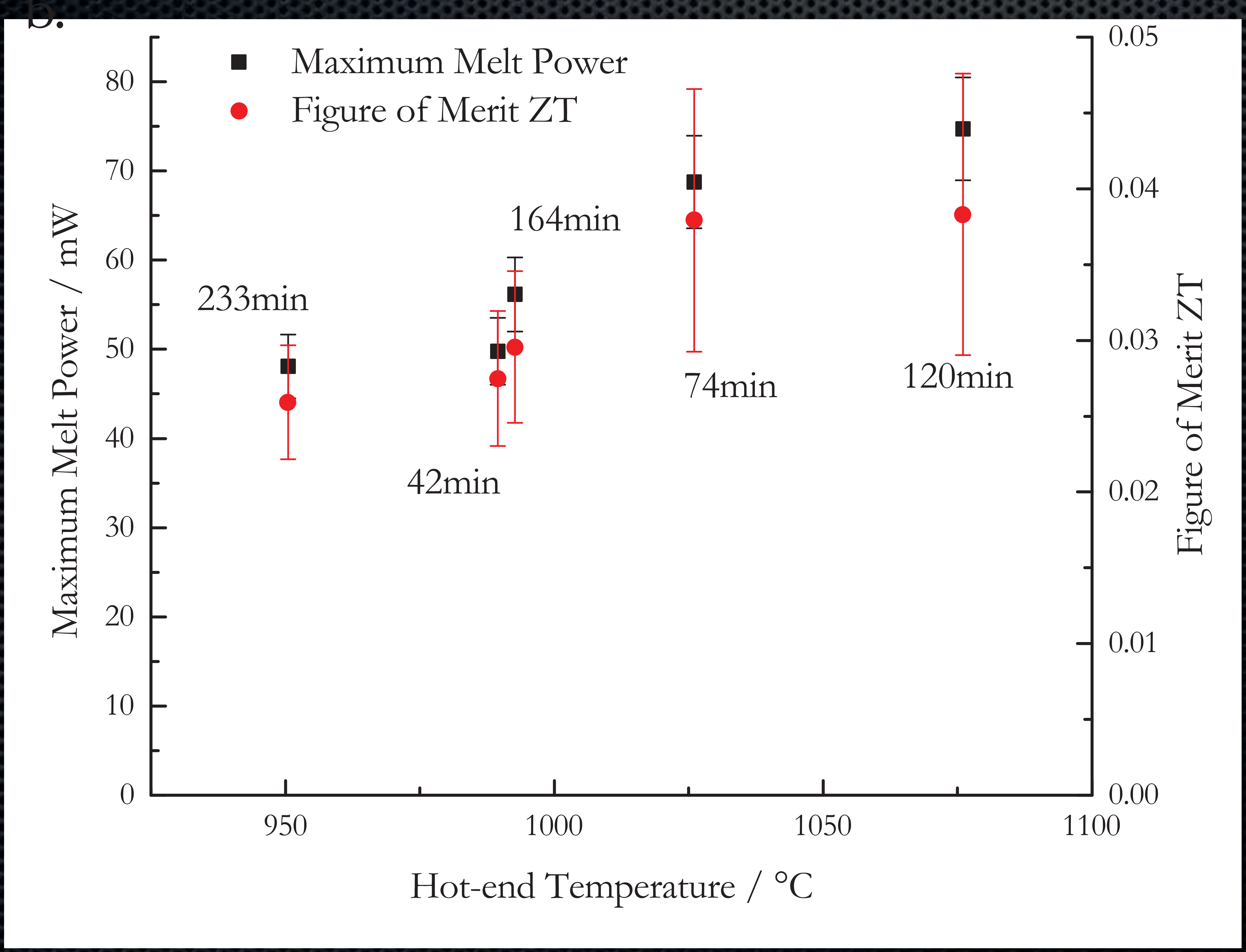
Results in agreement with known electronic properties



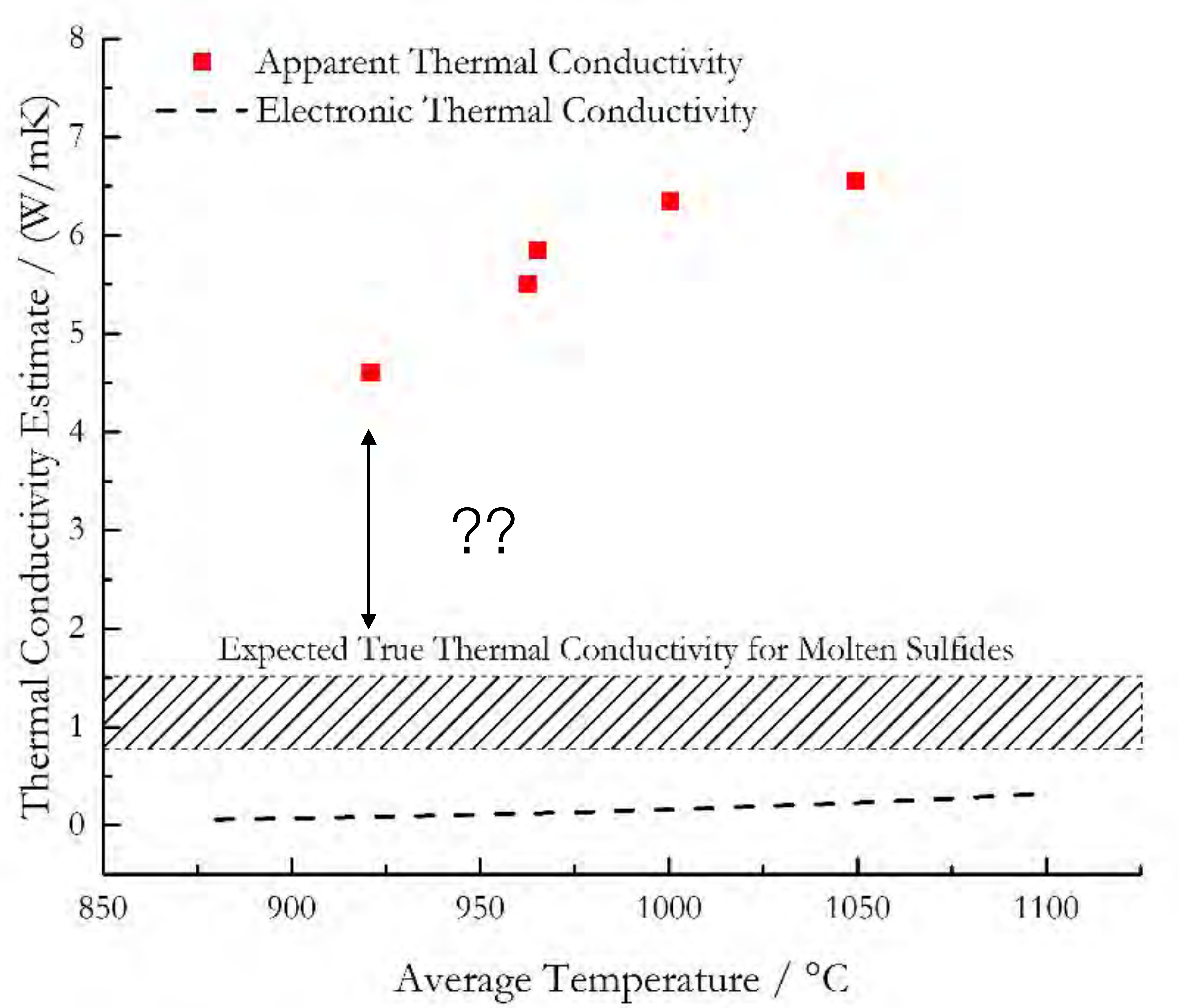


Materials limitations?

Good cyclability - what limits power conversion?



Thermal conductivity?



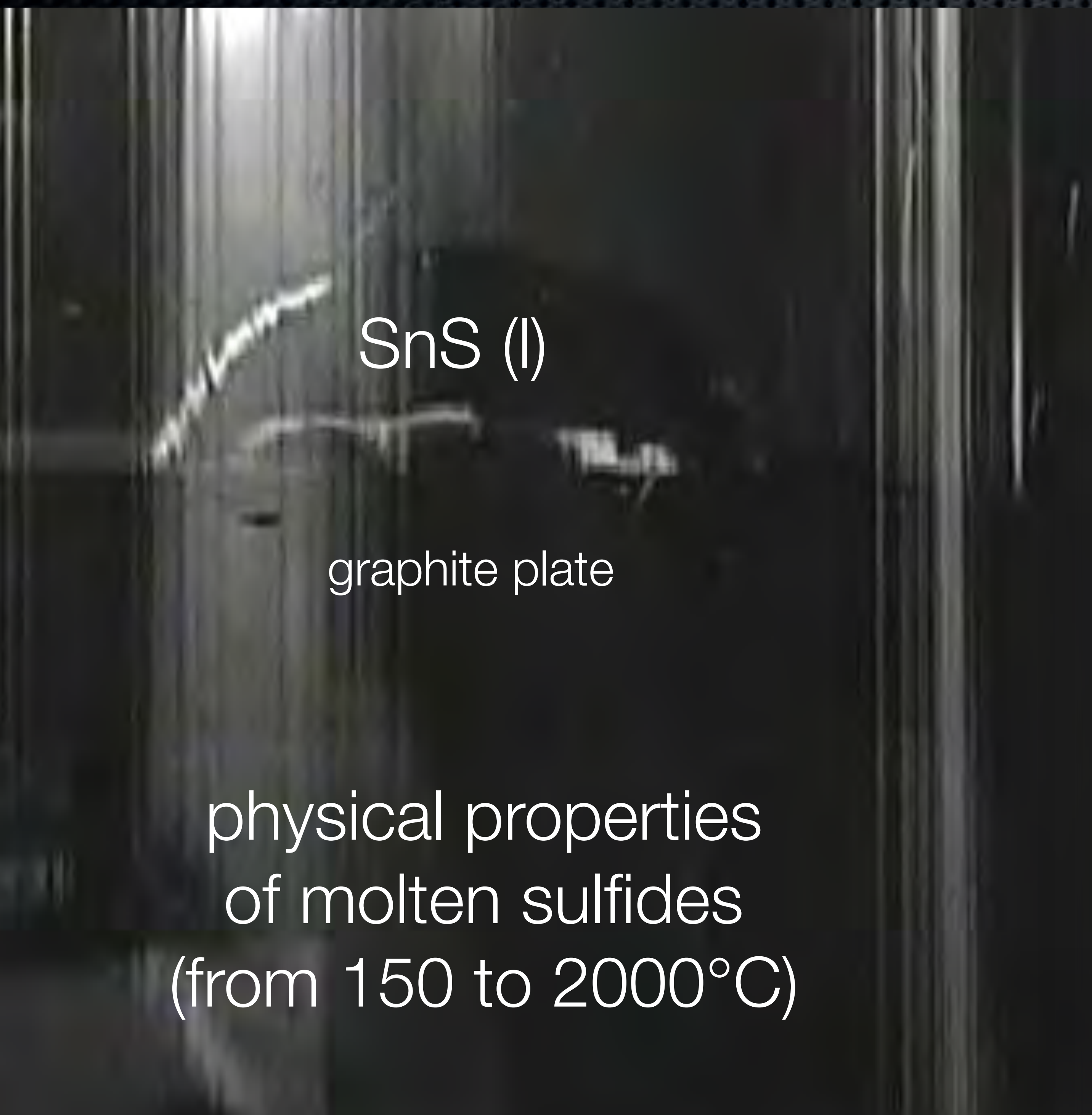
CONVECTION?

- need density, viscosity data

RADIATIVE?

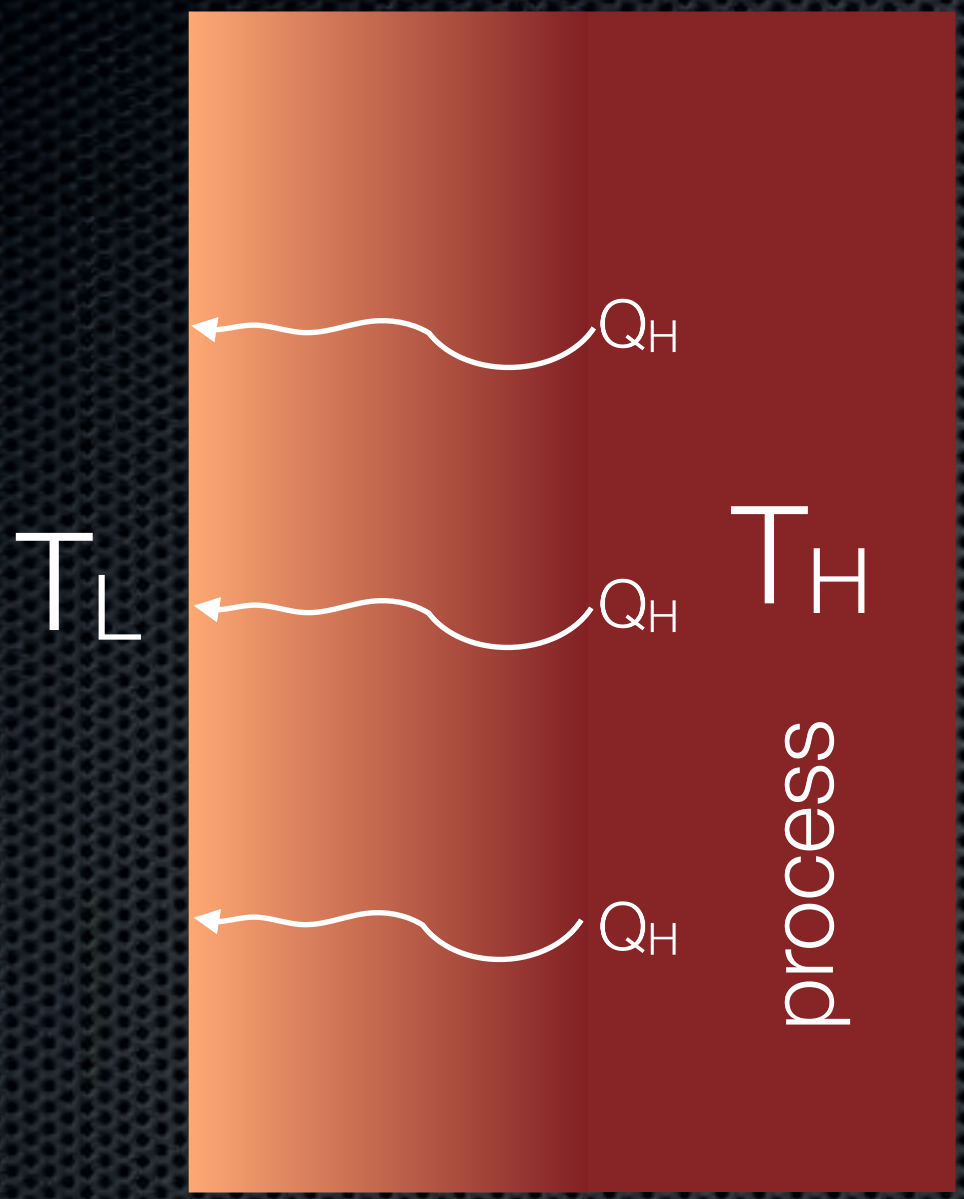
- Refractive index n
- Absorption coefficient α

Seeing the melt

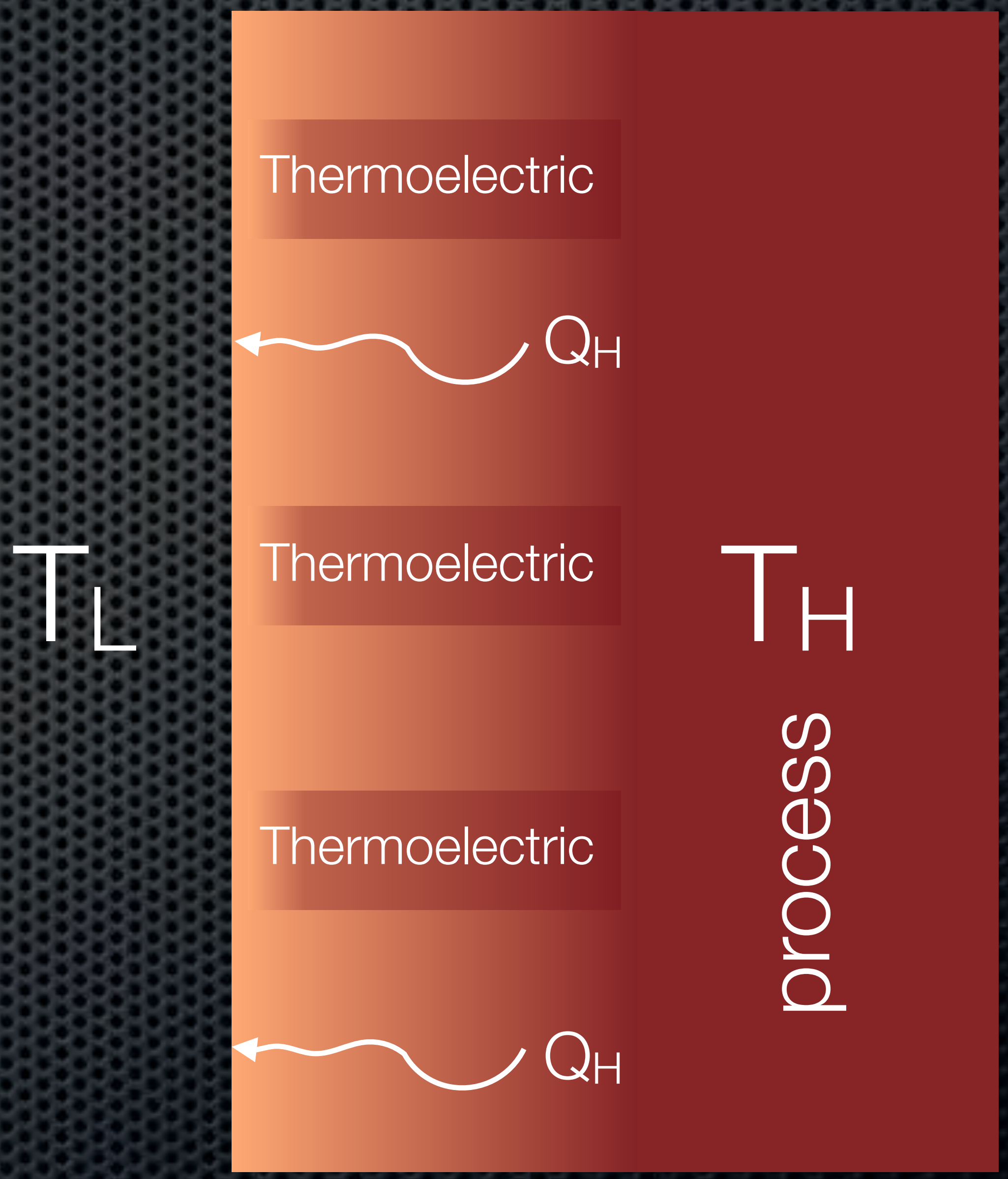


Process heat management?

conventional refractory



active refractory



- Q_H is fixed by max ΔT of refractory
- T_H limited by T_L location and ability to remove Q_C

- higher apparent thermal conductivity
- ability to be controlled by electricity
- can enable higher T_H, fast Q_H removal

Summary

- High temperature melts represent the ultimate state of condensed matter, pertinent to the entire metal supply chain (including oxidation products!)
- Existing predictive and experimental framework for properties is quickly evolving
- Novel media for heat, electrical or mass transfer in high temperature conditions can be designed and scaled-up promptly
- Scalability and implementation will be possible if it increases productivity of underlying process flow-diagram

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Acknowledgements

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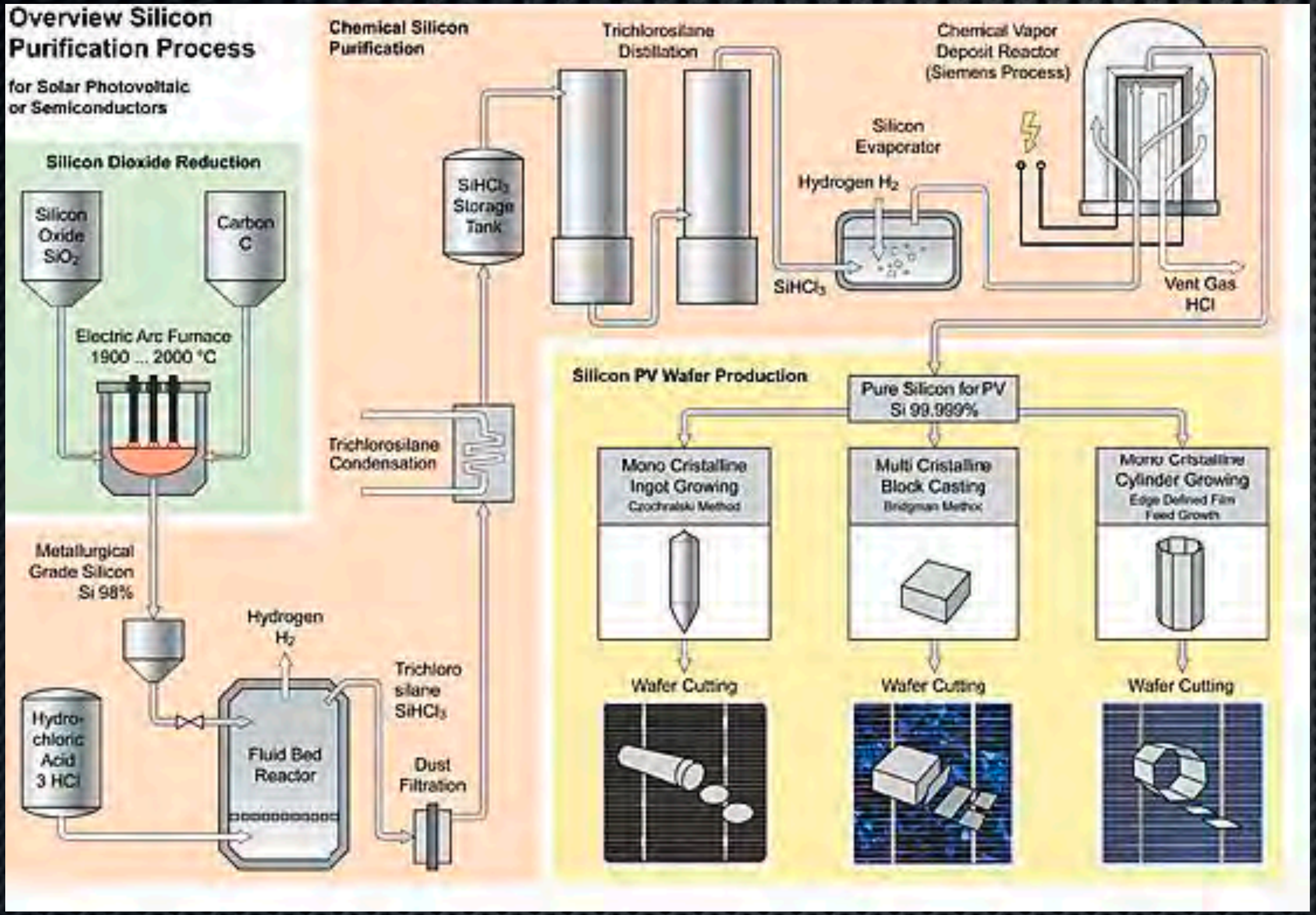
Dr. Cooper Rinzler - Mr. Youyang Zhang

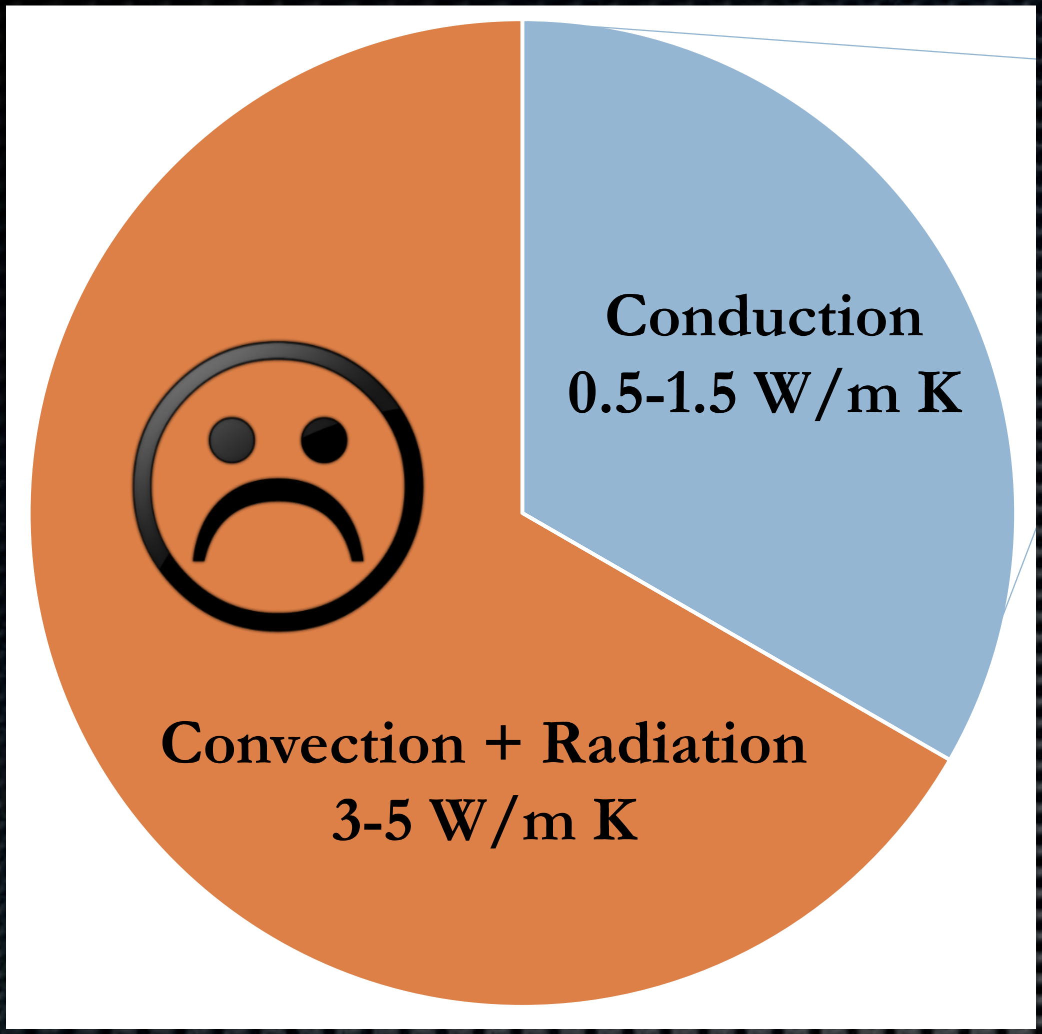
Materials processing

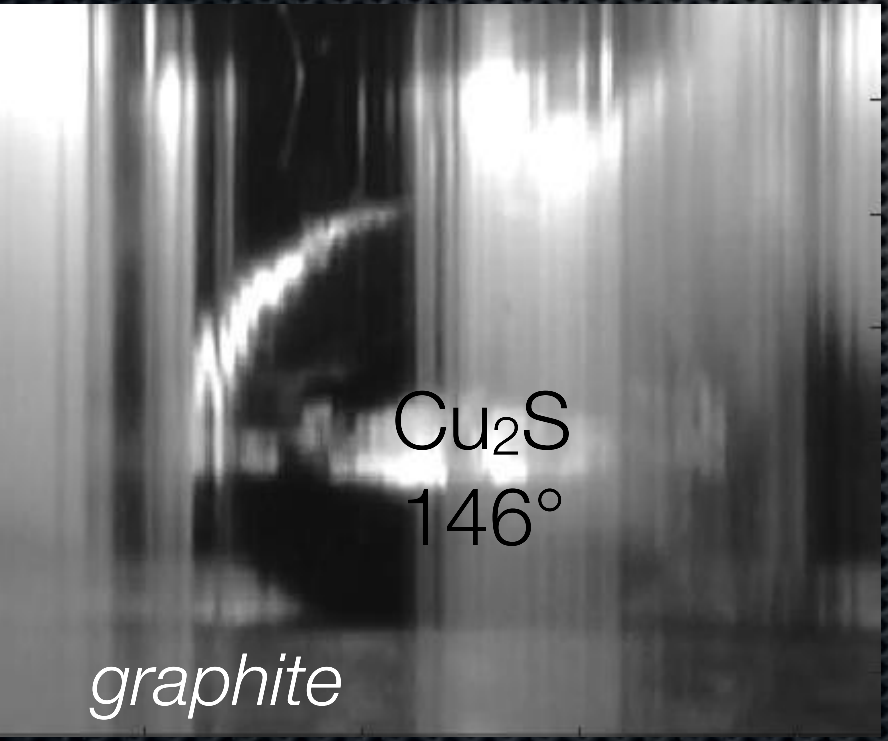
- realm of liquid state, high temperature, plasma, …

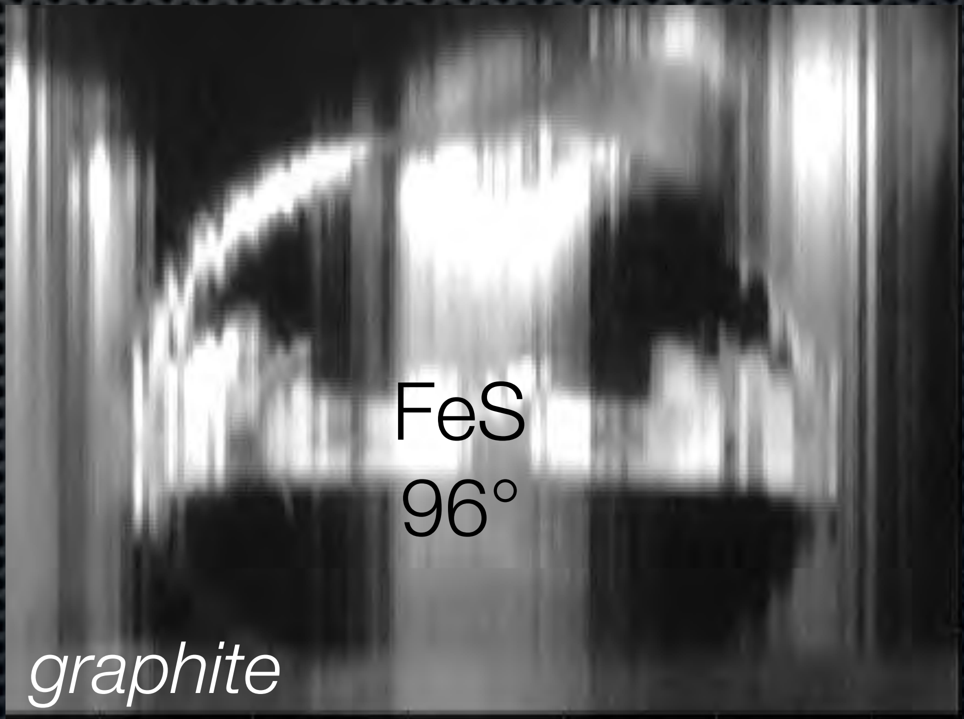


Electric Arc Furnace,
Ingot,
Plasma deposition,
EBeam (sublimation),
RT Process…

What is the state of the art in ‘high temperature’ materials science?

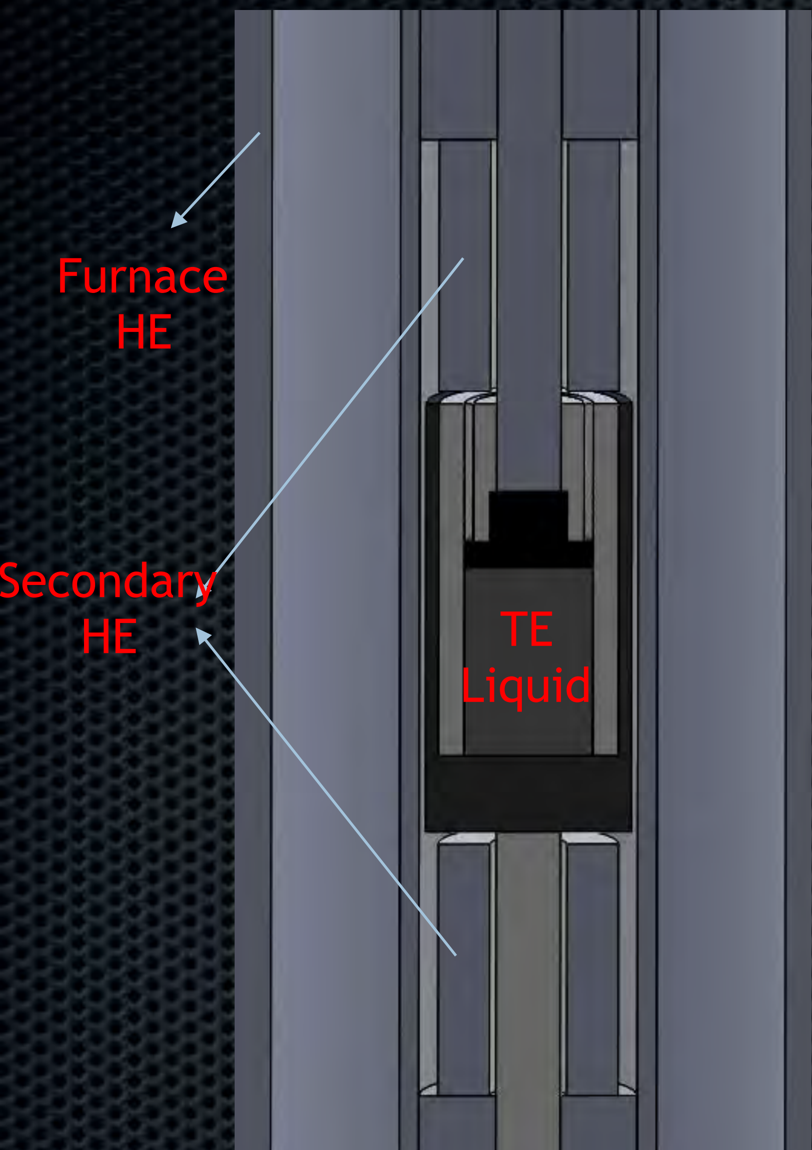

Conduction
0.5-1.5 W/m K
Convection + Radiation
3-5 W/m K

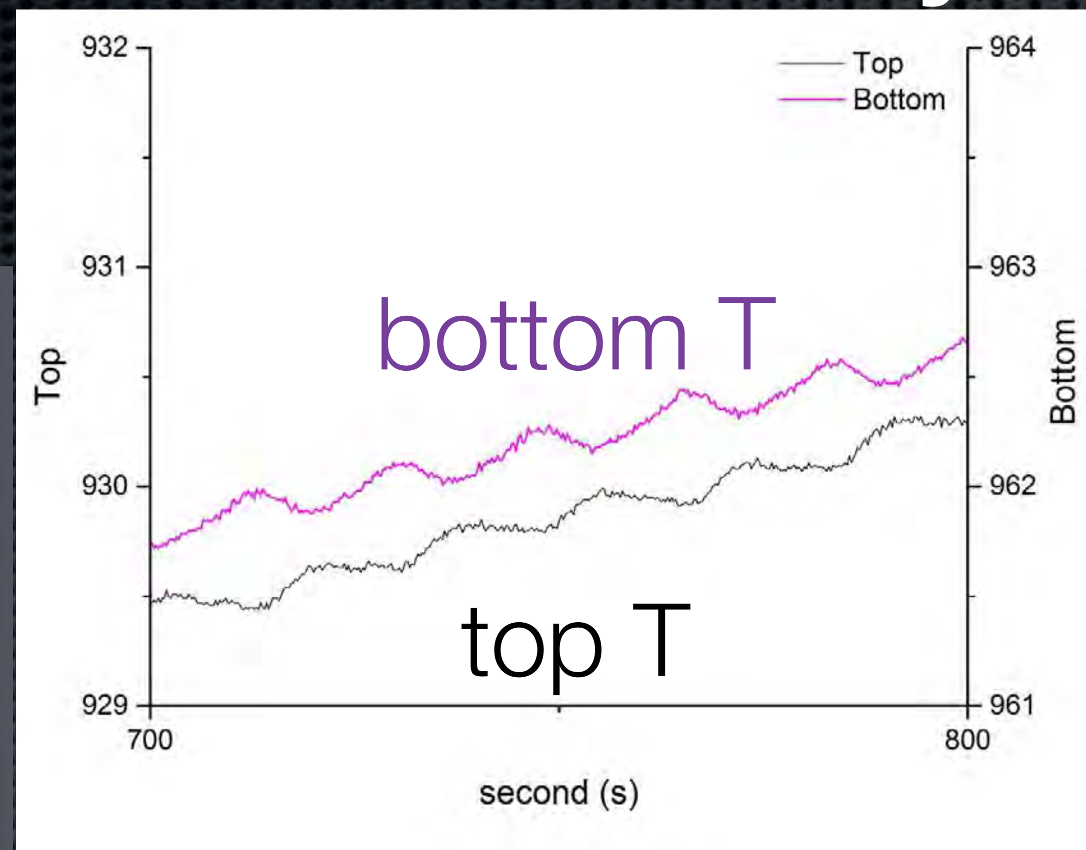

Cu_2S
146°
graphite


FeS
96°
graphite


Cu_2S-BaS-La_2S_3
76°
graphite

Thermal conductivity?





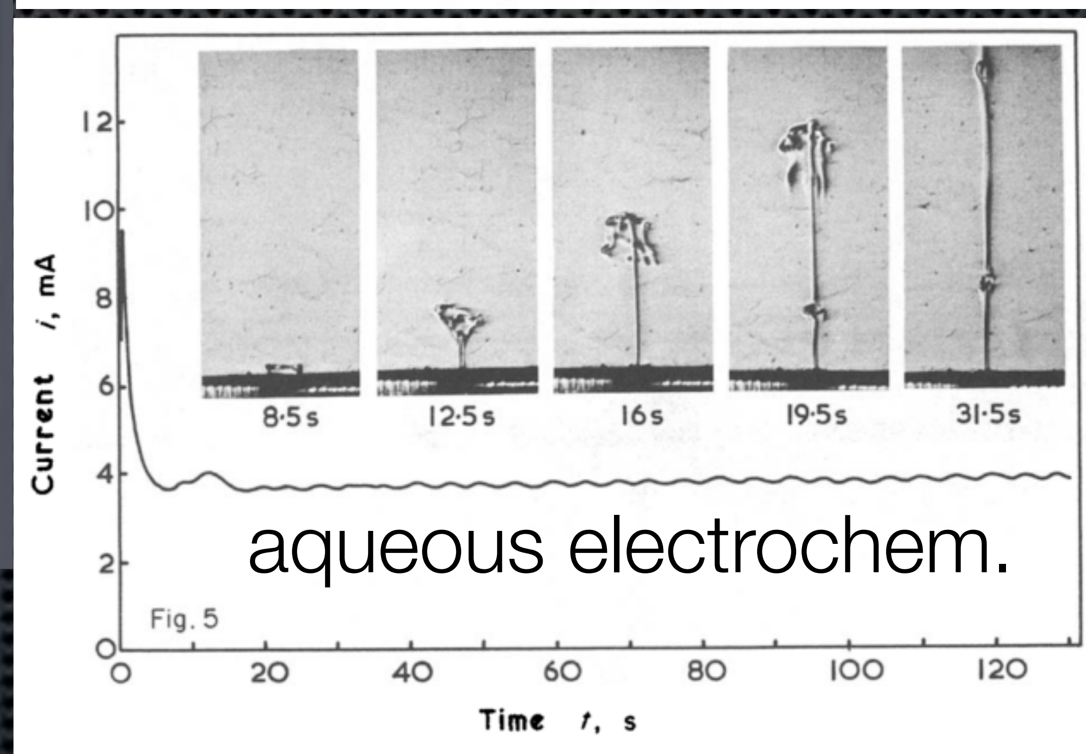


FIG. 5. Current–time plot and convection development for 2·5 mm electrode in 0·3 M solution, $Ra_d = 1{\cdot}0 \times 10^7$.

M. A. Patrick and A. A. Wragg, *Int. J. Heat Mass Transf.*, **18**, 1397–1407 (1975).

natural convection?

↓

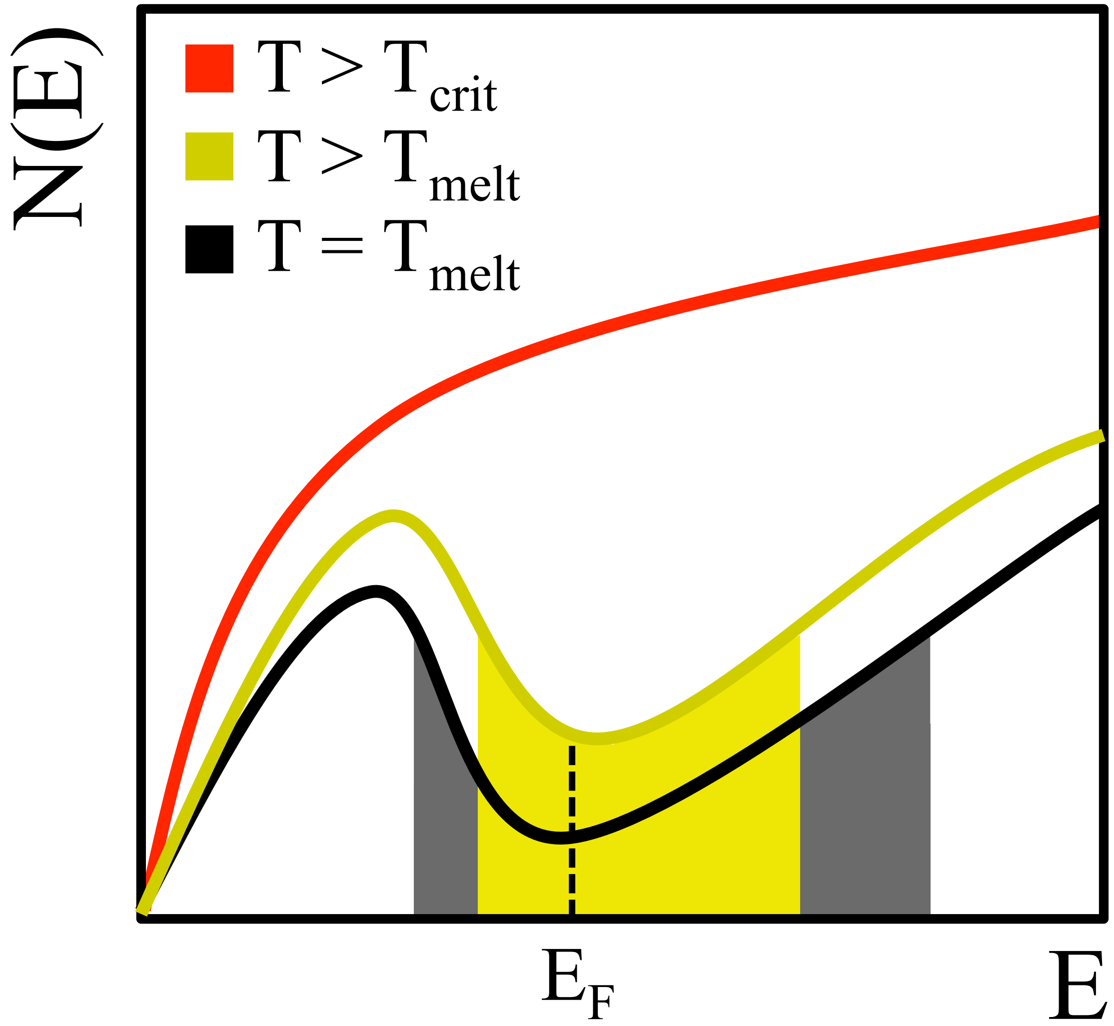
insight into density, viscosity, diffusivity

↓

seeing the melt?

Liquid semiconductors

Certain compounds maintain semi-conductivity upon melting…described by a ‘pseudo-gap’



Mott’s formulas
for amorphous SC

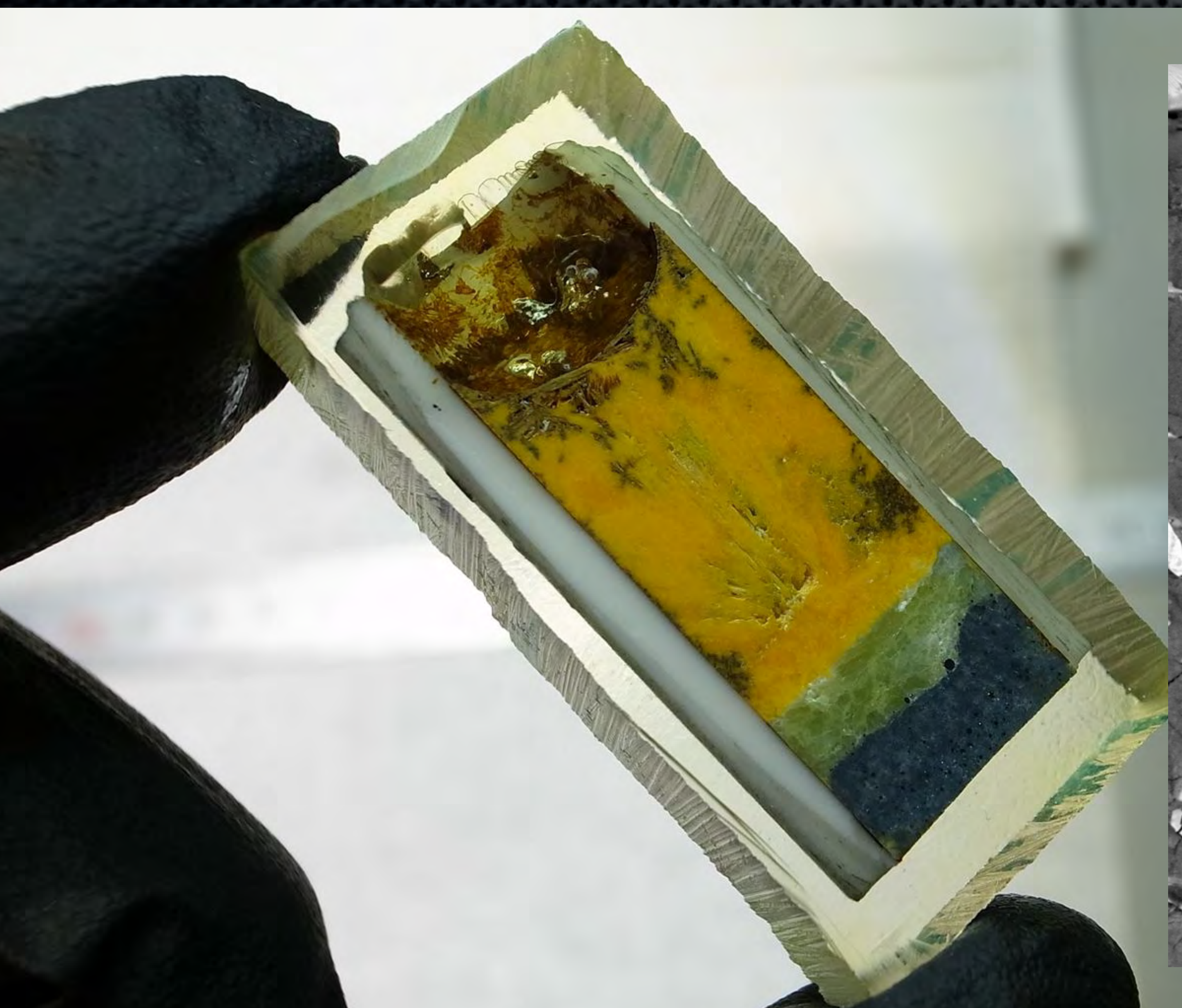
conductivity $\sigma = \sigma_{min} e^{\frac{-(E_0 - \gamma T)}{kT}}$

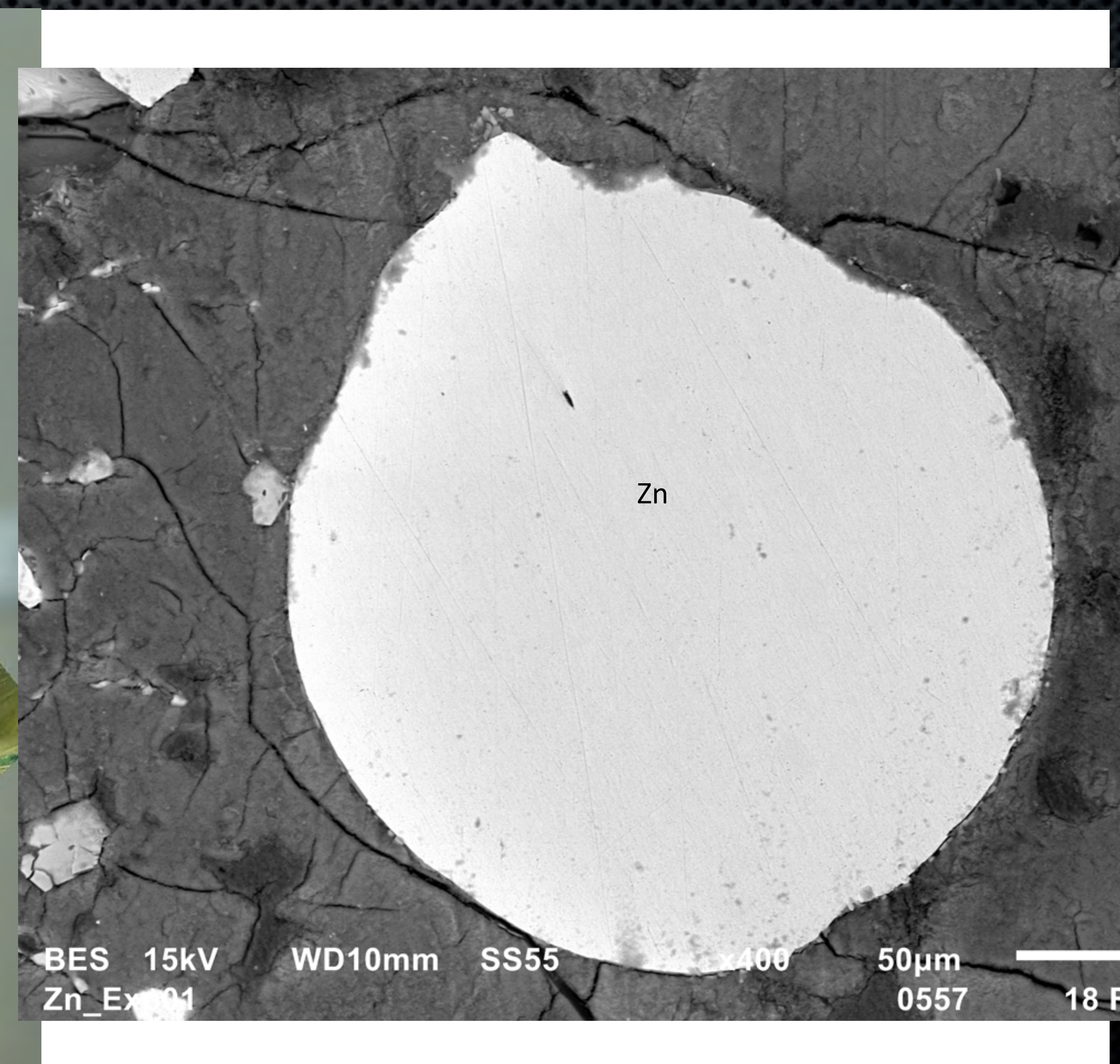
thermopower $\alpha = -\frac{k}{e}\left(\frac{E_0}{kT} - \frac{\gamma}{k} + 1\right)$

J. E. Enderby and A. C. Barnes (1990), Rep. Prog. Phys., 53, pp. 85–179
V. A. Alekseev, A. A. Andreev, and M. V Sadovskil, (1980), Sov. Phys. Usp., 23, no. 9, pp. 551–575
D. L. Price, (1990), Annu. Rev. Phys. Cher
P. W. Anderson, (1958), Phys. Rev. 109, pp.1492– 1505,

Molten sulfide electrolyte #2

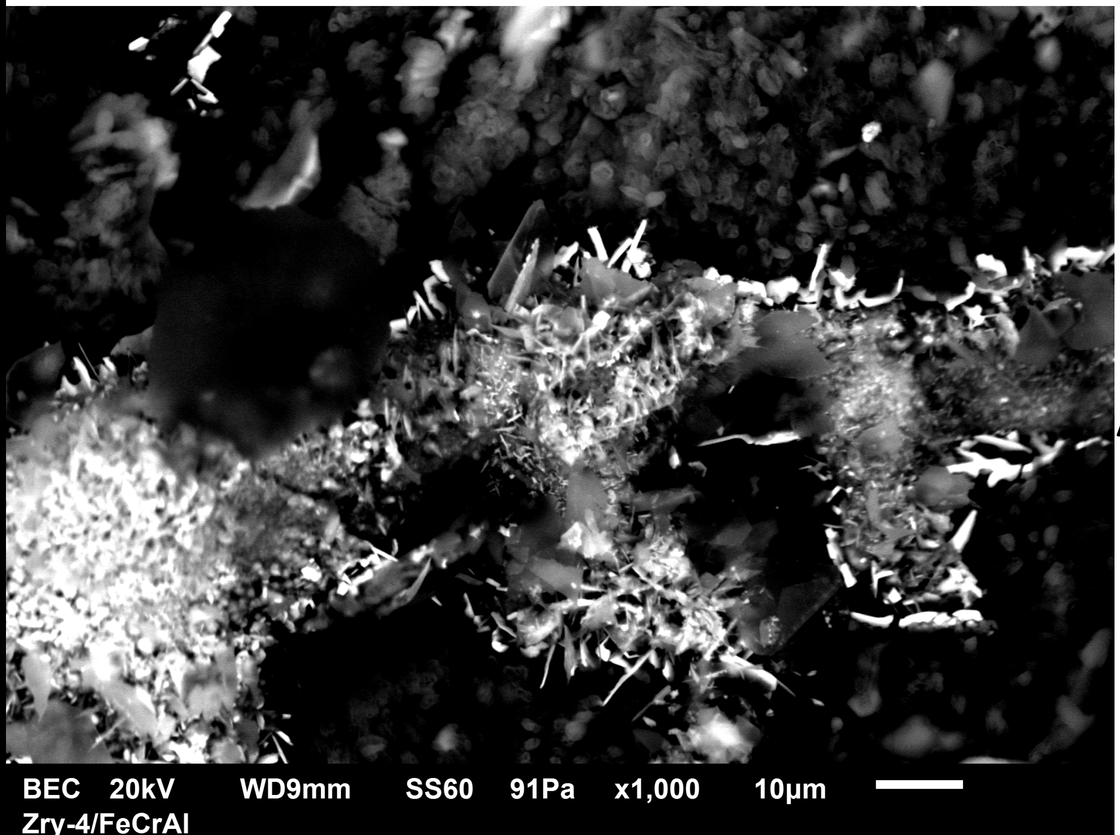
Na_2S-ZnS





Allanore et al., Presentation at the 11th Workshop on Reactive Metal Processing
February 20, 2016, Cambridge, MIT

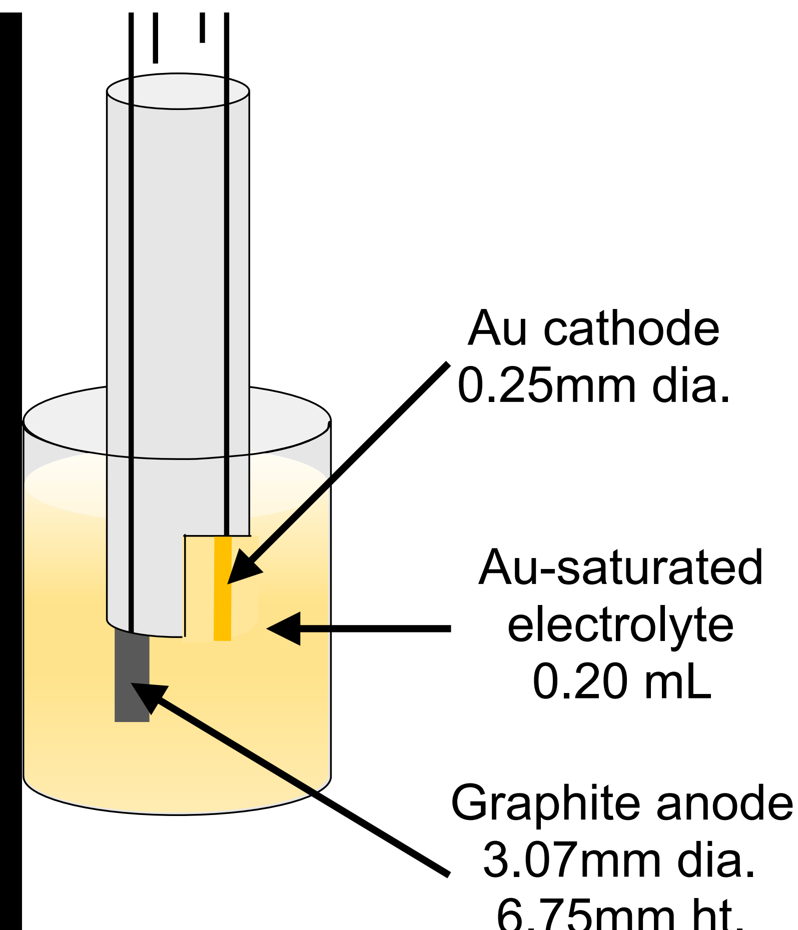
Silver: estimated concentration of 135 g/L

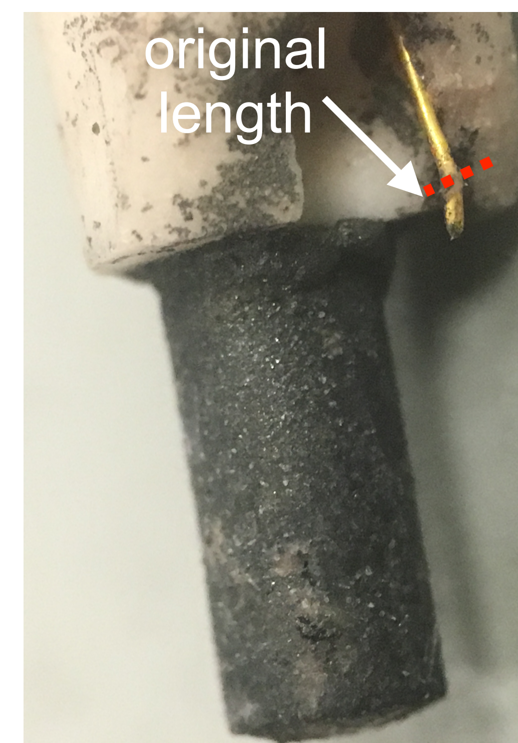


After 115 minutes of electrolysis, Ag "dendrites" were found near the cathode

additional possibilities demonstrated with Na_2S-ZnS

Gold: estimated concentration 278 g/L





Wagner & Allanore, Poster at the 68th International Society Meeting August 28, 2017, Providence (RI)