

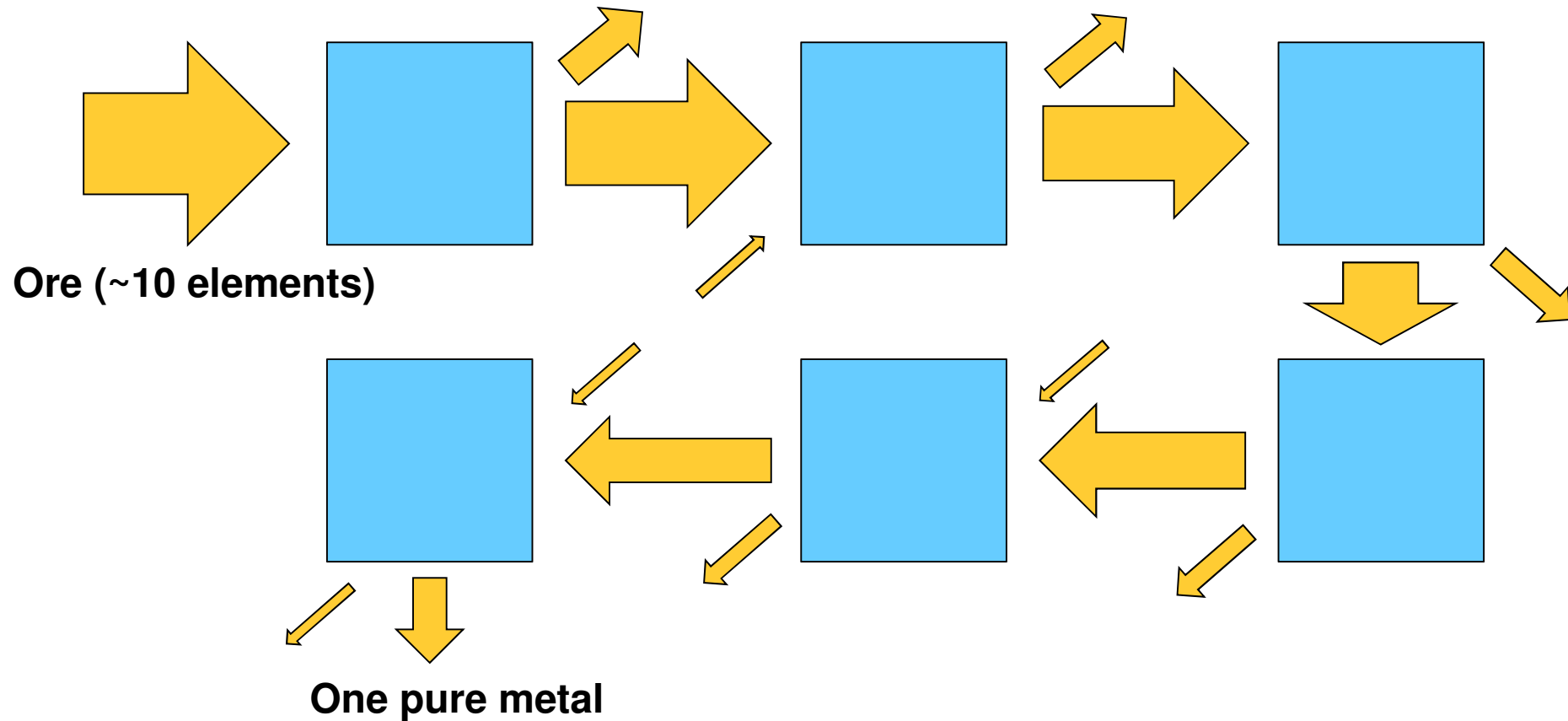
Scanning chemical compound space for radically new processing solutions: De-bismuthizing lead

Moritz to Baben

GTT-Technologies, Herzogenrath, Germany

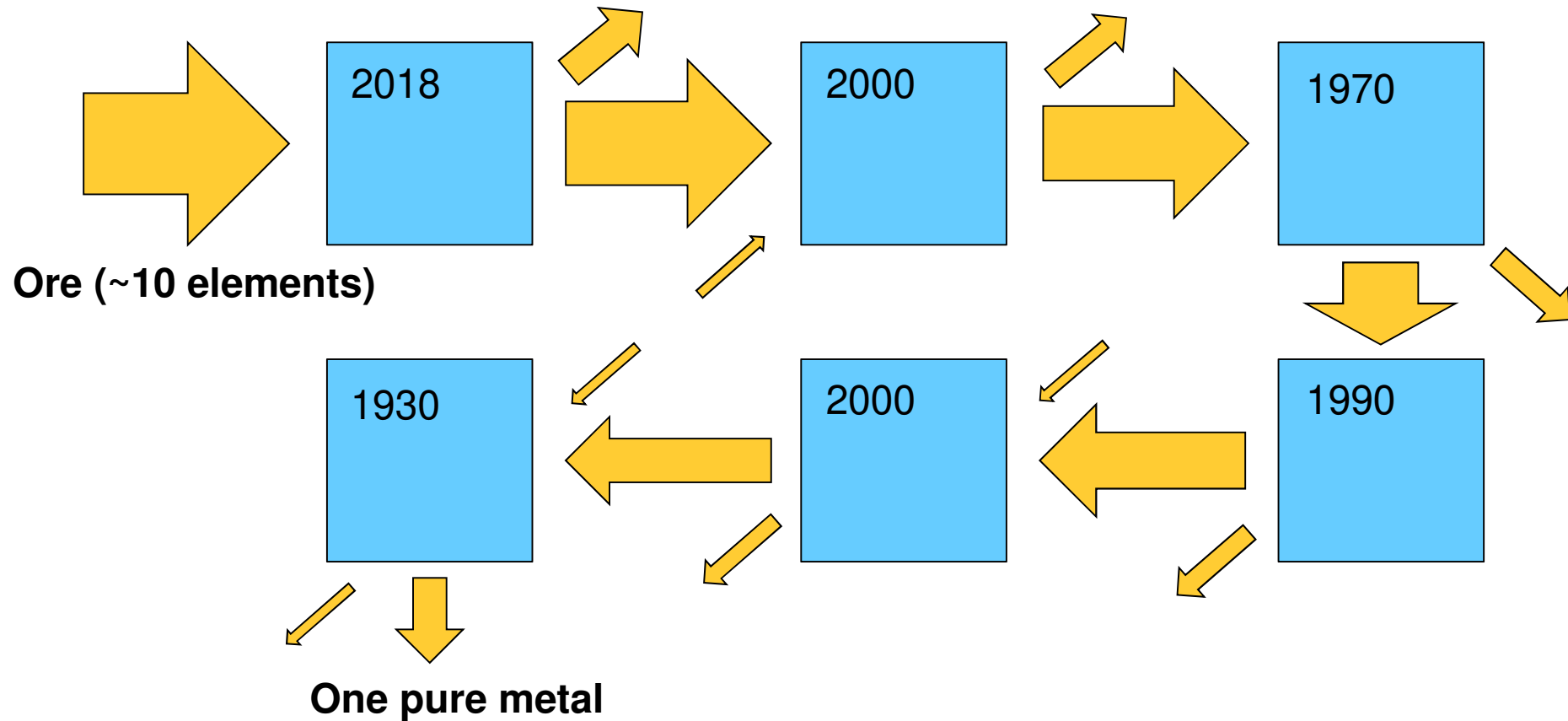


The art of metallurgical refining



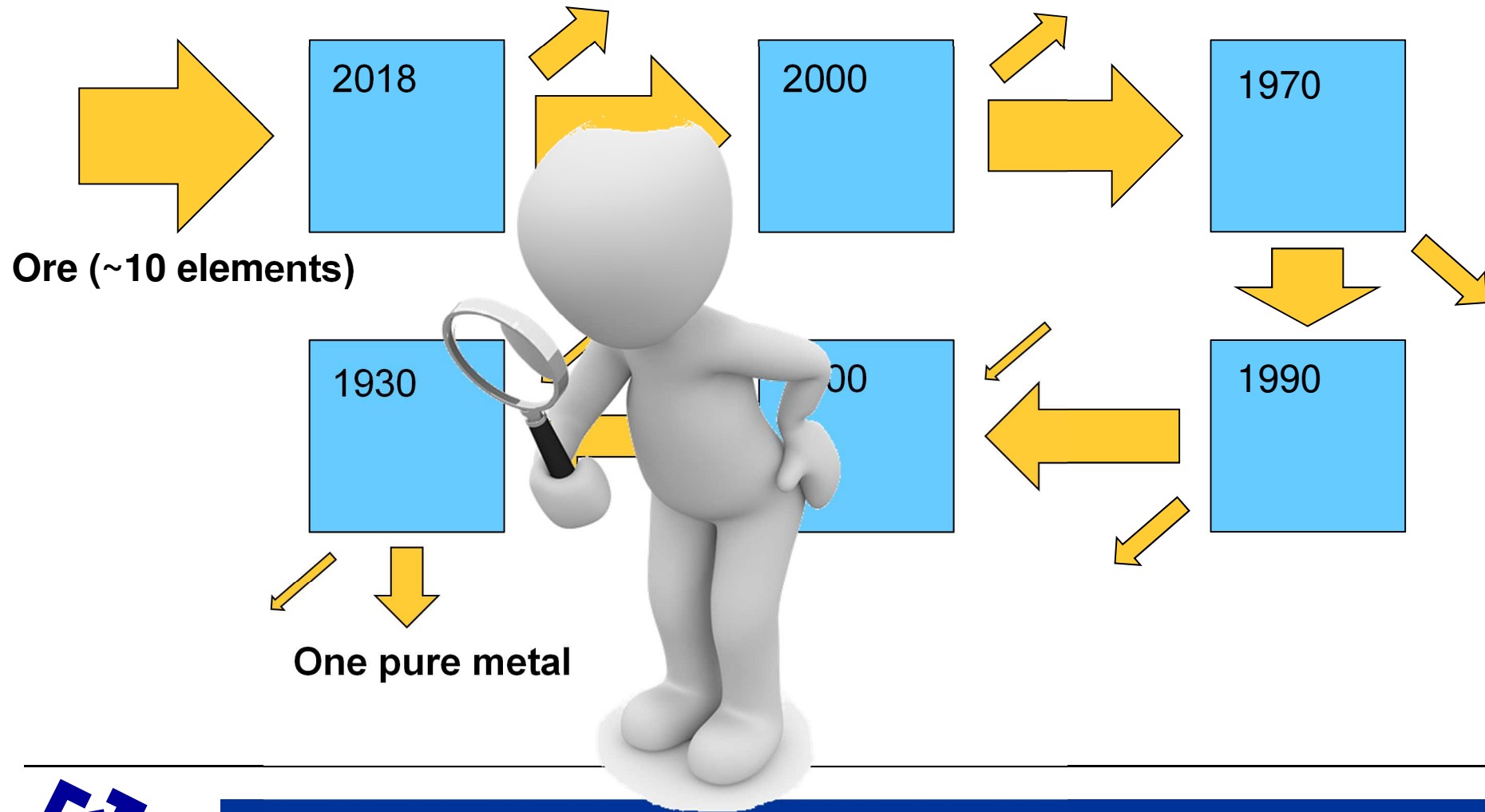
state of the

The art of metallurgical refining



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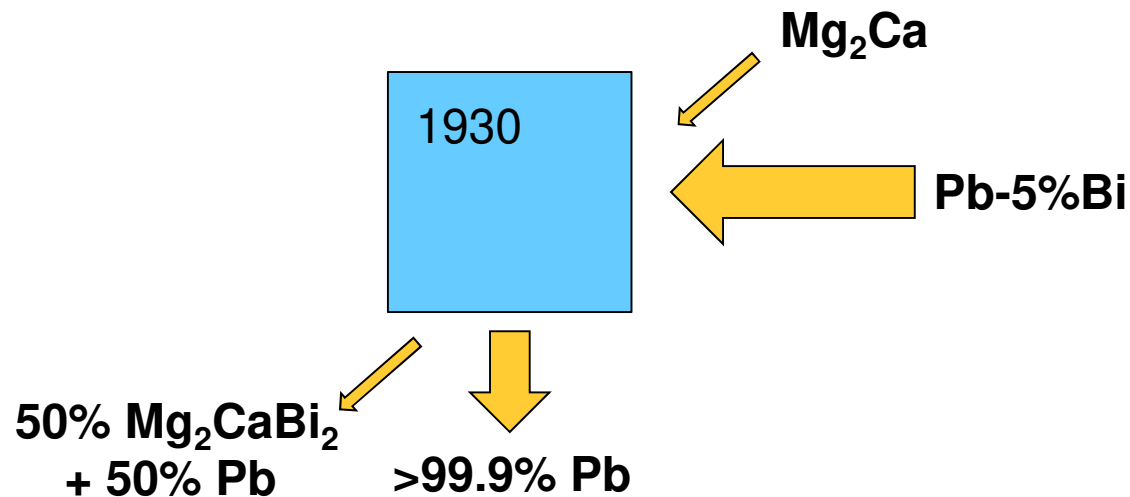


state of the The art of metallurgical refining

De-bismuthizing after Kroll-Betterton

Developed in the 1930s

Expensive and time-consuming - but it works!

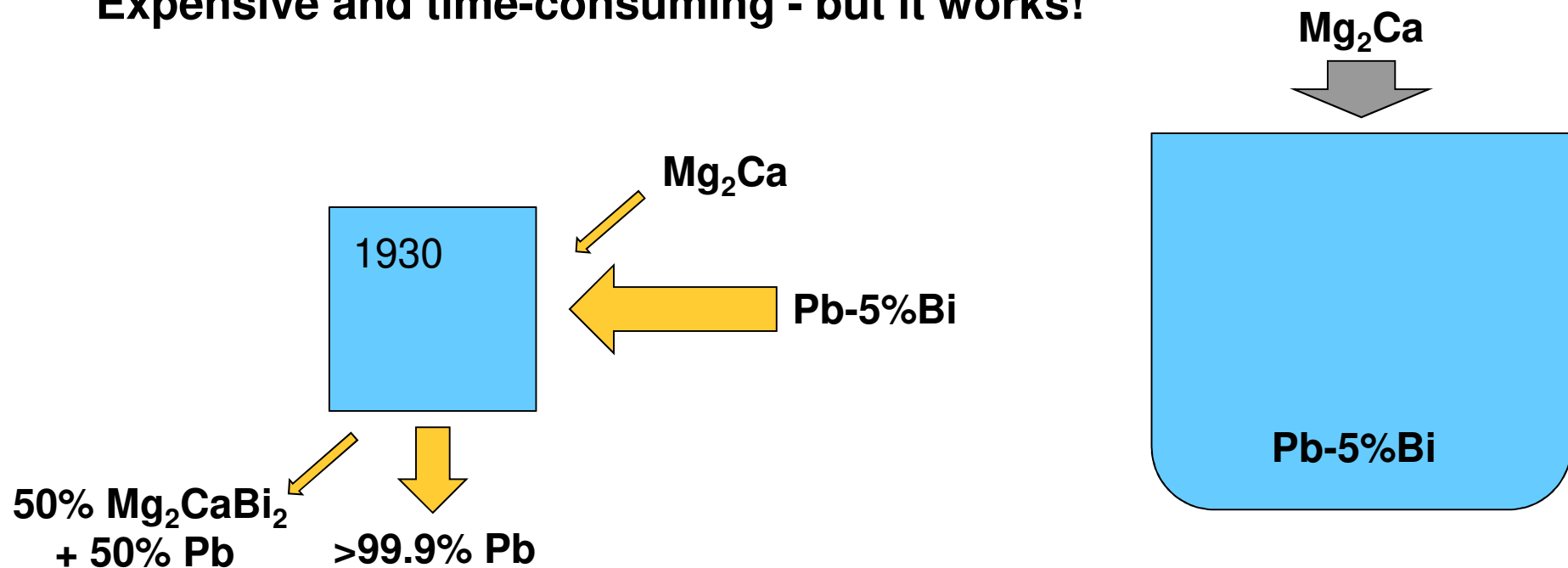


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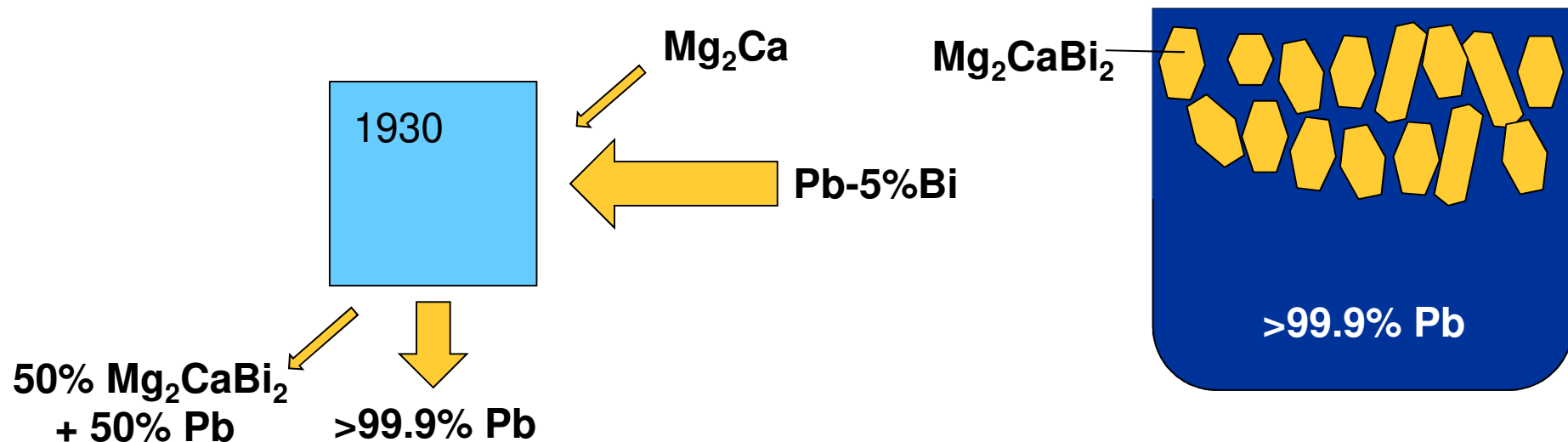


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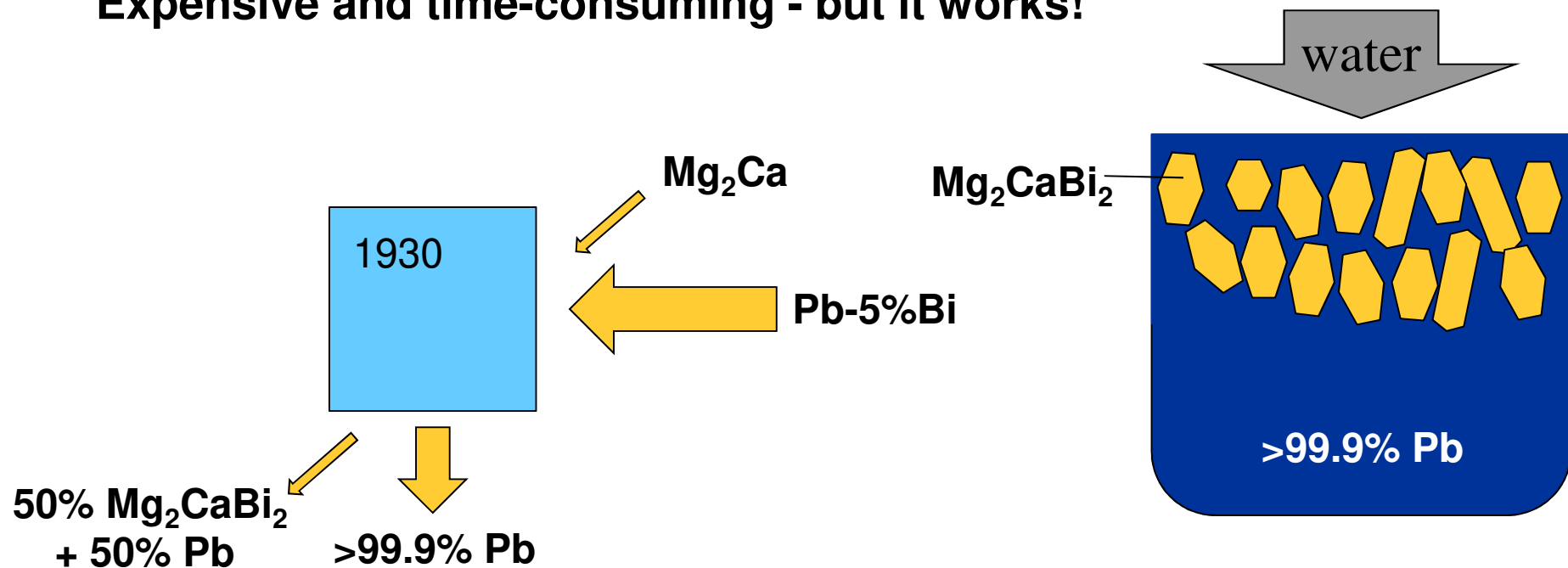


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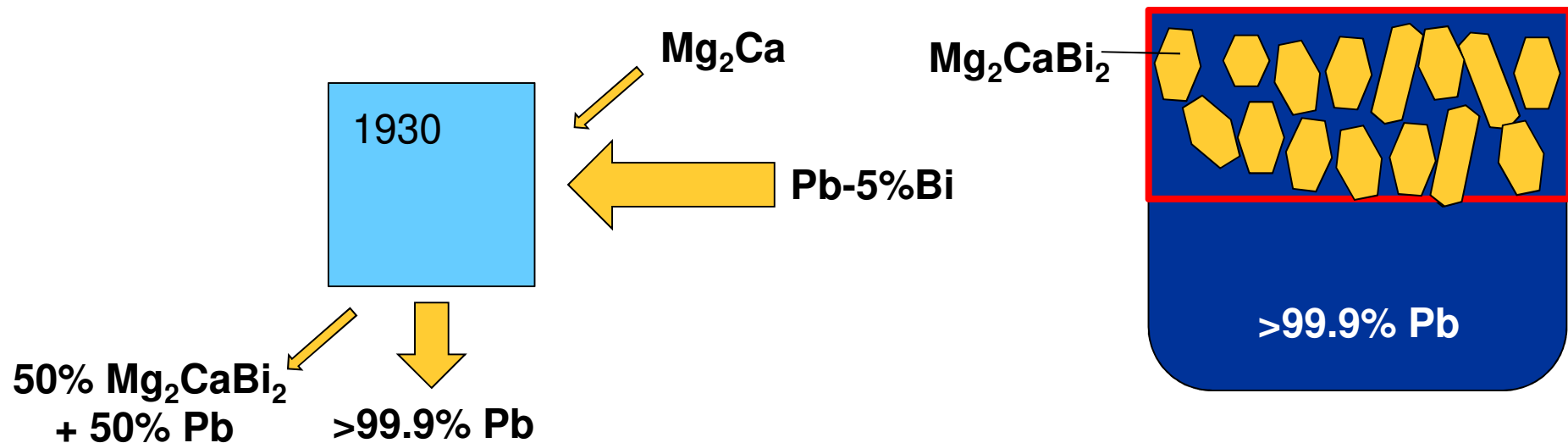


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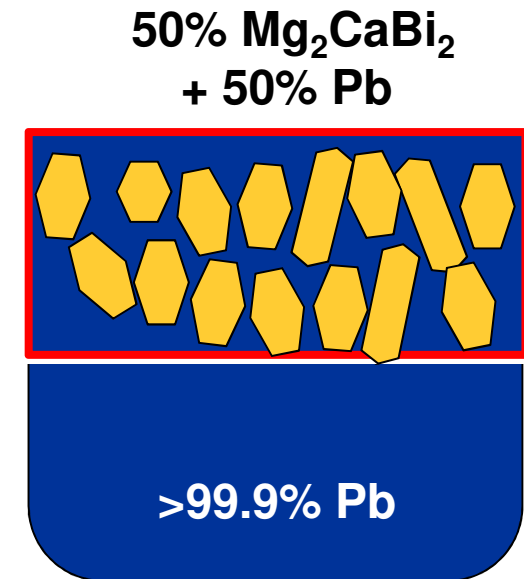
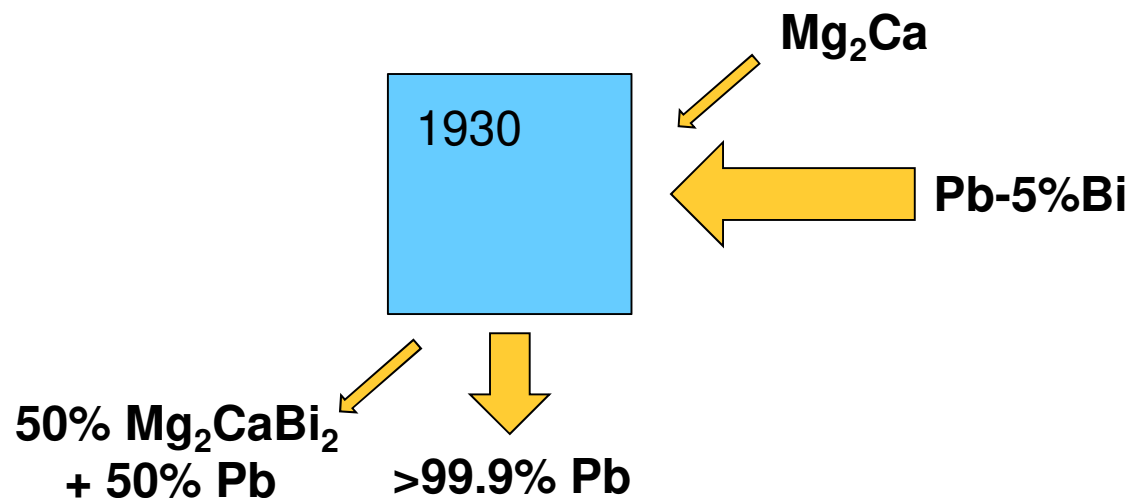


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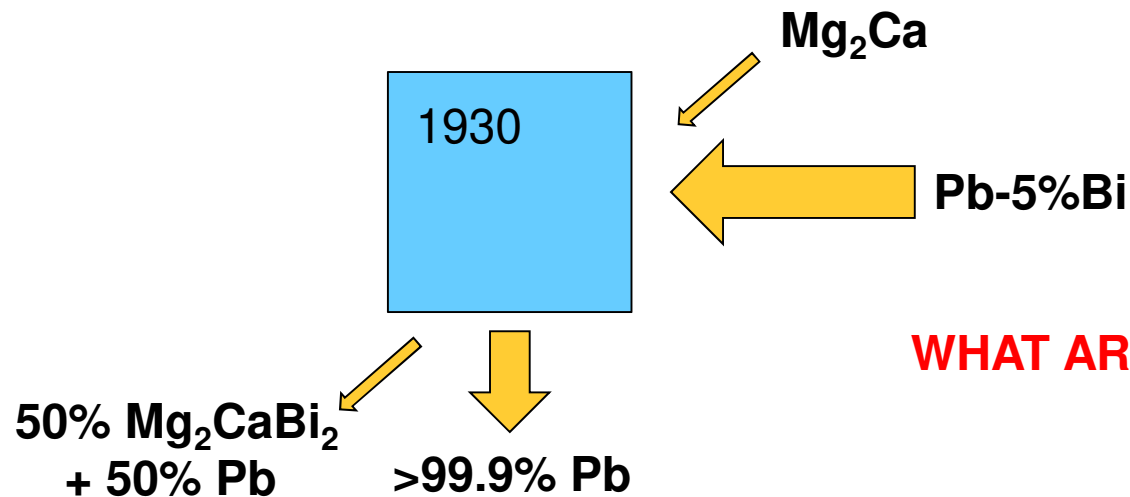


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WHAT ARE THE ALTERNATIVES?

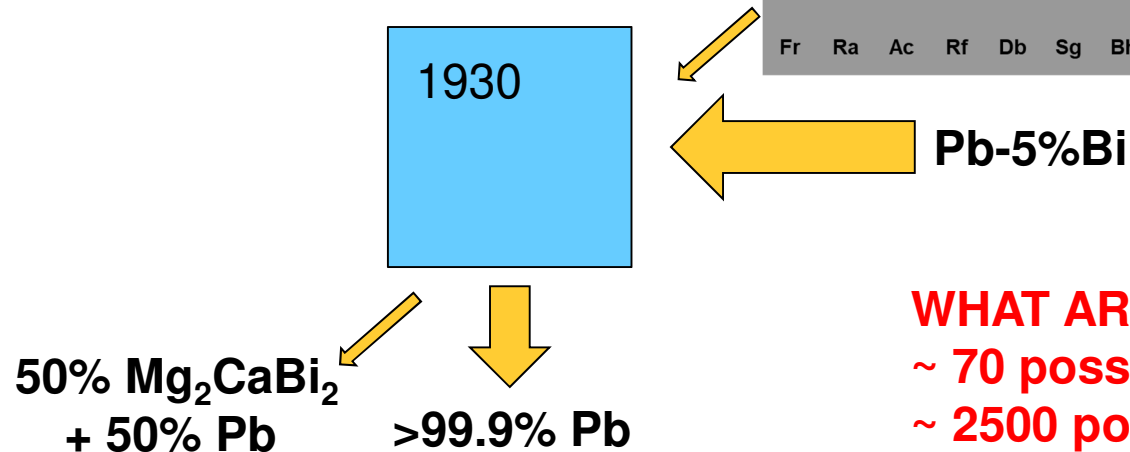


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De-bismuthizing after Kroll-Betterton

Developed in the 1930s
Expensive and time-consuming

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								



WHAT ARE THE ALTERNATIVES?

~ 70 possible elements

~ 2500 possible binary combinations



Chemical Compound Space

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Image from NASA (Hubble telescope)						



Chemical Compound Space

$$P \begin{pmatrix} X_H \\ X_{He} \\ X_{Li} \\ \vdots \\ X_{Ds} \end{pmatrix} = \begin{pmatrix} G \\ B \\ V \\ C_p \\ \vdots \end{pmatrix}$$
structure

$$P \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \odot / \otimes$$

H He
 Li Be B C N O F Ne
 Na Mg Al Si P S Cl Ar
 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
 Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

Image from NASA (Hubble telescope)



Chemical Compound Space

How do you navigate?

$$P \begin{pmatrix} X_H \\ X_{He} \\ X_{Li} \\ \vdots \\ X_{Ds} \end{pmatrix} = \begin{pmatrix} G \\ B \\ V \\ C_p \\ \vdots \end{pmatrix}$$
structure

$$P \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \odot / \otimes$$

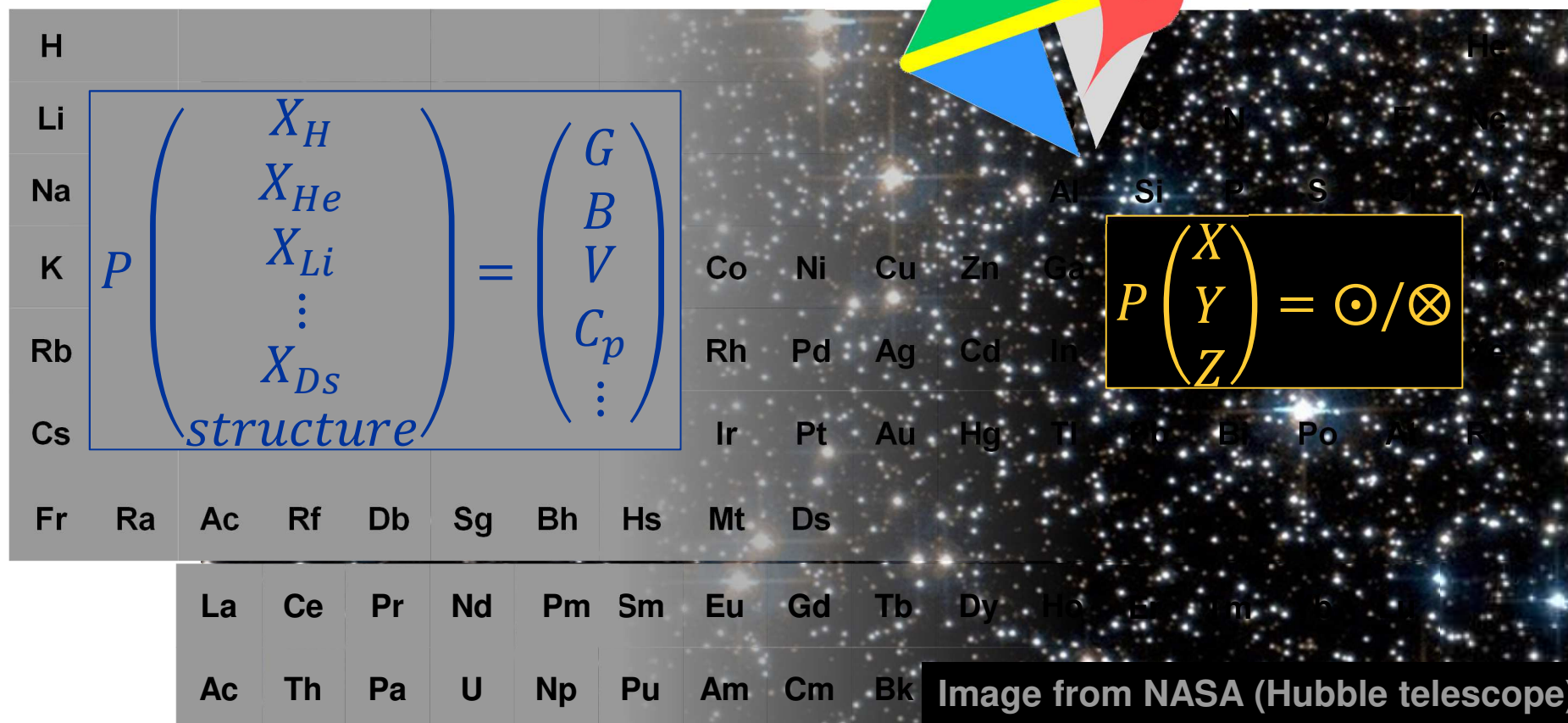
H He
 Li Be B C N O F Ne
 Na Mg Al Si P S Cl Ar
 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
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 Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

Image from NASA (Hubble telescope)



Chemical Compound Space

How do you navigate?



The periodic table is shown with elements labeled. A large blue box highlights the following matrix equation:

$$P \begin{pmatrix} X_H \\ X_{He} \\ X_{Li} \\ \vdots \\ X_{Ds} \\ \text{structure} \end{pmatrix} = \begin{pmatrix} G \\ B \\ V \\ C_p \\ \vdots \end{pmatrix}$$

A yellow box highlights the following matrix equation:

$$P \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \odot / \otimes$$

Image from NASA (Hubble telescope)



Chemical Compound Space

How do you navigate?

$$P \begin{pmatrix} X_H \\ X_{He} \\ X_{Li} \\ \vdots \\ X_{Ds} \end{pmatrix} = \begin{pmatrix} G \\ B \\ V \\ C_p \\ \vdots \end{pmatrix}$$
structure

$$P \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \odot / \otimes$$

H He
 Li Be B C N O F Ne
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 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
 Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
 Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No

Image from NASA (Hubble telescope)



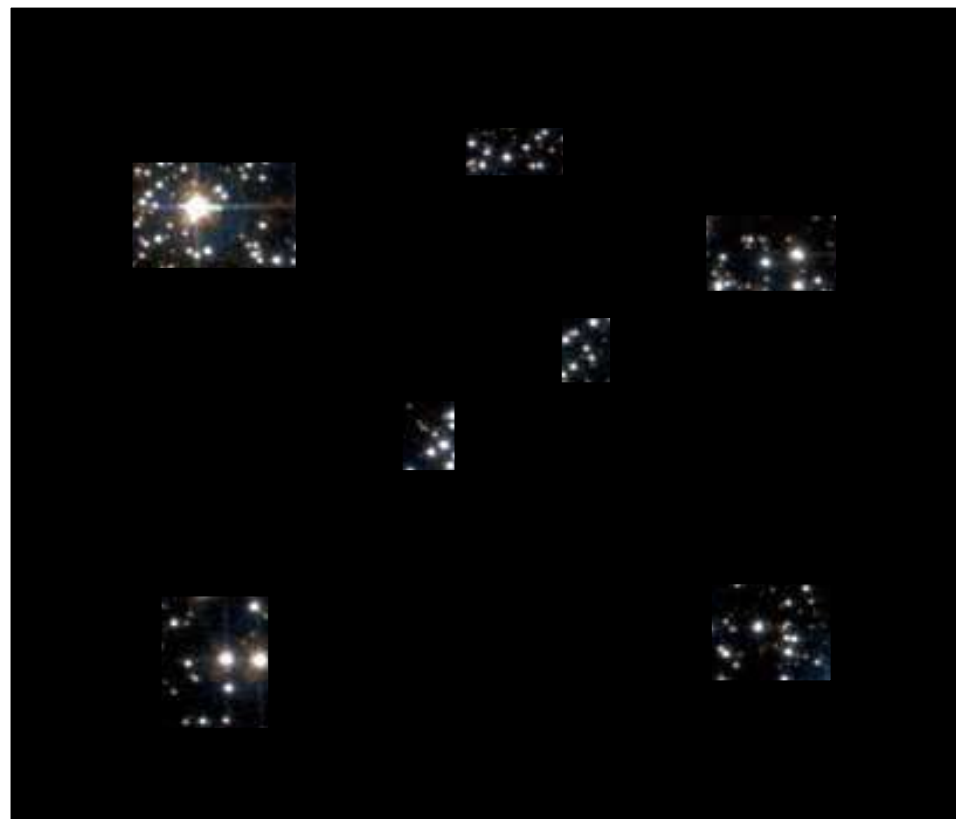
Chemical Compound Space

	CalPhaD
Number of phases	4868 (FactPS) 3768 (SGTE PS) 317 (SGTE Solutions)
T-ranges	298 K - 5000 K
Solution phases	solid liquid aqueous gas
origin	Experiments (Assessments since 1970s)



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Chemical Compound Space

	CalPhaD	Ab initio
Number of phases	4868 (FactPS) 3768 (SGTE PS) 317 (SGTE Solutions)	67'000 (materialsproject) 470'000 (oqmd) 1'680'000 (aflowlib)
T-ranges	298 K - 5000 K	0 K
Solution phases	solid liquid aqueous gas	---
origin	Experiments (Assessments since 1970s)	Materials Genome Initiative (since 2011)



Chemical Compound Space

**New
database**

	CalPhaD	Ab initio	aiMP 1.0
Number of phases	4868 (FactPS) 3768 (SGTE PS) 317 (SGTE Solutions)	67'000 (materialsproject) 470'000 (oqmd) 1'680'000 (aflowlib)	67'000
T-ranges	298 K - 5000 K	0 K	298 - 5000 K
Solution phases	solid liquid aqueous gas	---	--- (soon: solid)
origin	Experiments (Assessments since 1970s)	Materials Genome Initiative (since 2011)	materialsproject.org + extrapolation



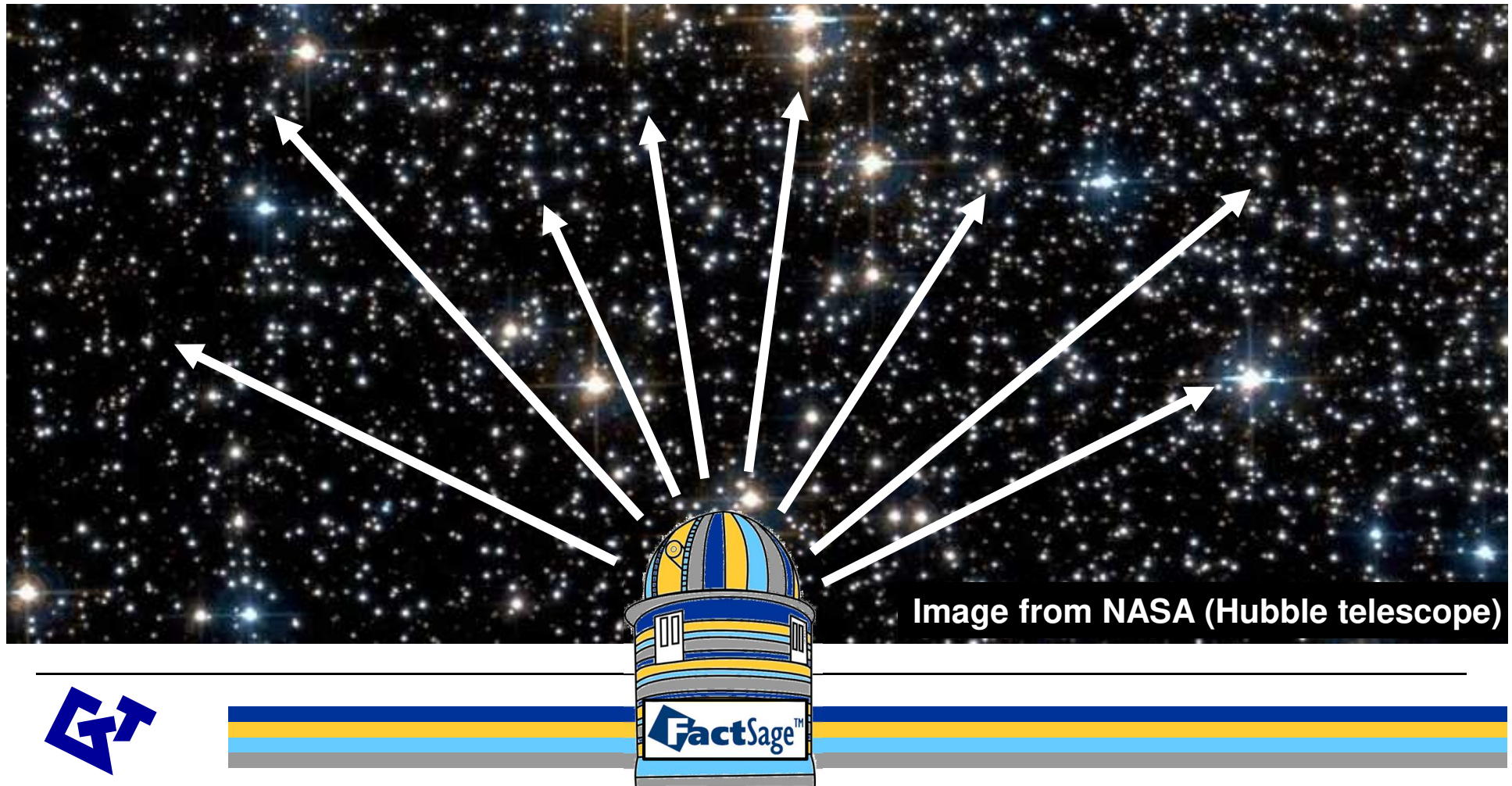
Chemical Compound Space

**New
database**

		aiMP 1.0
Number of phases		67'000
T-ranges		298 - 5000 K
Solution phases		--- (soon: solid)
origin		materialsproject.org + extrapolation



Materials Informatics



From *ab initio* to CalPhaD

$$G(T) = H(T) - TS(T)$$

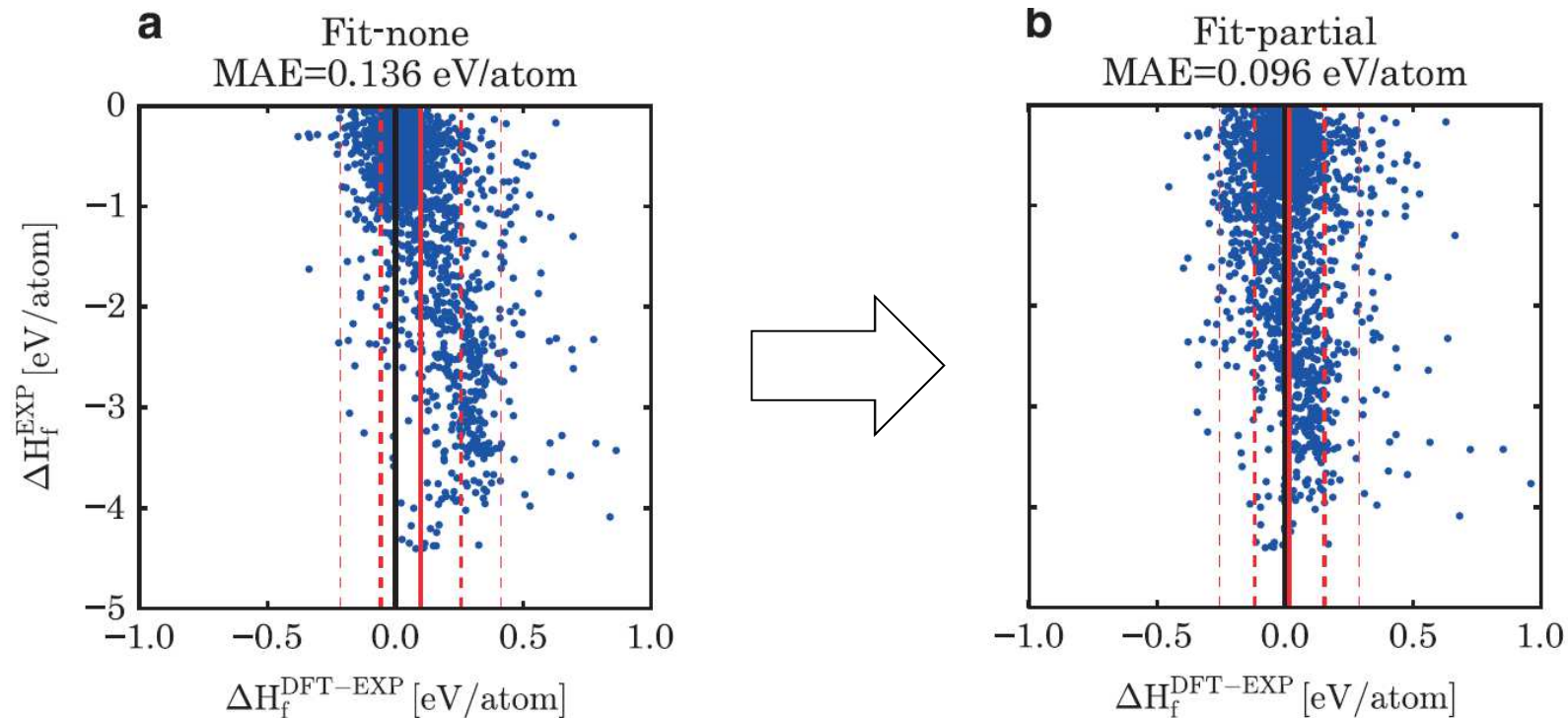
$$H(T) = H^{0K} + \int_{0K}^T C_P(T) dT \quad \Rightarrow \quad \boxed{H^{0K}}; C_p(T) \rightarrow \text{DFT!}$$

$$S(T) = S^{0K} + \int_{0K}^T \frac{C_P(T)}{T} dT \quad \Rightarrow \quad S^{0K}, C_p(T) = 0 \text{ (3rd law)}$$



Accuracy of *ab initio* enthalpies

For some elements (e.g. O) the most stable state changes between 0K and 298K. → Correct H^{298K} for all oxides etc. [3]



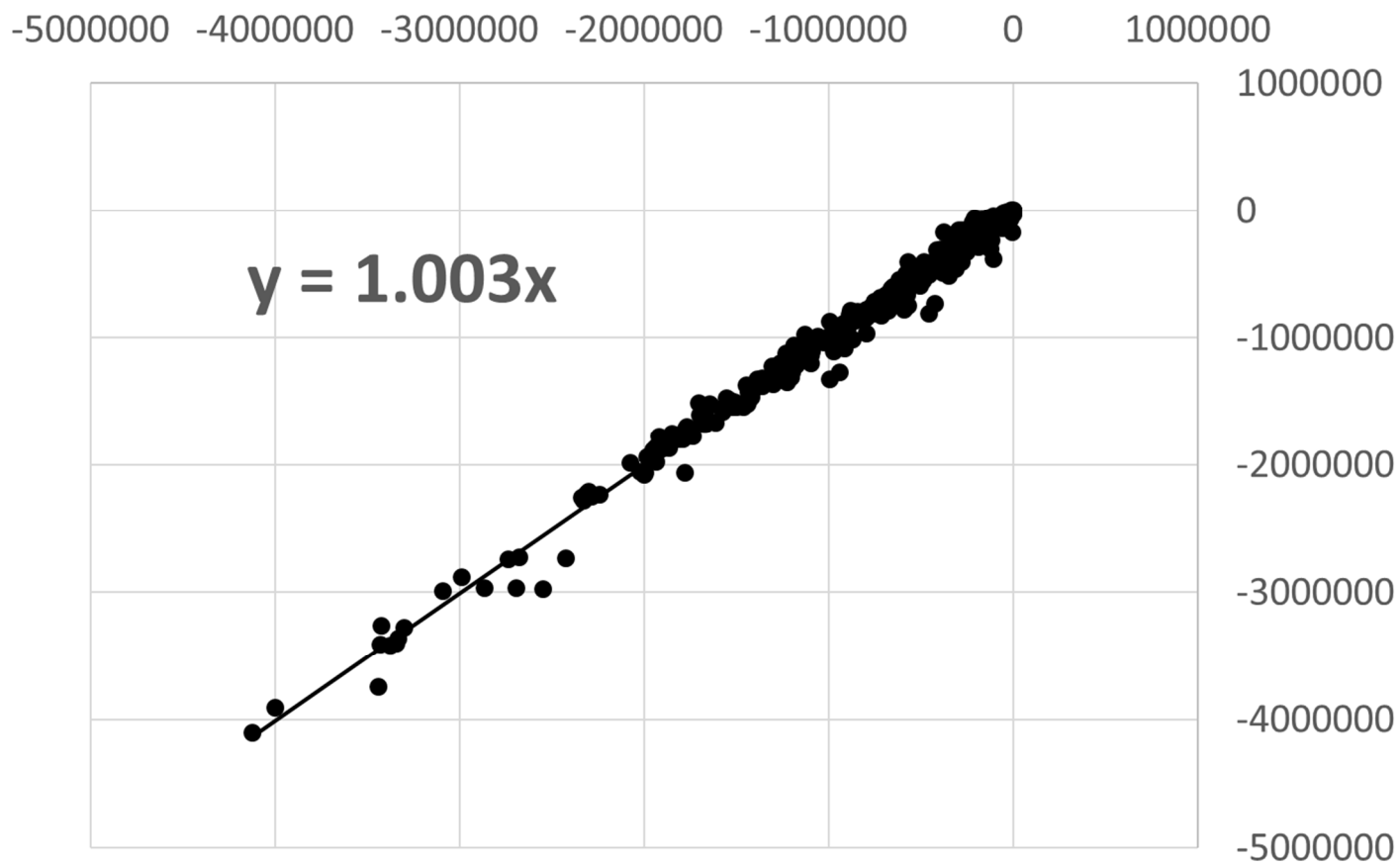
[1] S. Kirklin et al., npj Computational Materials 1 (2015) 15010.

oqmd.org



Accuracy of *ab initio* enthalpies

ΔH_f [J/mol] SGTE Pure Substance database



ΔH_f [J/mol] materialsproject.org
with empirical corrections



From *ab initio* to CalPhaD

$$G(T) = H(T) - TS(T)$$

$$H(T) = H^{0K} + \int_{0K}^T C_P(T) dT \quad \Rightarrow \quad H^{0K}, C_p(T) \rightarrow \text{DFT!}$$

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From *ab initio* to CalPhaD

$$G(T) = H(T) - TS(T) \quad 298 \text{ K} < T < 5000 \text{ K}$$

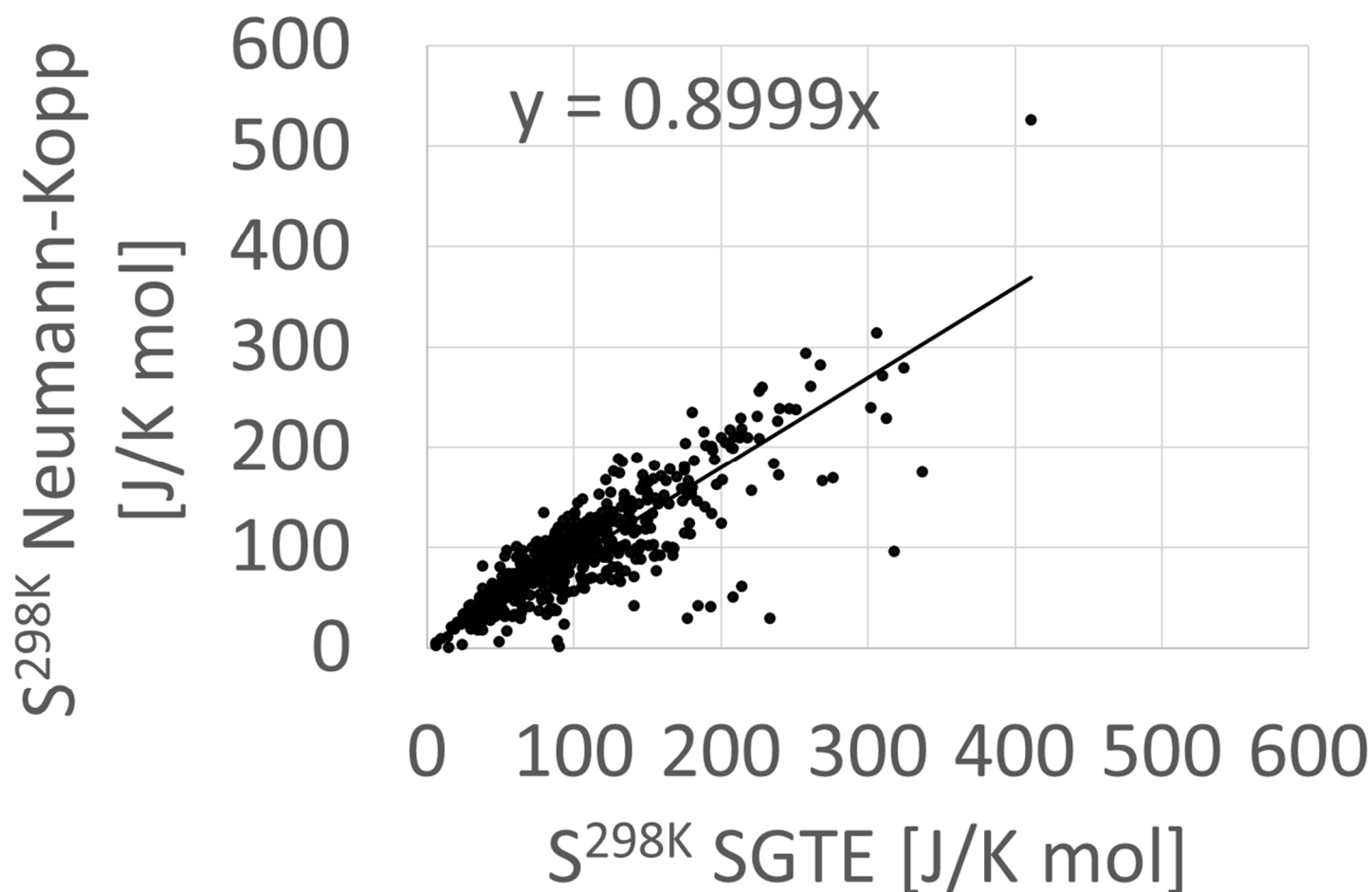
$$H(T) = H^{298\text{K}} + \int_{298\text{K}}^T C_P(T) dT \quad \Rightarrow \quad H^{298\text{K}}, C_p(T) \rightarrow \text{DFT!}$$

$$S(T) = S^{298\text{K}} + \int_{298\text{K}}^T \frac{C_P(T)}{T} dT \quad \Rightarrow \quad \boxed{S^{298\text{K}}}, C_p(T)$$

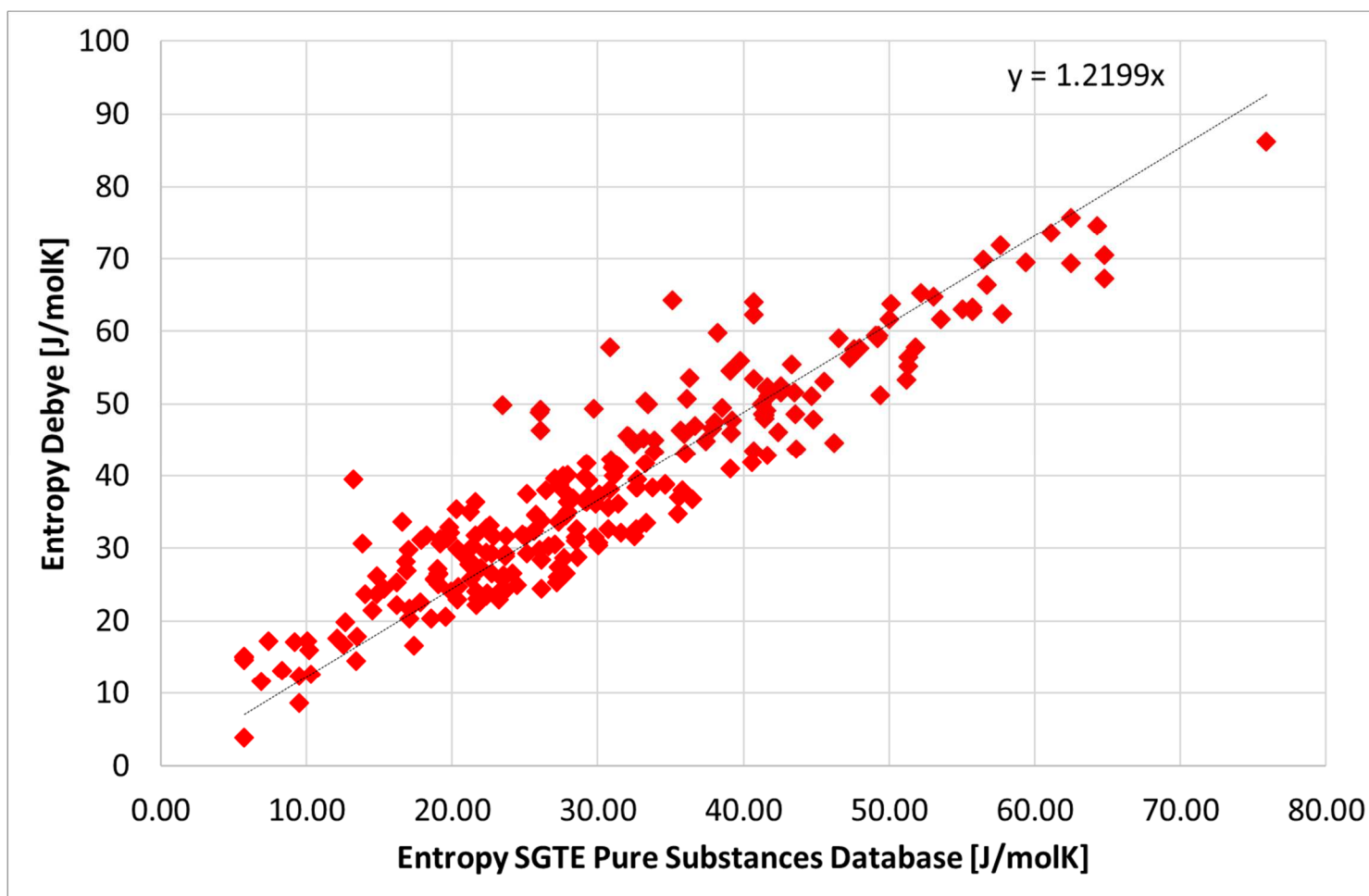
~~= 0 (3rd law)~~




Neumann-Kopp for S^{298K}



Alternative: S^{298K} from Debye model



Chemical Compound Space

		aiMP 1.0
Number of phases		67'000
T-ranges		298 - 5000 K
Solution phases		--- (soon: solid)
origin		materialsproject.org + extrapolation

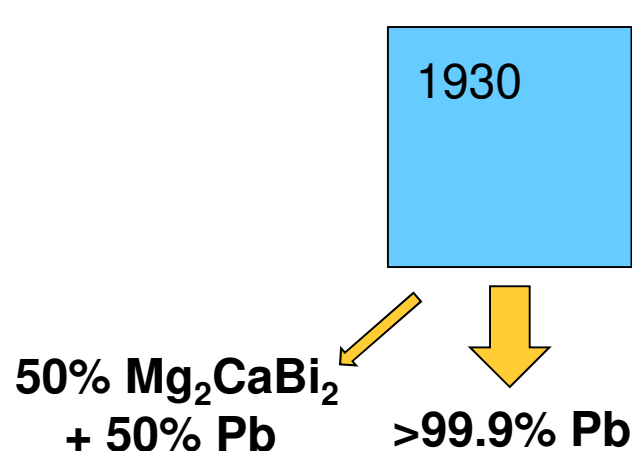


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		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	



Pb-5%Bi

WHAT ARE THE ALTERNATIVES?

~ 70 possible elements

~ 2500 possible binary combinations



Rational Process and Materials Design


MATERIALS INFORMATICS:

Test ALL ~2500 combinations Pb-Bi-X-Y

aiMP1.0 + SGTE Solutions + 50 lines of simple macro code in



→ 53 systems Pb-Bi-X-Y as good as Pb-Bi-Ca-Mg

H		MATERIALS INFORMATICS: Test ALL ~2500 combinations Pb-Bi-X-Y																He
Li	Be	aiMP1.0 + SGTE Solutions + 50 lines of simple macro code in																Ne
Na	Mg																	Ar
K	Ca	→ 53 systems Pb-Bi-X-Y as good as Pb-Bi-Ca-Mg																Kr
Rb	Sr																	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Rational Process and Materials Design

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Li	Be																	B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
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Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds														
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						



Conclusions

- aiMP is a CalPhaD compatible database integrated in FactSage based on
 - materialsproject.org
 - Empirical corrections to *ab initio* calculated enthalpy of formation
 - Empirical models for C_p and $S^{298K\#}$
- aiMP can be used for quickly scanning chemical compound space for radically different processing solutions



Thank you for your attention!

