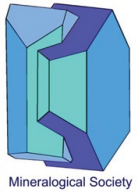
PHASE EQUILIBRIUM MODELING
APPROACHES AND PITFALLS

Part 1: Overview of thermodynamic databases

Pierre Lanari

Virtual workshop, May 10th to 14th 2021

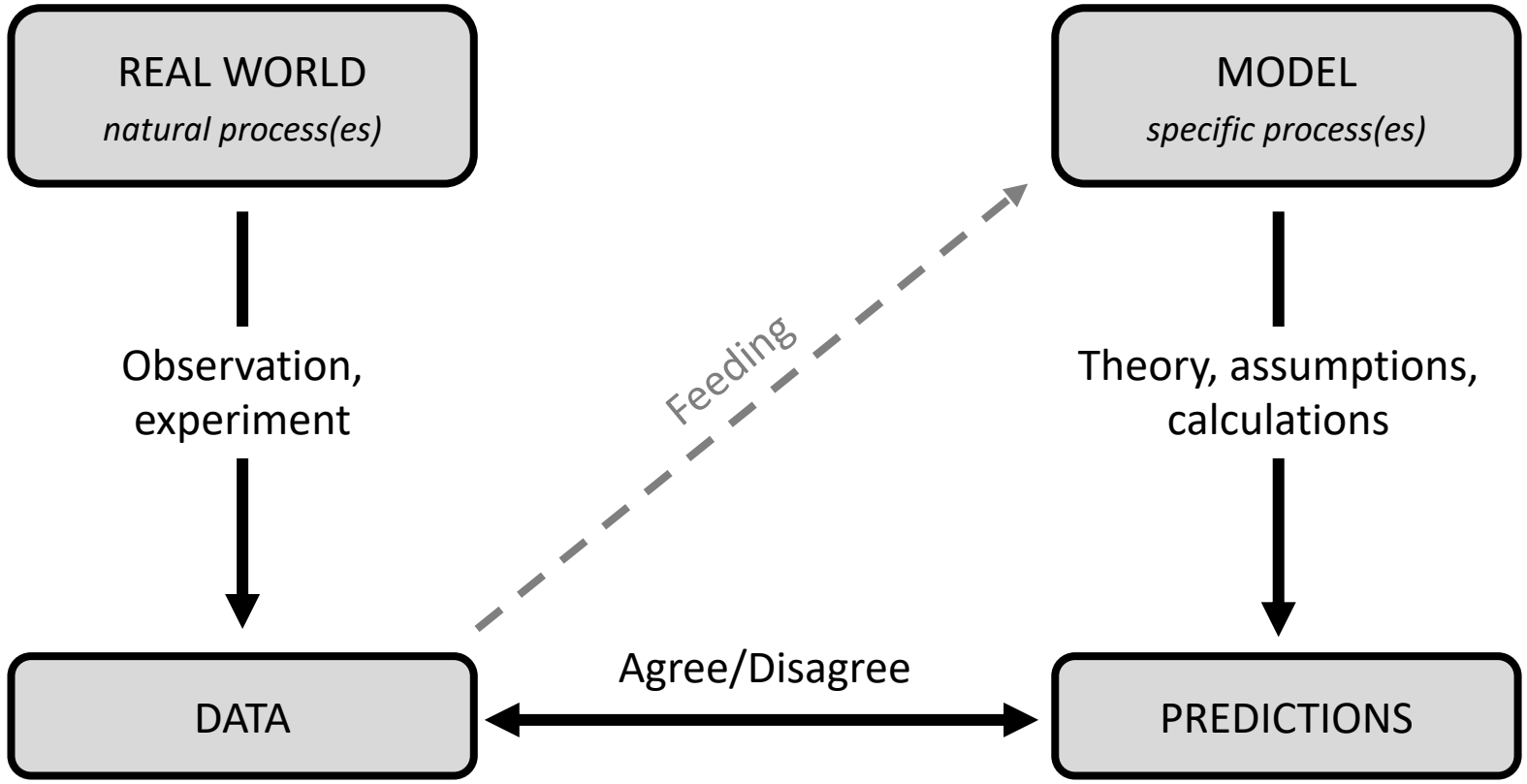
Objectives of this lecture

- Help understanding each part of a thermodynamic database
- Obtain a detailed view of the current offer in thermodynamic databases and modeling programs
- Understand some of the challenges of internal consistency and uncertainty evaluation
- Target future needs and research directions

As a beginner/novice in petrological modeling I should definitively be aware of this!

Part 1

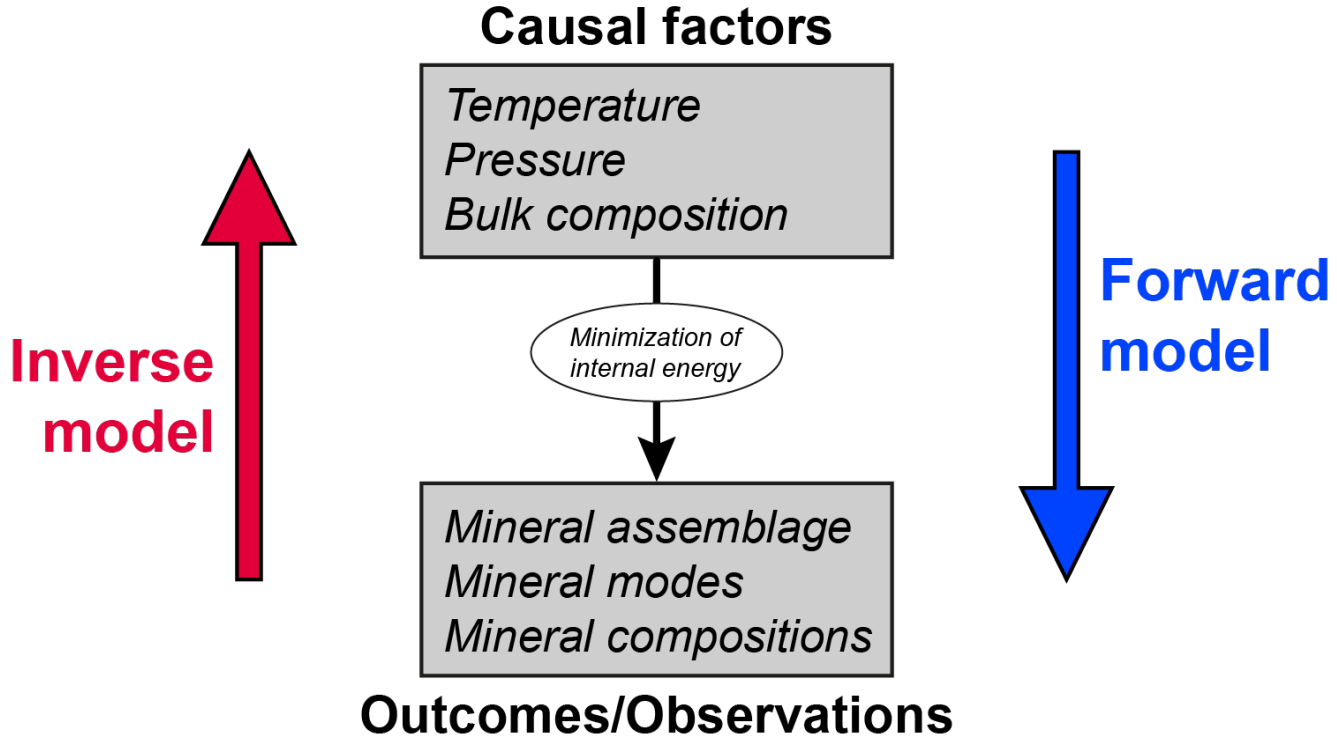
A **scientific model** is an imperfect or idealized representation of a physical system



Models must have a robust physical basis and be coupled with experiment/observation

Part 1

Modeling strategies based on equilibrium thermodynamics commonly used in metamorphic petrology



e.g. multi-equilibrium thermobarometry

THERMOCALC winTWQ

e.g. mineral assemblage diagrams (phase diagrams, pseudosections)

THERMOCALC Theriak-Domino Perple_X

Equilibrium condition: Minimization of one of the several energies in the system

At fixed pressure (*P)* and temperature (*T)*, the Gibbs energy is minimized at equilibrium

Apparent Gibbs energy of a phase

$$\Delta_a G^{P,T} = \Delta_f G^{P,T} + RT\ln(a)$$

$\Delta_a G^{P,T}$ is the apparent Gibbs energy of a mineral phase; $\Delta_f G^{P,T}$ is the standard Gibbs energy of formation of a phase from its constituent elements in their standard states; R the universal gas constant; a the activity of a phase in a solution.

- *Standard Gibbs energy of formation* of a phase (composition-independent term)

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,\mathrm{d}T - T\int_{T_0}^{T} \frac{Cp}{T}\,\mathrm{d}T + \int_{P_0}^{P} V\,\mathrm{d}P$$

$\Delta_f H^{P_0,T_0}$ and S^{P_0,T_0} are the enthalpy of formation from the elements or oxides and standard entropy at P_0 (1 bar) and T_0 (298.15 K); Cp is the heat capacity and V the molar volume of the phase

- *Activity* of a phase (composition-dependent term)

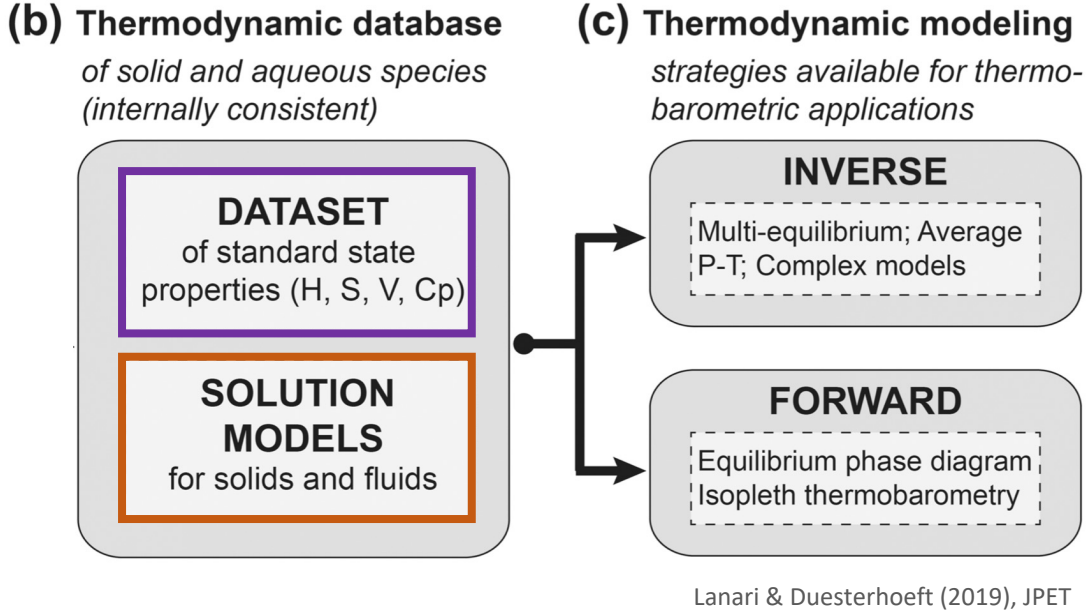
$$RT\ln(p)$$

For example, ideal activity with *p* the proportion of the phase in the solution

Composition-independent term

$$\Delta_a G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,dT - T\int_{T_0}^{T} \frac{Cp}{T}\,dT + \int_{P_0}^{P} V\,dP + RT\ln(a)$$

Composition-dependent term



Lanari & Duesterhoeft (2019), JPET

Any <u>thermodynamic database</u> of petrological interest must include:

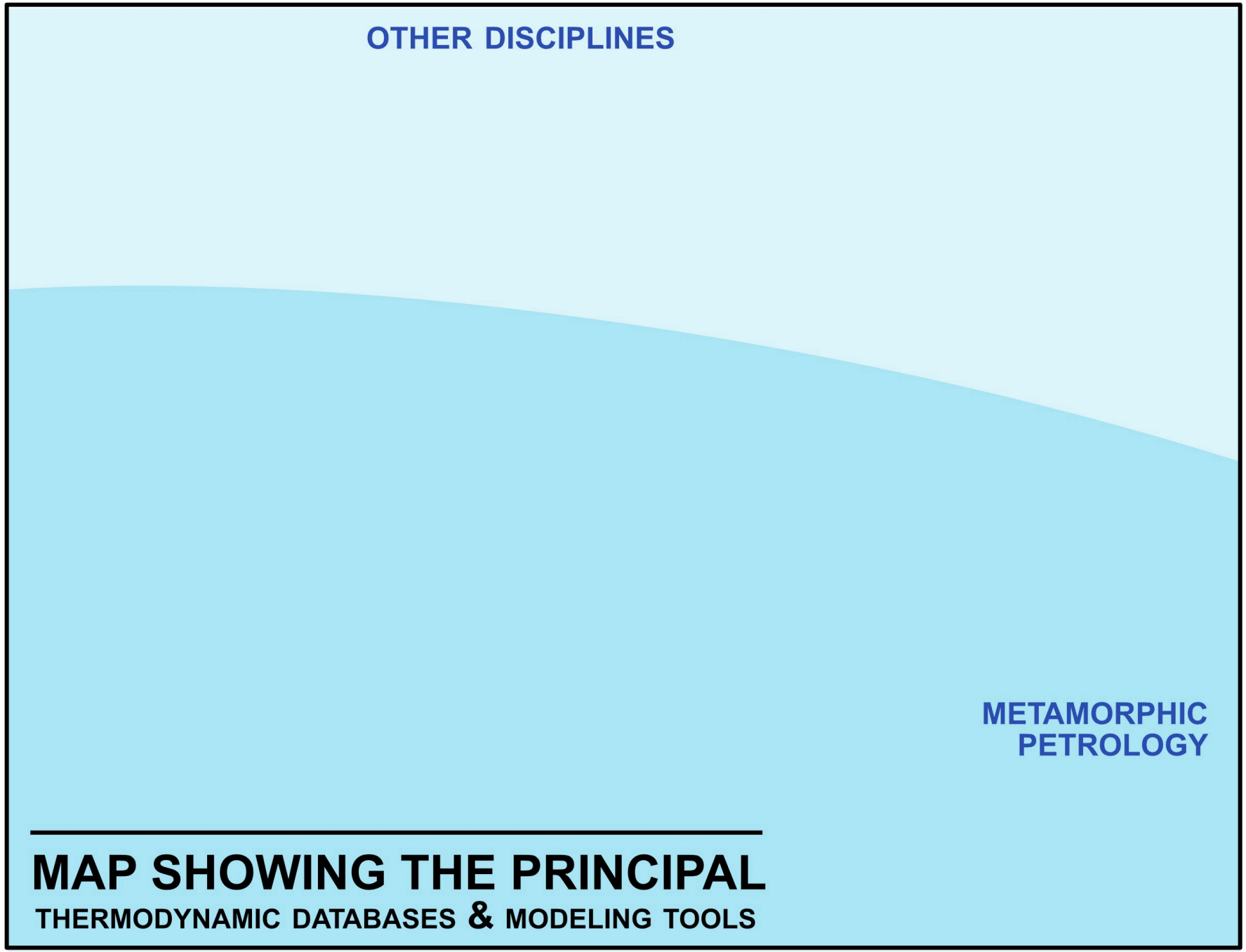
A dataset of standard state properties

- Enthalpy of formation, standard entropy and volume
- Heat capacity and volume functions

Solution models (activity or *a–X* models)

- Calculate the composition dependent term depending on the composition of the solution
- Includes ideal and non-ideal contributions

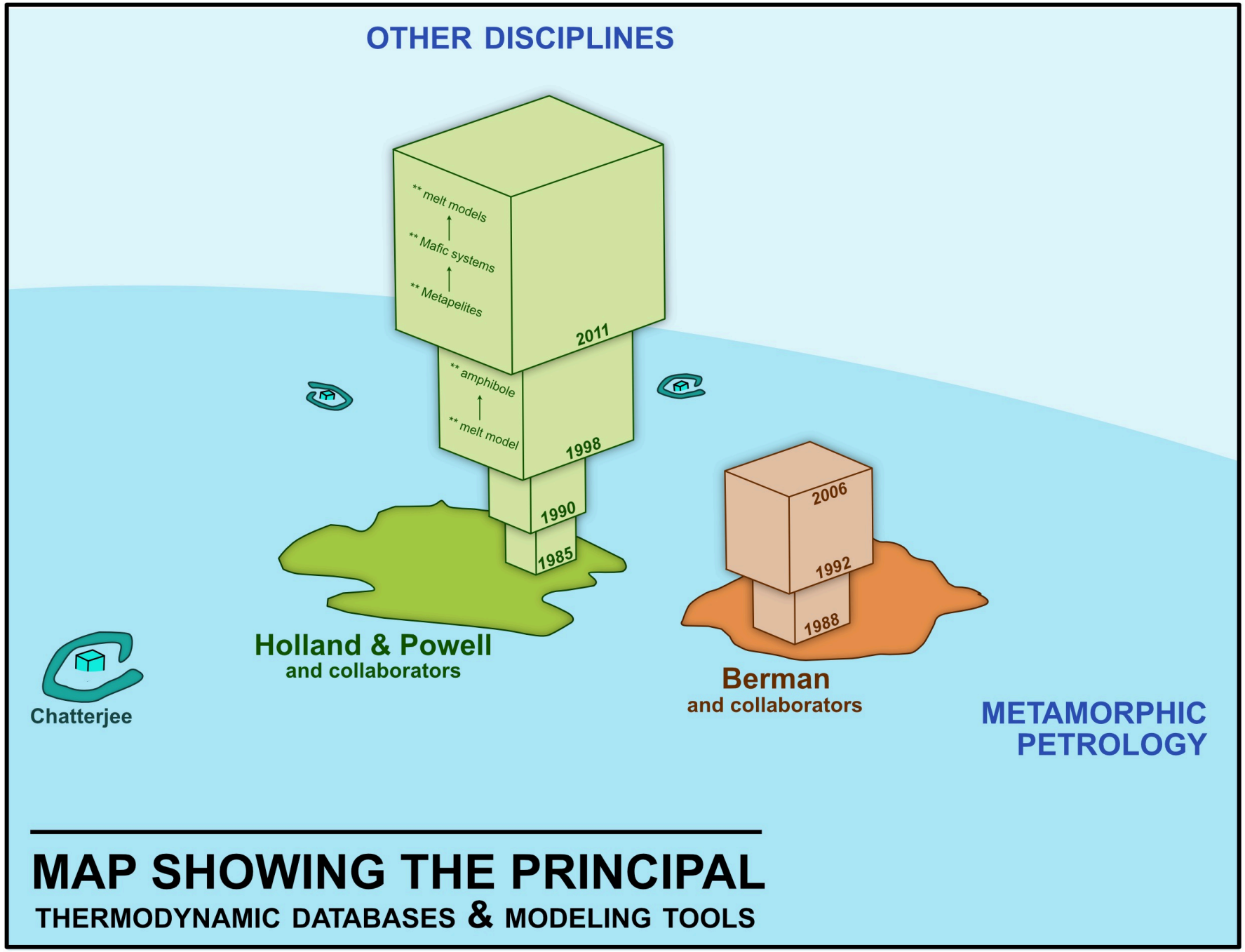
Part 1



PHASE EQUILIBRIUM MODELING

AN INTRODUCTION TO PETROLOGICAL MODELLING

Part 1



MAP SHOWING THE PRINCIPAL
THERMODYNAMIC DATABASES & MODELING TOOLS

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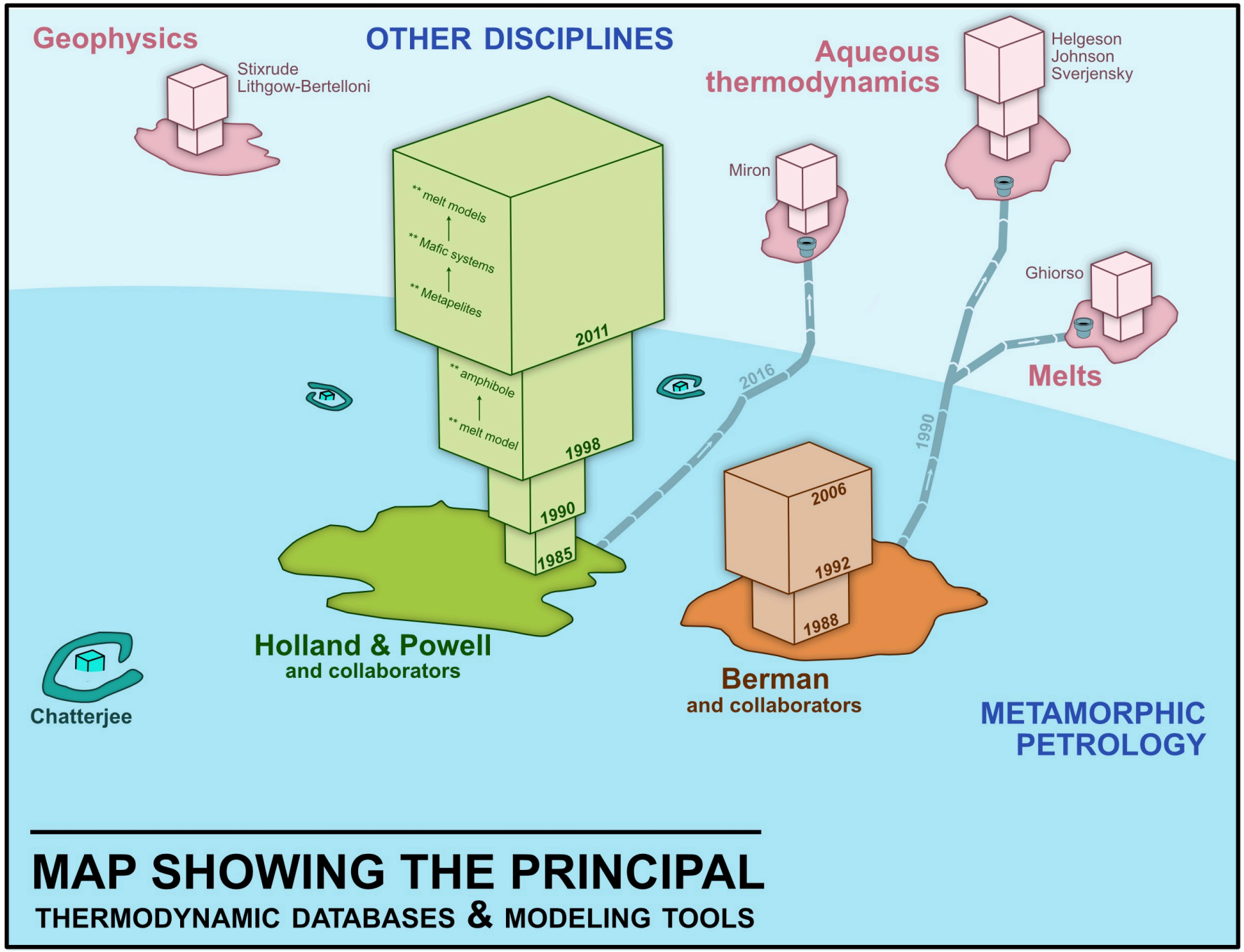

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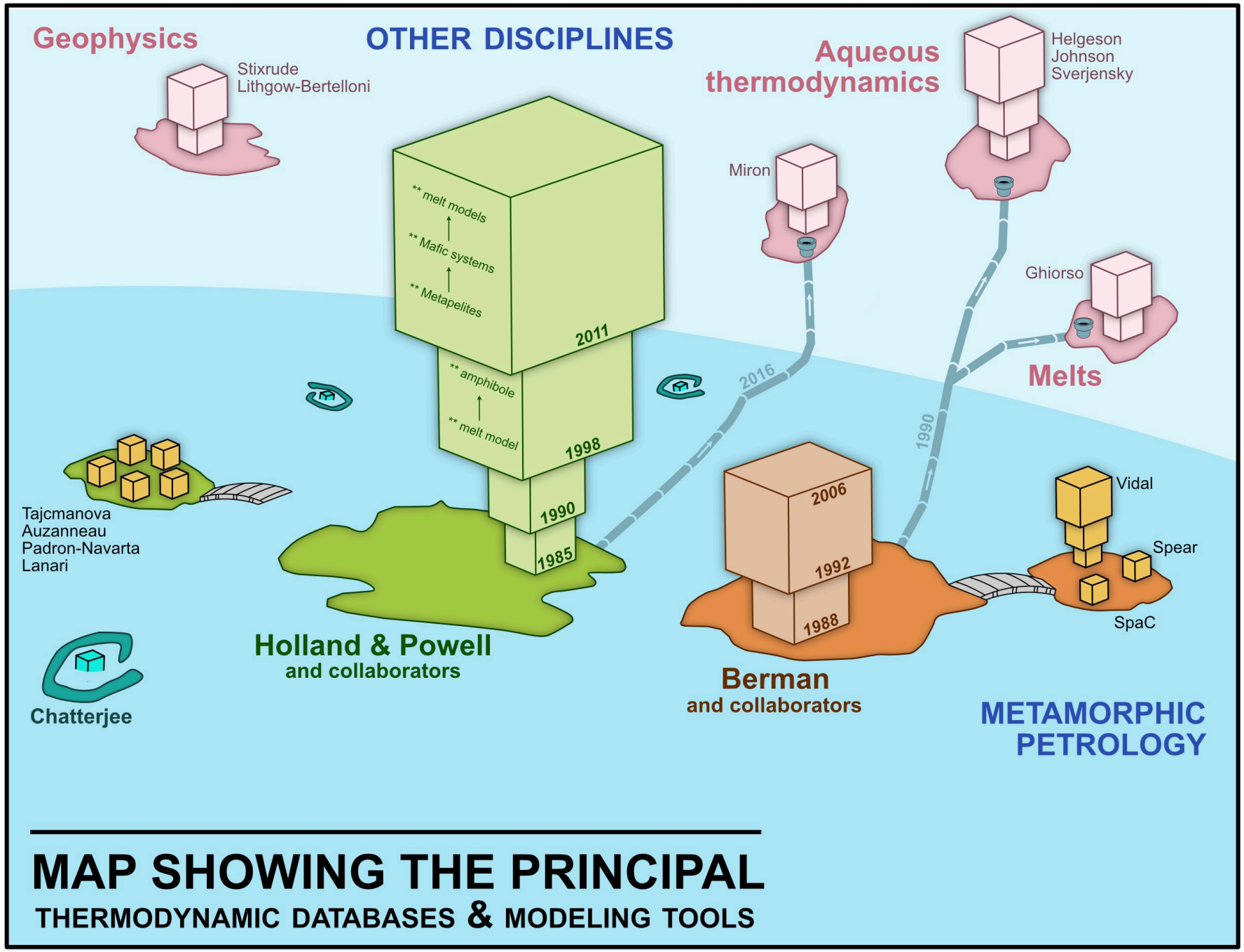

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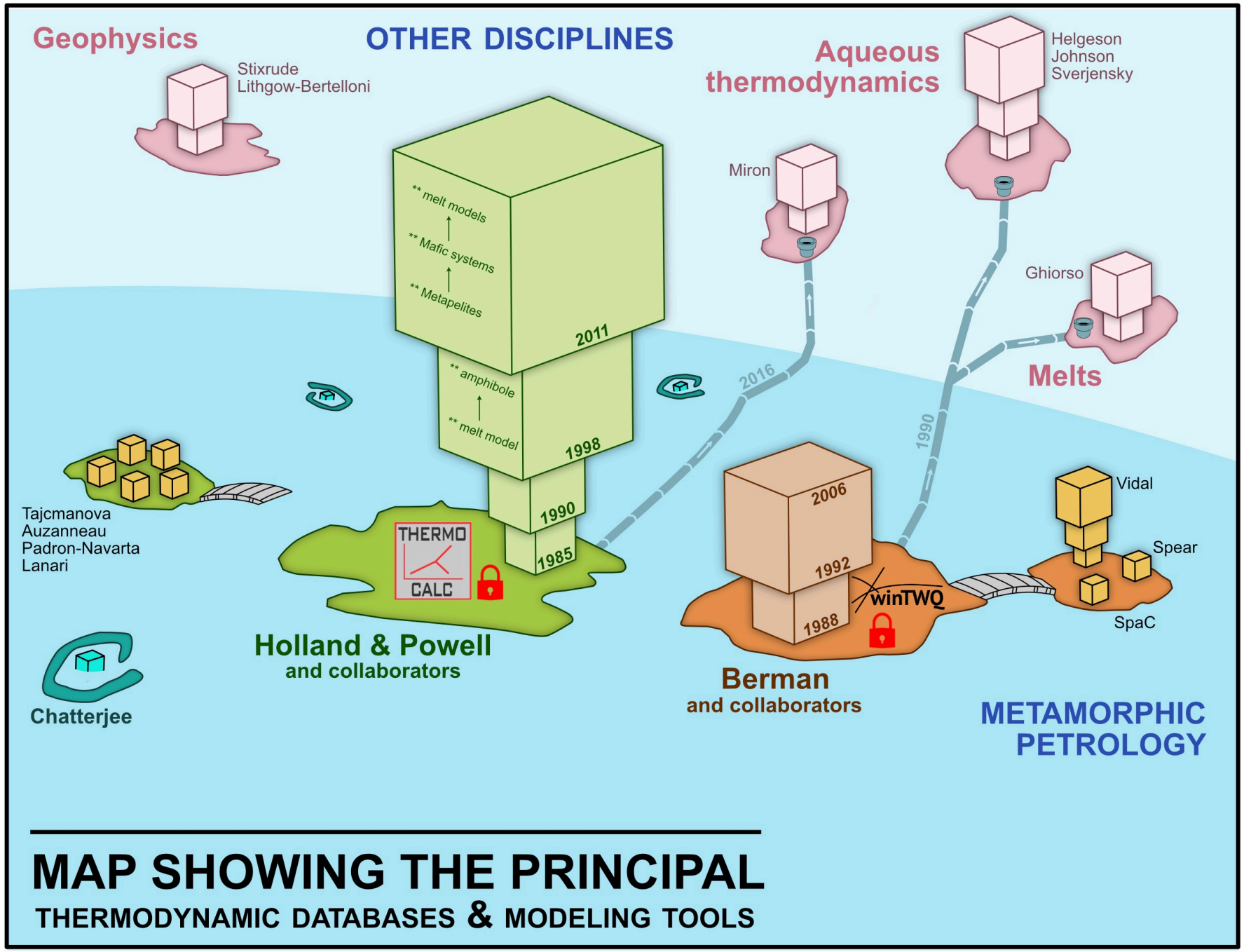

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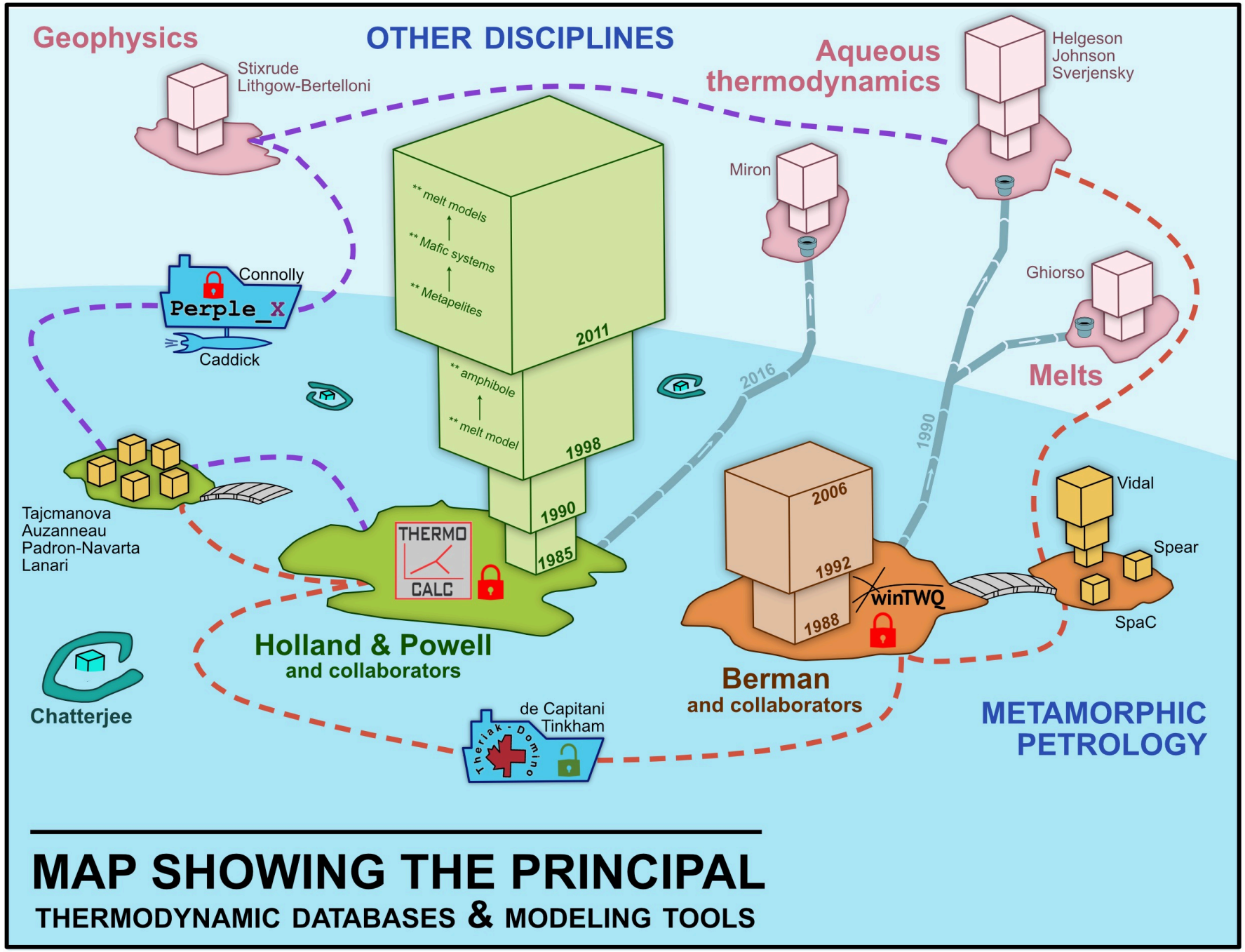

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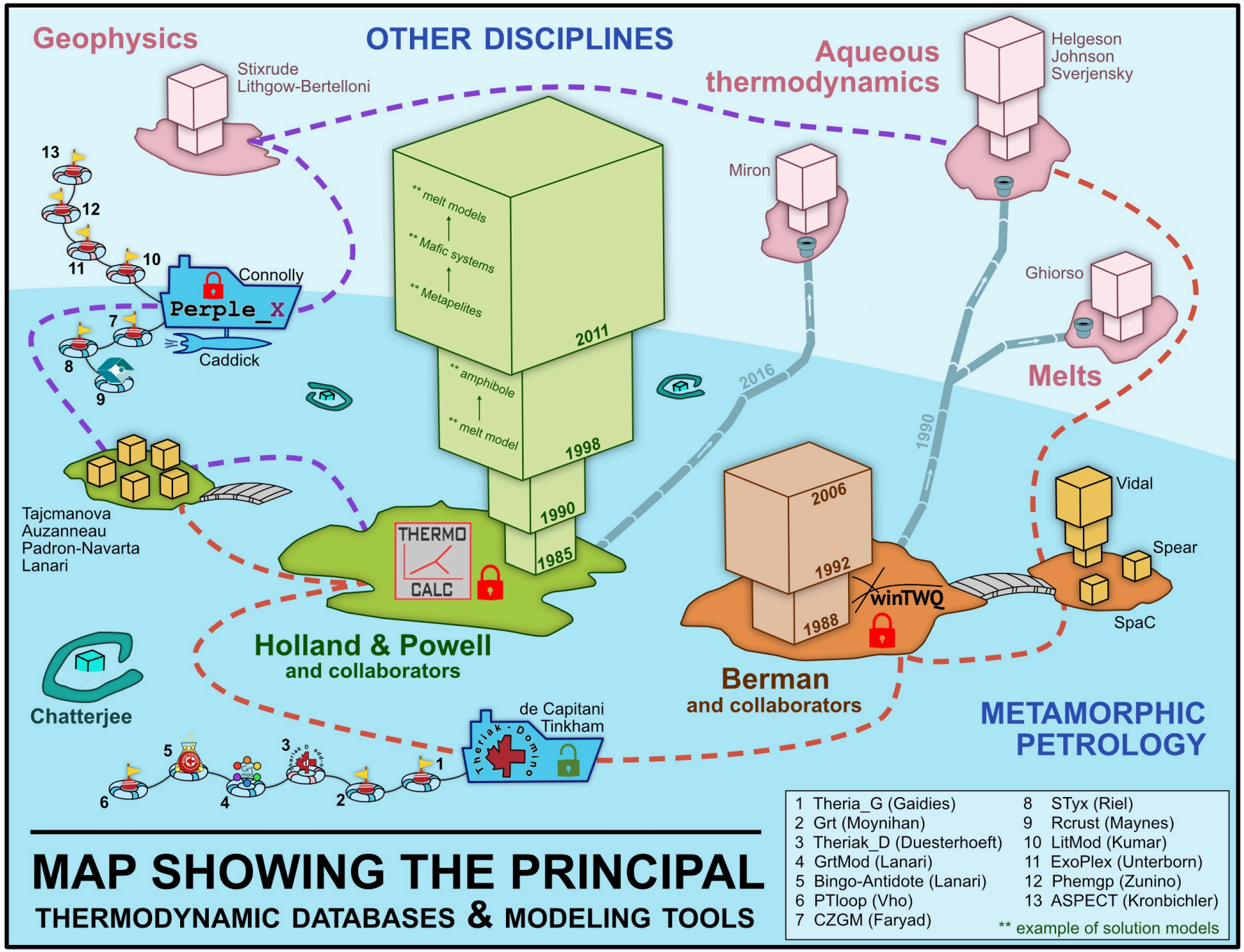

Internally consistent dataset

Table 2a. Molar thermodynamic properties (units: kJ, K, kbar) of the end-members whose formulae can be found in Table 1.

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				$\alpha\kappa$				ℓ
						a	b	c	d	α_0	κ_0	κ_0'	κ_0''	
Garnet and olivine	Almandine (alm)	−5260.65	1.31	342.00	11.525	0.6773	0	−3772.7	−5.0440	2.12	1900.0	2.98	−0.0016	
	Andradite (andr)	−5769.08	1.56	316.40	13.204	0.6386	0	−4955.1	−3.9892	2.86	1588.0	5.68	−0.0036	
	grossular (gr)	−6642.95	1.46	255.00	12.535	0.6260	0	−5779.2	−4.0029	2.20	1720.0	5.53	−0.0032	
	Knorringite (knor)	−5687.75	3.88	317.00	11.738	0.6130	0.3606	−4178.0	−3.7294	2.37	1743.0	4.05	−0.0023	
	Majorite (maj)	−6050.33	9.62	255.20	11.457	0.7136	−0.0997	−1158.2	−6.6223	1.83	1600.0	4.56	−0.0028	
	Pyrope (py)	−6282.13	1.06	269.50	11.313	0.6335	0	−5196.1	−4.3152	2.37	1743.0	4.05	−0.0023	
	Spessartine (spss)	−5693.65	3.14	335.30	11.792	0.6469	0	−4525.8	−4.4528	2.27	1740.0	6.68	−0.0038	
	Clinohumite (chum)	−9609.82	2.49	443.00	19.785	1.0700	−1.6533	−7899.6	−7.3739	2.91	1194.0	4.79	−0.0040	
	Fayalite (fa)	−1477.74	0.68	151.00	4.631	0.2011	1.7330	−1960.6	−0.9009	2.82	1256.0	4.68	−0.0037	
	Forsterite (fo)	−2172.57	0.57	95.10	4.366	0.2333	0.1494	−603.8	−1.8697	2.85	1285.0	3.84	−0.0030	
	Larnite (lrn)	−2307.04	0.90	127.60	5.160	0.2475	−0.3206	0	−2.0519	2.90	985.0	4.07	−0.0041	1
	Monticellite (mont)	−2251.31	0.52	109.50	5.148	0.2507	−1.0433	−797.2	−1.9961	2.87	1134.0	3.87	−0.0034	
	Tephroite (teph)	−1733.95	1.05	155.90	4.899	0.2196	0	−1292.7	−1.3083	2.86	1256.0	4.68	−0.0037	
Aluminosilicates	Andalusite (and)	−2588.72	0.68	92.70	5.153	0.2773	−0.6588	−1914.1	−2.2656	1.81	1442.0	6.89	−0.0048	
	Kyanite (ky)	−2593.02	0.67	83.50	4.414	0.2794	−0.7124	−2055.6	−2.2894	1.92	1601.0	4.05	−0.0025	
	Sillimanite (sill)	−2585.85	0.68	95.40	4.986	0.2802	−0.6900	−1375.7	−2.3994	1.12	1640.0	5.06	−0.0031	2
	Mullite (amul)	−2485.51	0.91	113.00	5.083	0.2448	0.0968	−2533.3	−1.6416	1.36	1740.0	4.00	−0.0023	
	Mullite (smul)	−2569.28	0.69	101.50	4.987	0.2802	−0.6900	−1375.7	−2.3994	1.36	1740.0	4.00	−0.0023	
	Chloritoid (fctd)	−3208.31	0.80	167.00	6.980	0.4161	−0.3477	−2835.9	−3.3603	2.80	1456.0	4.06	−0.0028	
	Chloritoid (mctd)	−3549.31	0.75	146.00	6.875	0.4174	−0.3771	−2920.6	−3.4178	2.63	1456.0	4.06	−0.0028	
	Chloritoid (mnctd)	−3336.20	1.68	166.00	7.175	0.4644	−1.2654	−1147.2	−4.3410	2.60	1456.0	4.06	−0.0028	
	Staurolite (fst)	−23 755.04	6.34	1010.00	44.880	2.8800	−5.6595	−10642.0	−25.3730	1.83	1800.0	4.76	−0.0026	
	Staurolite (mnst)	−24 246.42	8.60	1034.00	45.460	2.8733	−8.9064	−12688.0	−24.7490	2.09	1800.0	4.76	−0.0026	
	Staurolite (mst)	−25 124.32	6.28	910.00	44.260	2.8205	−5.9366	−13774.0	−24.1260	1.81	1684.0	4.05	−0.0024	
	Topaz (tpz)	−2900.76	0.96	100.50	5.339	0.3877	−0.7120	−857.2	−3.7442	1.57	1315.0	4.06	−0.0031	

Holland & Powell (2011), JMG

PHASE EQUILIBRIUM MODELING

AN INTRODUCTION TO PETROLOGICAL MODELLING

Part 1

J. metamorphic Geol. 1985, **3**, 343–370

An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results

T. J. B. HOLLAND, *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK*
ROGER POWELL, *Department of Geology, University of Melbourne, Parkville, Victoria 3052, Australia*

J. metamorphic Geol., 1990, **8**, 89–124

An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O–Na_2O–CaO–MgO–MnO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2–C–H_2–O_2

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J. metamorphic Geol., 1998, **16**, 309–343

An internally consistent thermodynamic data set for phases of petrological interest

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[2]*School of Earth Sciences, University of Melbourne, Parkville, Victoria 3052, Australia*

Journal of METAMORPHIC GEOLOGY

J. metamorphic Geol., 2011, **29**, 333–383 doi:10.1111/j.1525-1314.2010.00923.x

An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids

T. J. B. HOLLAND[1] AND R. POWELL[2]
[1]*Department of Earth Sciences, University of Cambridge, Cambridge, CB2 3EQ, UK*
[2]*School of Earth Sciences, The University of Melbourne, Victoria 3010, Australia (powell@unimelb.edu.au)*

Internally-Consistent Thermodynamic Data for Minerals in the System Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2

by R. G. BERMAN*

Department of Geological Sciences, University of British Columbia, Vancouver, B. C. Canada V6T 2B4

(*Received 16 March 1987; revised typescript accepted 7 October 1987*)

Contrib Mineral Petrol (1998) 133: 149–168

Niranjan D. Chatterjee · Ralf Krüger · Gerd Haller
Walter Olbricht

The Bayesian approach to an internally consistent thermodynamic database: theory, database, and generation of phase diagrams

Eur. J. Mineral.
1997, **9**, 175-223

Internally consistent thermodynamic data for rock-forming minerals in the system SiO_2-TiO_2-Al_2O_3-Fe_2O_3-CaO-MgO-FeO-K_2O-Na_2O-H_2O-CO_2

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+ compatible solution models & updates

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	Reference	Updates	Technique	Phases	Si	Al	Mg	Ca	Na	K	Ti	Fe	Fe3	Mn	Cr	Li	Be	Zn	Zr	Ni	Cu	Cu_3	Cl	S	H_2O	CO_2	O_2	Citations Google Scholar*
HP85	Holland & Powell (1985)	none	REG	43	x	x	x	x	x	x															x	x		225
B88	Berman (1988)	*JUN92; DEC06*	MAP	67	x	x	x	x	x	x	x	x	x												x	x		2138
HP90	Holland & Powell (1985)	none	REG	123	x	x	x	x	x	x	x	x	x	x											x	x	x	1273
G97	Gottschalk (1997)	none	IREG	94	x	x	x	x	x	x	x	x	x												x	x	x	180
C98	Chatterjee *et al.* (1998)	none	BAYES	148	x	x	x	x	x	x	x	x	x	x	x	x	x	x							x	x	x	79
HP98	Holland & Powell (1998)	*ds3.2; ds5.5*	REG	189	x	x	x	x	x	x	x	x	x	x					x	x					x	x	x	3707
HP11	Holland & Powell (2011)	*ds6.2*	REG	254	x	x	x	x	x	x	x	x	x	x	x				x	x	x	x	x	x	x	x	x	419

IREG is an iterative REG.
*In December 2017.

Lanari & Duesterhoeft (2019), JPET

Experimental data and optimization of standard state properties: constraints

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,\mathrm{d}T - T\int_{T_0}^{T} \frac{Cp}{T}\,\mathrm{d}T + \int_{P_0}^{P} V\,\mathrm{d}P$$

- **Direct measurement** of phase property

  Thermochemical, thermophysical, and volumetric properties of phase (e.g. calorimetric measurements for Cp and S; X-ray diffraction for V)

- **Approximation** based on fundamental relations "enthalpy and entropy of reactions"

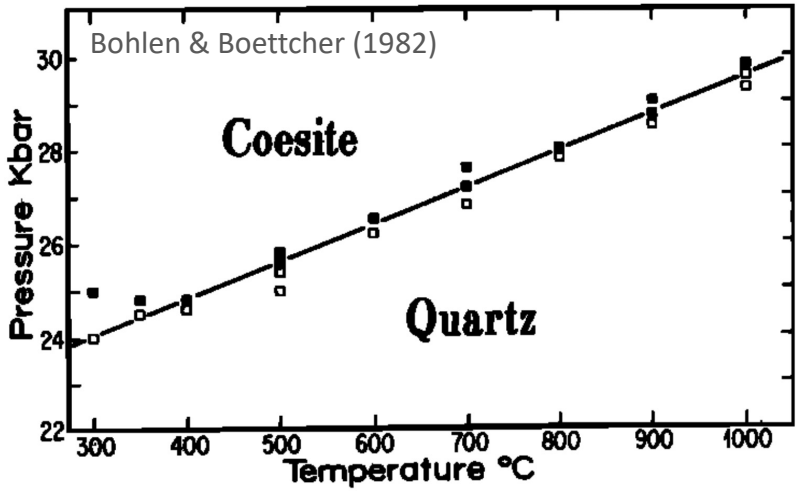
  $\Delta_f H^{P_0,T_0}$ of Qz = $\Delta H_f\ SiO_2$

  $\Delta_f H^{P_0,T_0}$ of And = $\Delta H_f\ SiO_2 + \Delta H_f\ Al_2O_3$

  Requires data for each polyhedral type; tabulated for enthalpy (large uncertainties): Chermak & Rimstidt (1989) for entropy: Holland (1989)

- **Indirect experiment** of reaction property data based on reaction reversal (bracketing) experiment

  e.g. reaction Qz = Coe



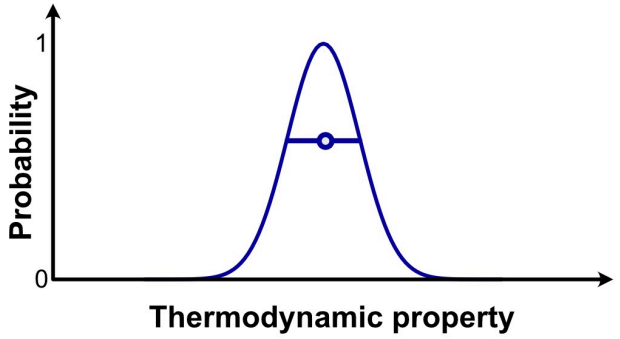
  Additional reactions:

  e.g. reaction Ab = Jd + Qz

Experimental data and optimization of standard state properties: uncertainties

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,\mathrm{d}T - T\int_{T_0}^{T} \frac{Cp}{T}\,\mathrm{d}T + \int_{P_0}^{P} V\,\mathrm{d}P$$

- **Direct measurement** of phase property



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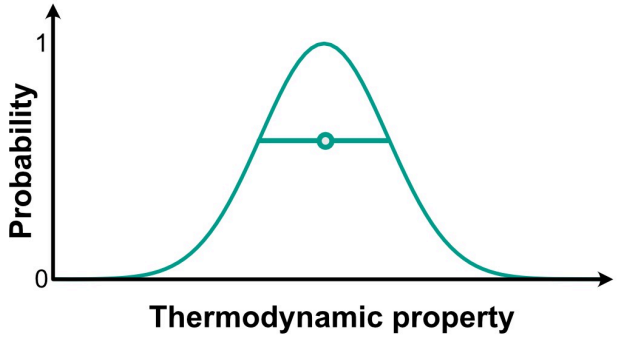

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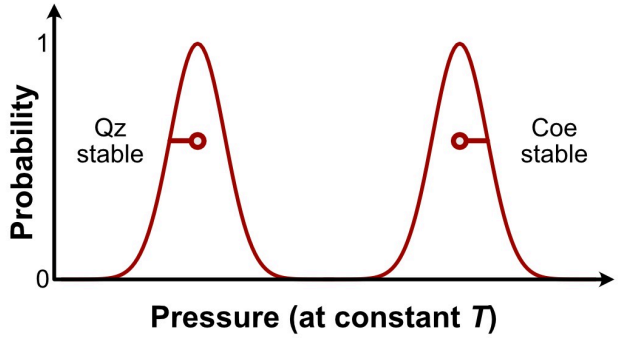
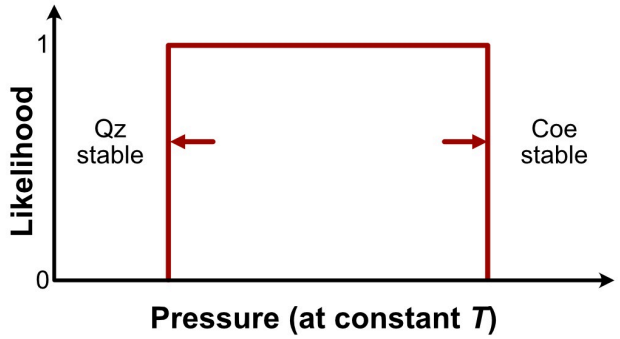




Phase Equilibrium Modeling

An introduction to petrological modelling

Part 1

Holland & Powell (1985)

REG

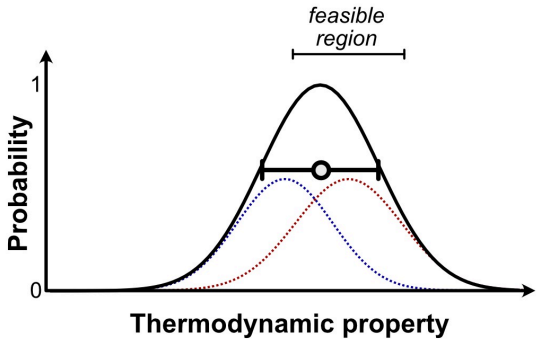
Least square regression

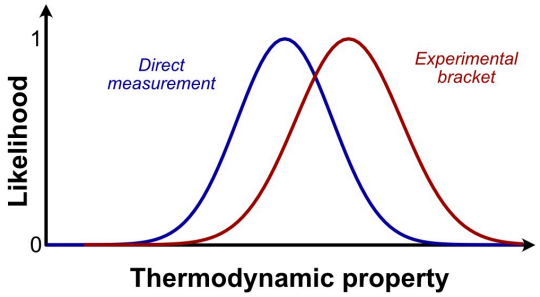
The weighted mid-points of brackets are treated as positions where $\Delta_r G^{P,T} = 0$

Minimize square of residuals: unique solution and it does not ensure consistency

Pseudo-uncertainties extracted from the variance-covariance matrix

Easy to calculate





Berman et al. (1986)

MAP

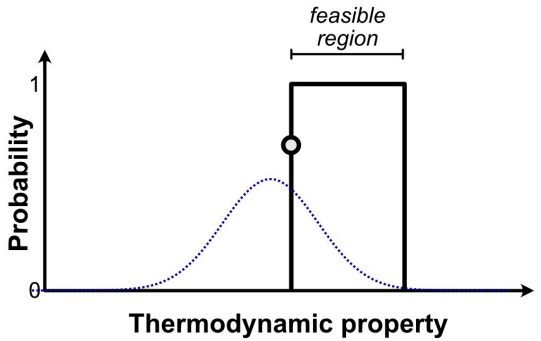
Mathematical programming

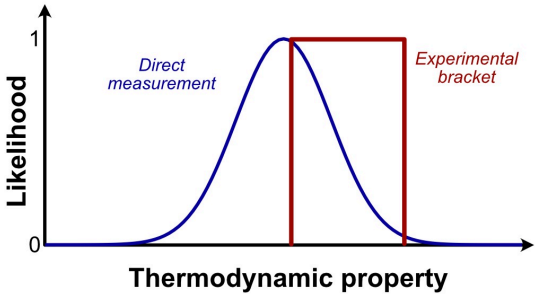
Each half-bracket is treated as a statement of inequality in $\Delta_r G^{P,T}$

Range of solution with MAP, which ensures the consistency with all selected data

No uncertainties

Easy to calculate, but requires some preparation and checking





Chatterjee et al., (1998)

BAYES

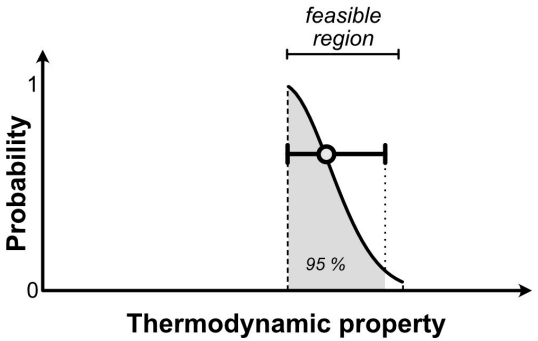
Bayes method

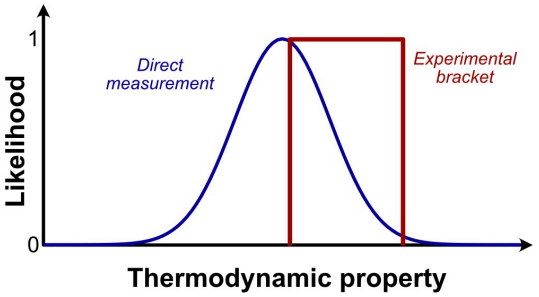
Each half-bracket is treated as a statement of inequality in $\Delta_r G^{P,T}$

Approximate the mean of the posterior distribution and the uncertainty region

Uncertainties extracted from the variance-covariance matrix

Complex to calculate, requires extensive Monte-Carlo mapping





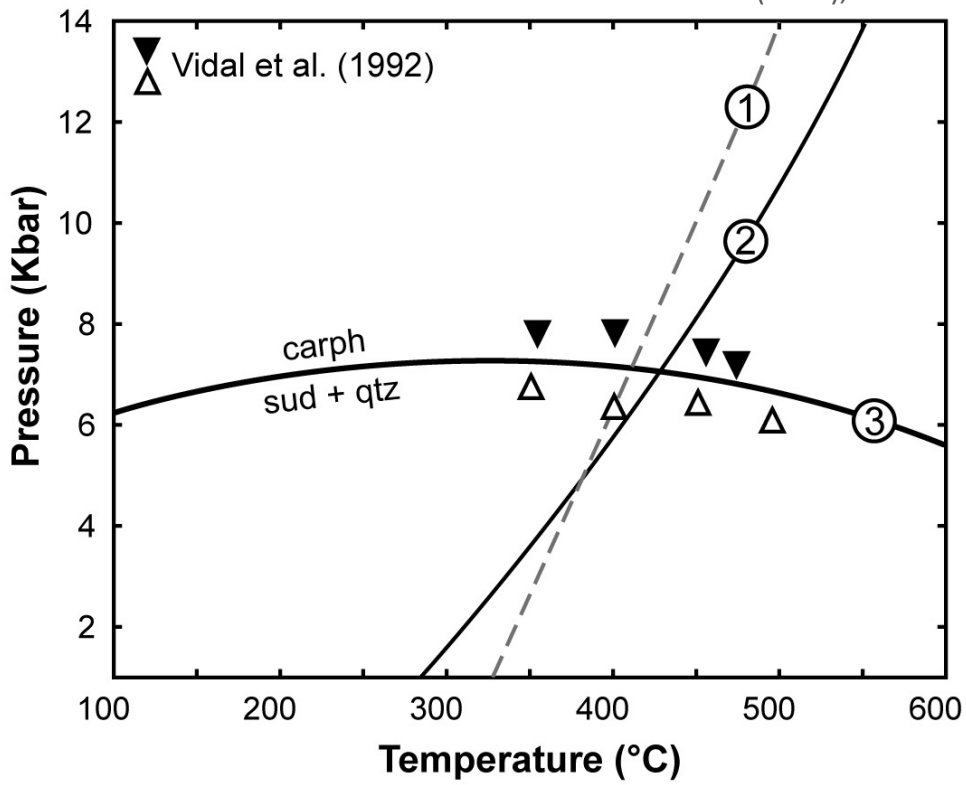
Example: only $\Delta_f H^{P_0,T_0}$ values are adjusted during the global optimization in REG.

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,dT - T\int_{T_0}^{T} \frac{Cp}{T}\,dT + \int_{P_0}^{P} V\,dP$$

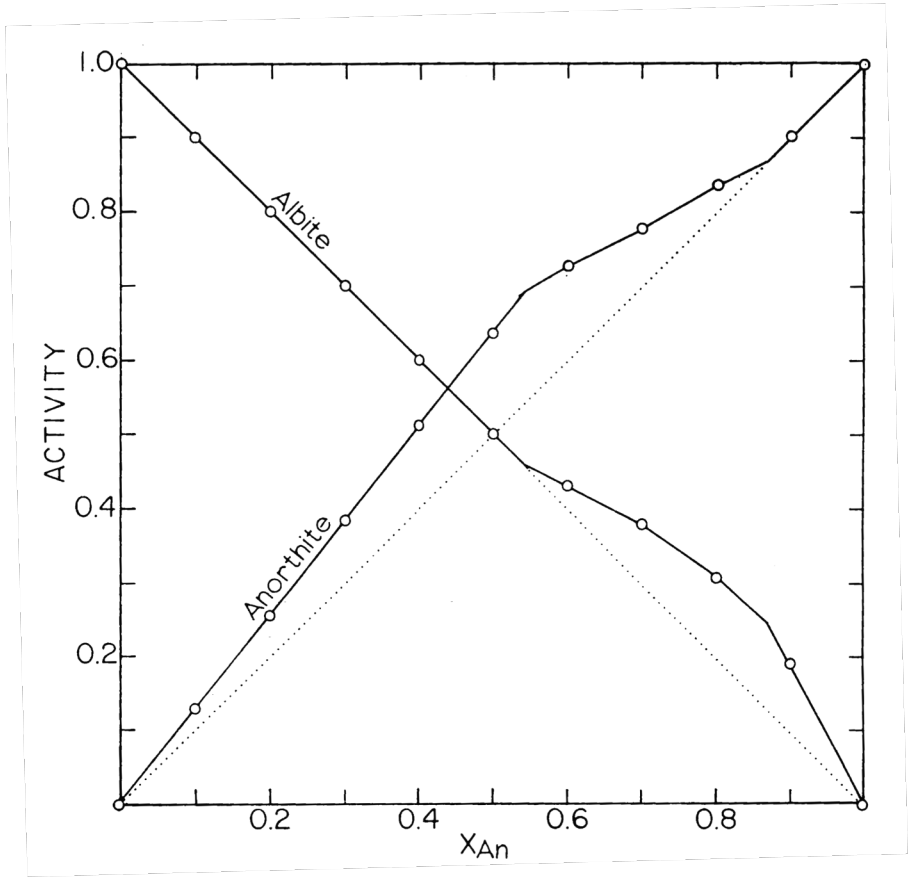
$\sigma_{\Delta_f H}$

- If any other thermodynamic property or function holds a large uncertainty or its value incorrectly determined, it will add to the total uncertainty of $\Delta_f H^{P_0,T_0}$ (e.g. S^{P_0,T_0})
- No inequalities, the $\Delta_r G^{P,T}$ is used instead
- There are cases for which these errors remain undetected!

Lanari et al. (2014), CMP



Activity models



Orville (1972), AJS

Activity models

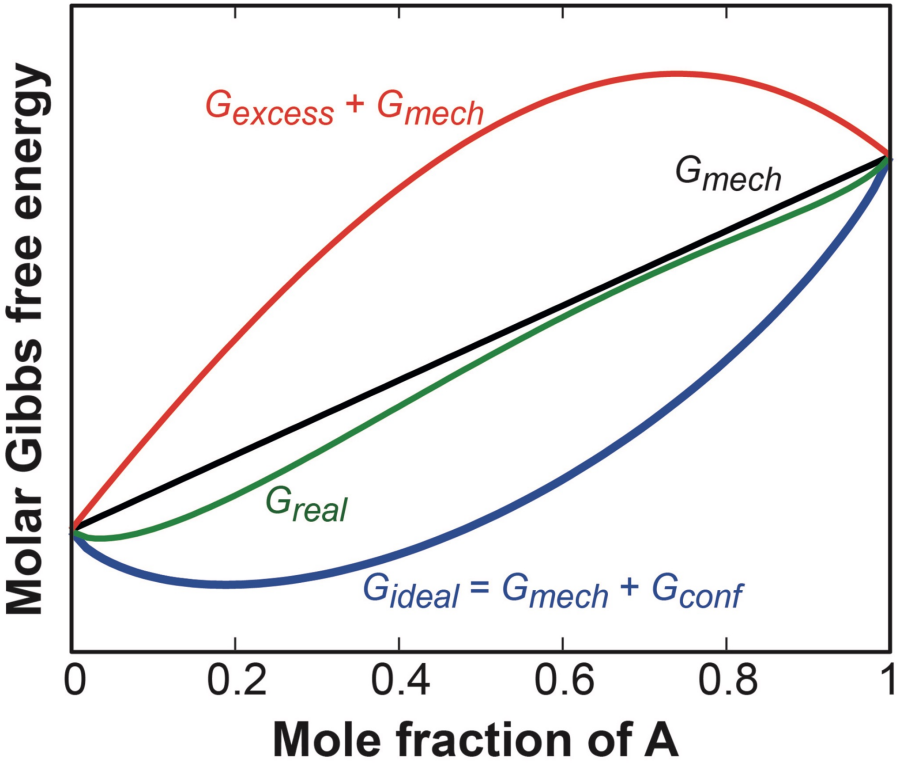
- Mechanical mixture

$$G_{\text{mech}} = X_1 \Delta_f G_1^{P,T} + X_2 \Delta_f G_2^{P,T}$$

- Reaction at given *P* and *T* without heat effect ($\Delta H_f = 0$) to form a single phase (ideal):

$$G_{\text{conf}} = -T\Delta S_{\text{sol}}$$

In the case of ideal mixing volume and enthalpies are the sum of the components ($\Delta H_{\text{ideal mixing}} = \Delta V_{\text{ideal mixing}} = 0$); entropy of the new solution increases with a larger number of possible arrangements.



- Excess energy (non-ideal) e.g. using *regular* and *asymmetrical sub-regular* models with three independent interaction energy parameters (Margules parameters):

$$W_G = \mathrm{W_H} - T\mathrm{W_S} + PW_V$$

Example: asymmetric multicomponent formulation Holland & Powell (2003)

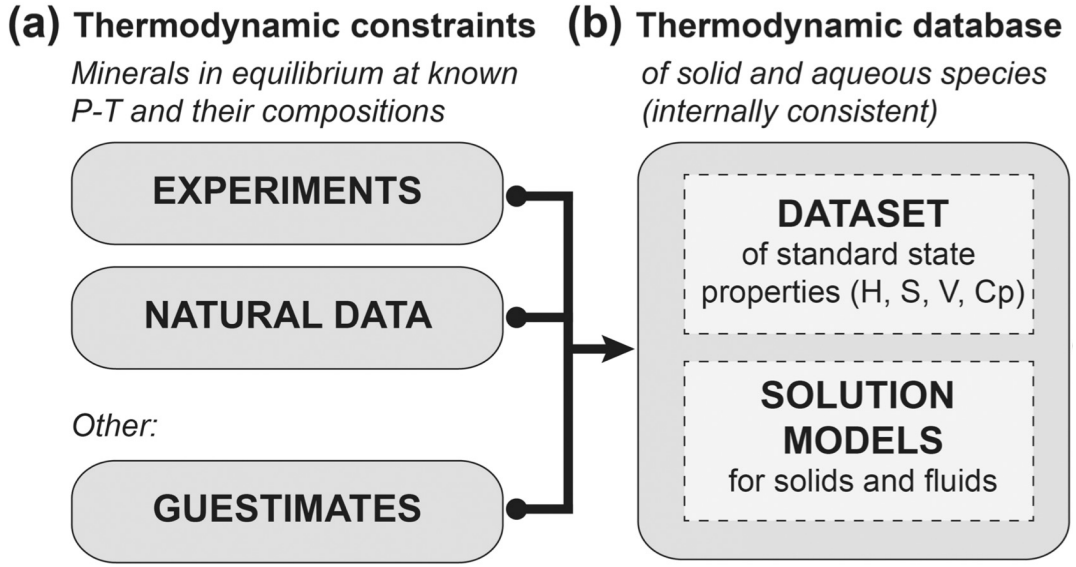
$$G_{excess} = \sum_{i=1}^{n-1} \sum_{j>1}^{n} \phi_i \phi_j \frac{2\sum_{l=1}^{n} \alpha_1 p_1}{\alpha_i + \alpha_j} W_{i,j}$$

	End-members	Margules (W)
Simple SS model	5	10 (x3)
Clinoamphibole (Green et al. 2016)	10	45 (x3)

Derivation of solution models for a given dataset (second step after the dataset)

Example: dataset ds6.2 (Holland & Powell 2011)

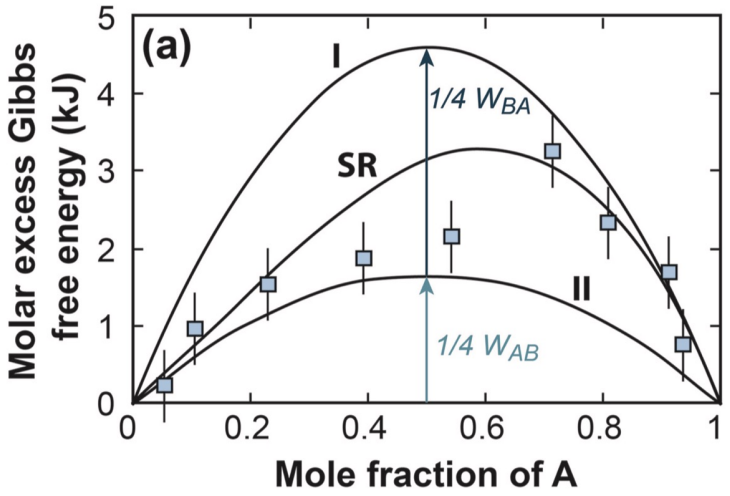
- Solution models for metapelites White et al. (2014a,b) JMG
- Solution models for mafic systems: Green et al. (2016), JMG



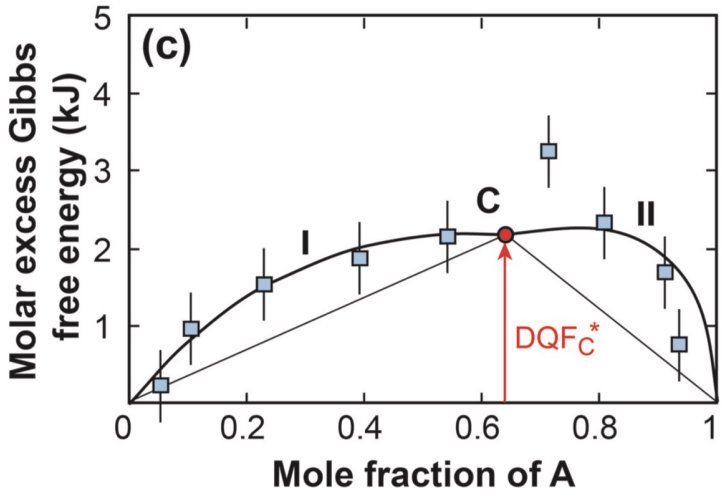
In practice several parameters are not optimized using an algorithm, but are either parametrized (e.g. Powell et al. 2014) or manually adjusted by trial and error and based on guestimates.

Part 1

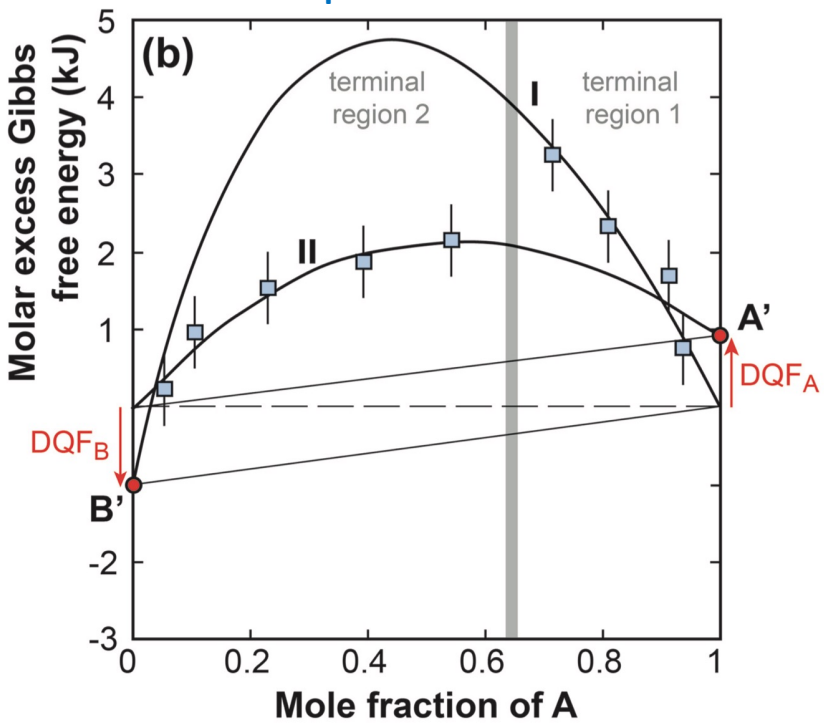
Regular and subregular models



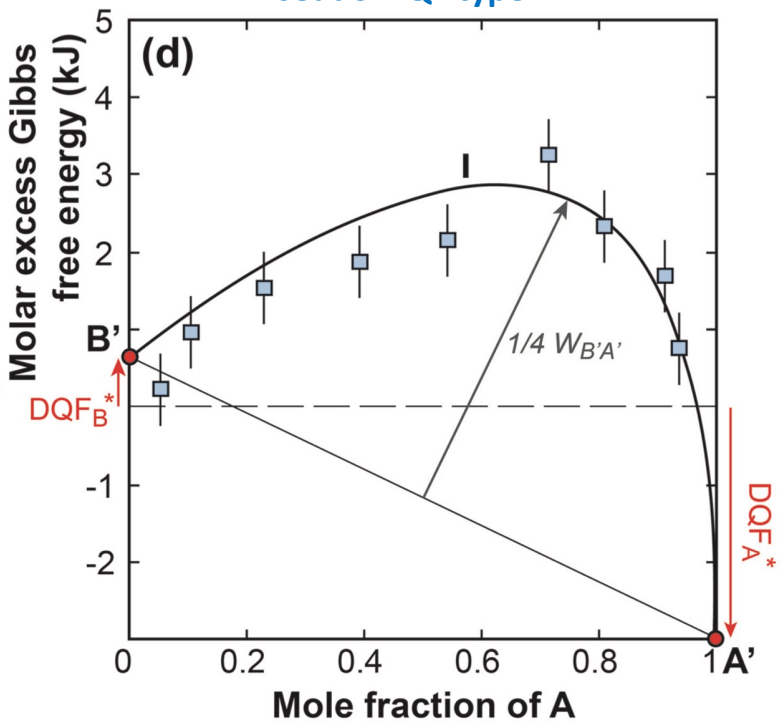
Pseudo-DQF type 1



Darken's quadratic formulation

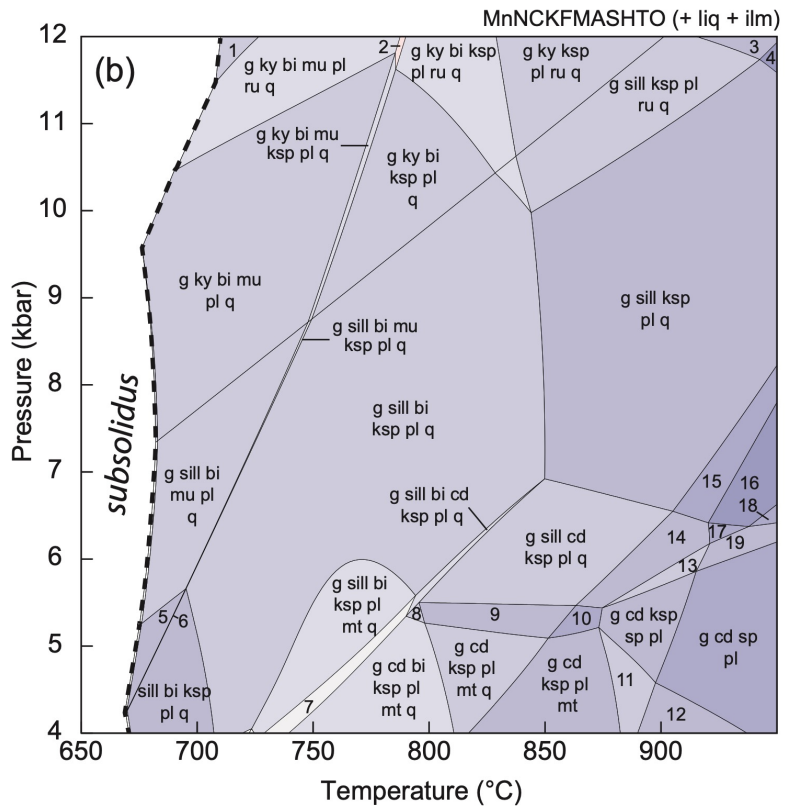


Pseudo-DQF type 2



Lanari & Duesterhoeft (2019), JPET

Thermodynamic databases



1: g bi mu pl ru q
2: g ky bi mu ksp pl ru q
3: g sill ksp ru q
4: g sill ksp q
5: sill bi mu pl q
6: sill ksp bi mu pl q
7: g sill cd bi ksp pl mt q
8: g cd bi ksp pl q
9: g cd ksp pl q
10: g cd ksp pl
11: g cd ksp sp pl mt
12: g cd sp pl mt
13: g sill cd ksp sp pl
14: g sill cd ksp pl
15: g sill ksp pl
16: g sill pl
17: g sill cd pl
18: g sill sp pl
19: g sill cd sp pl

Yakymchuk (2017), Geosc. Can.

Example: dataset HP98 (Holland & Powell 1998) + solution models:

Solution model	Reference
Chlorite	Holland et al. (1998)
Orthopyroxene	Powell & Holland (1999); White et al. (2002)
Chloritoid	White et al. (2000)
Melt	White et al. (2001; 2007)**
White mica	Coggon & Holland (2002)**
Feldspar	Holland & Powell (2003); Baldwin et al. (2005)
Clinopyroxene	Green, Holland & Powell (2007); Diener & Powell (2012)
Garnet, Ilmenite, Biotite, Spinel	White et al. (2007)**
Amphibole	Dale et al. (2003; 2005); Diener, Powell & White (2007); Diener & Powell (2012)

** some of the standard state properties were adjusted

Non-official solution models:

Solution model	Reference
Biotite	Tajcmanova et al. (2009)
White mica	Auzanneau et al. (2010)
Antigorite	Padron-Navarta et al. (2013)
Chlorite	Lanari et al. (2014)

→ Internal consistency (as defined here) is usually not rigorously tested

Example: dataset ds6.2 (Holland & Powell 2011)

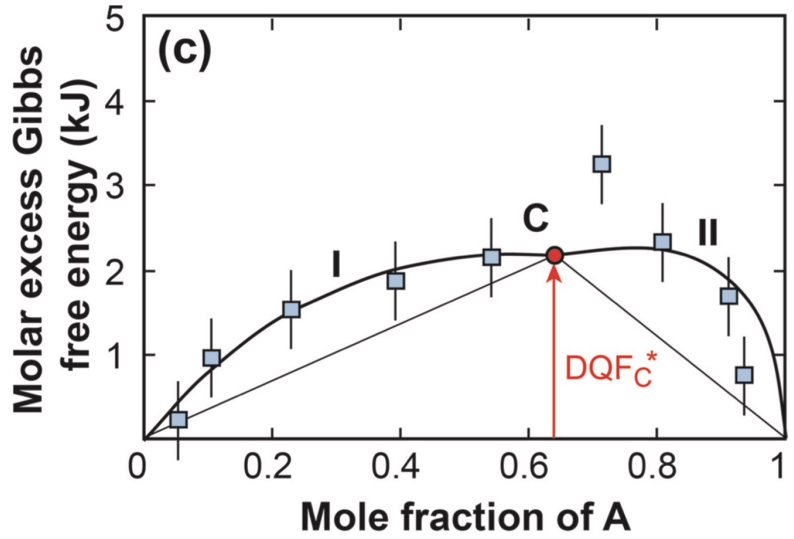
- Solution models for metapelites White et al. (2014) JMG

biotite

	M3					M12		T		V	
	Mg	Fe	Fe3	Ti	Al	Mg	Fe	Si	Al	OH	O
phl	1	0	0	0	0	2	0	1	1	2	0
ann	0	1	0	0	0	0	2	1	1	2	0
obi*	0	1	0	0	0	2	0	1	1	2	0
east	0	0	0	0	1	2	0	0	2	2	0
tbi*	0	0	0	1	0	2	0	1	1	0	2
fbi*	0	0	1	0	0	2	0	0	2	2	0

** phase not present in the internally-consistent dataset*

Pseudo-DQF type 1



Calculation of the apparent Gibbs energy for non-dataset endmembers:

$$G_{\mathrm{obi}} = \frac{1}{3} G_{\mathrm{ann}} + \frac{2}{3} G_{\mathrm{phl}} - 2\ \mathrm{kJ}$$

Reaction 1 obi = 1/3 ann + 2/3 phl + excess enthalpy term (ΔH)

$$G_{\mathrm{fbi}} = G_{\mathrm{east}} + \frac{1}{2} G_{\mathrm{and}} - \frac{1}{2} G_{\mathrm{grs}} - 3\ \mathrm{kJ}$$

$$G_{\mathrm{tbi}} = G_{\mathrm{phl}} + G_{\mathrm{ru}} - G_{\mathrm{br}} + 55\ \mathrm{kJ}$$

Example: dataset ds6.2 (Holland & Powell 2011)

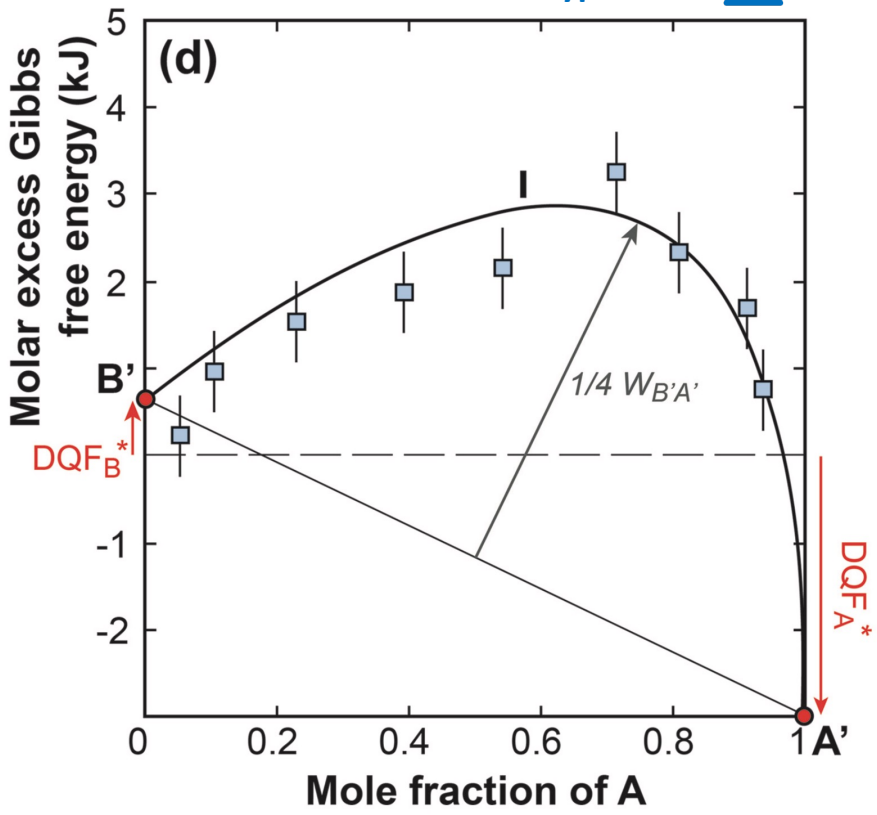
- Solution models for metapelites White et al. (2014) JMG

biotite

	M3					M12		T		V	
	Mg	Fe	Fe3	Ti	Al	Mg	Fe	Si	Al	OH	O
phl	1	0	0	0	0	2	0	1	1	2	0
ann	0	1	0	0	0	0	2	1	1	2	0
obi*	0	1	0	0	0	2	0	1	1	2	0
east	0	0	0	0	1	2	0	0	2	2	0
tbi*	0	0	0	1	0	2	0	1	1	0	2
fbi*	0	0	1	0	0	2	0	0	2	2	0

** phase not present in the internally-consistent dataset*

Pseudo-DQF type 2



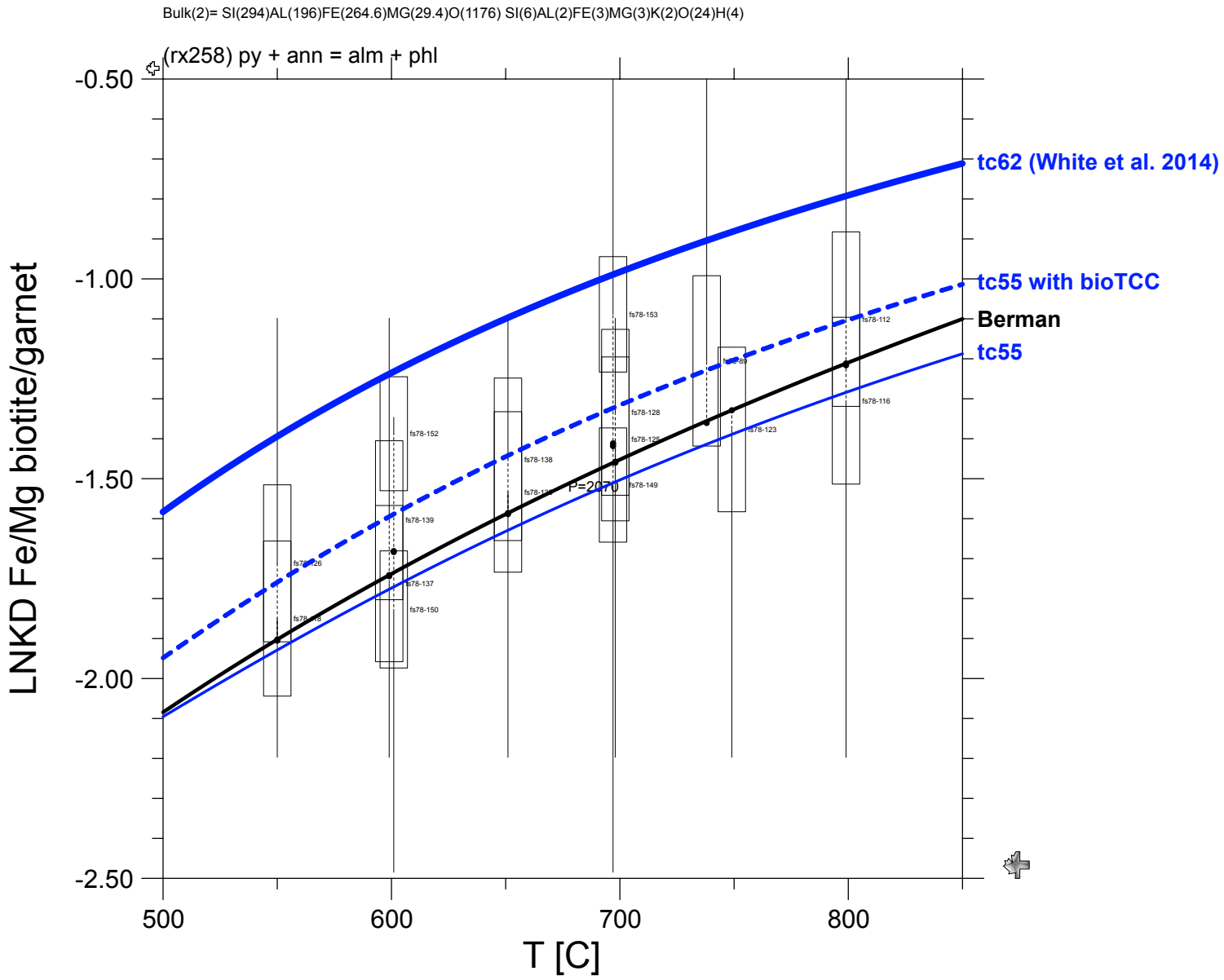
In addition, the enthalpy of annite had to be modified by $DQF_{ann} = -3$ kJ to make the phase equilibria behave sensibly, in particular because otherwise a number of well-constrained biotite-breakdown melting reactions occurred to unreasonably low T for FeO-rich biotite compositions. The necessity for this modification suggests a shortcoming in the a–x relations for biotite, but attempts to adjust the a–x relations to remove the necessity for this modification have so far been unsuccessful.

White et al. (2014), JMG

How does that affect internal consistency?

Part 1

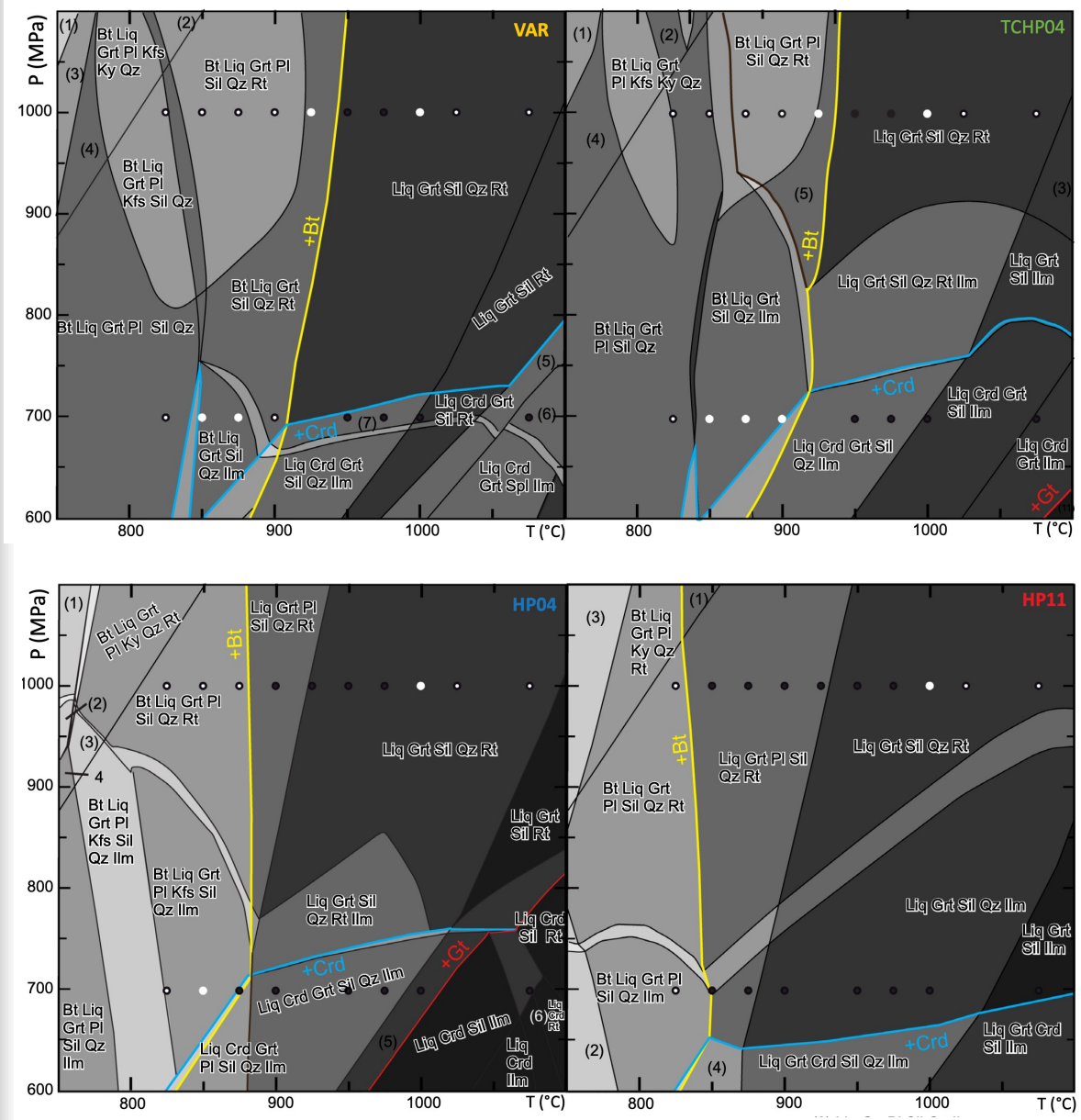
Database check (HP11 + W14) against primary data using **THERION** (from C. de Capitani)



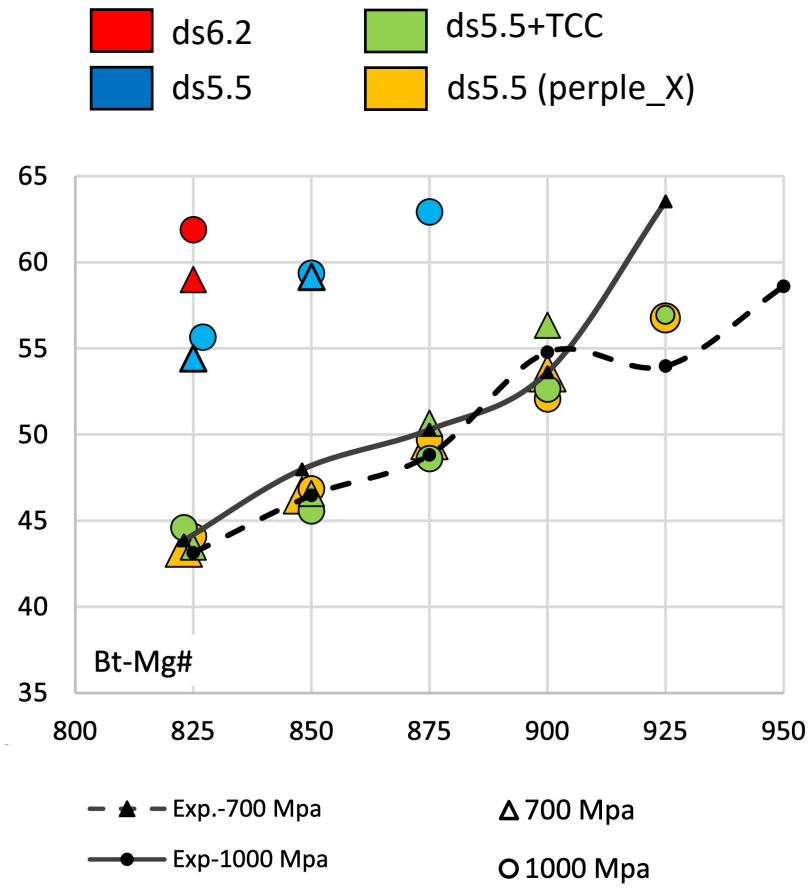
This figure was generated using THERION; experimental data are from Ferry & Spear (1978), CMP

Test of several databases against experimental data by Gervais & Trapy (2021)

e.g. experimental data from Patiño-Douce and Johnston (1991)



Mineral compositions



Gervais & Trapy (2021), CMP

Berman

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - TS^{P_0,T_0} + \int_{T_0}^{T} Cp\,dT - T\int_{T_0}^{T} \frac{Cp}{T}\,dT + \int_{P_0}^{P} V\,dP$$

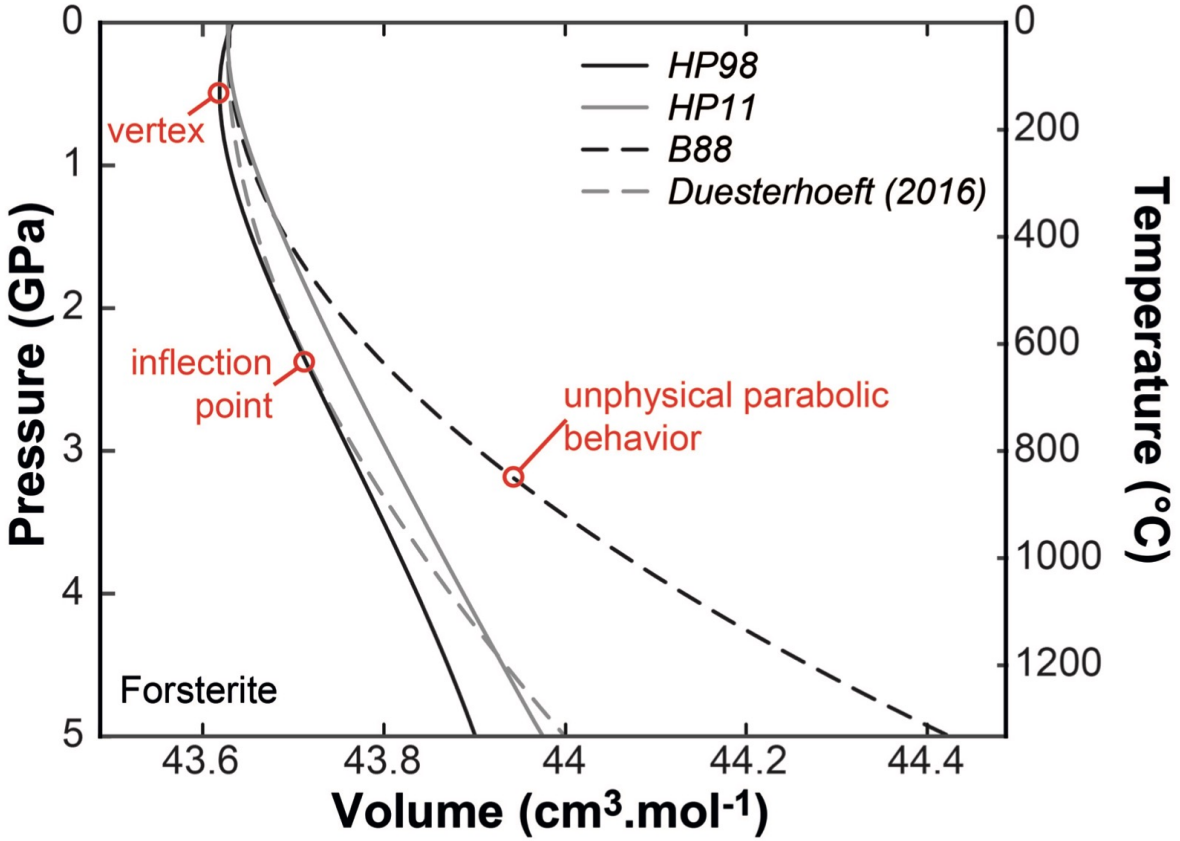
Holland & Powell

$\sigma_{\Delta_f H}$

For phase equilibrium modeling we need to calculate the apparent Gibbs energy of formation.

How reliable are other thermodynamic properties and functions?

- Volume



Lanari & Duesterhoeft (2019), JPET

Part 1

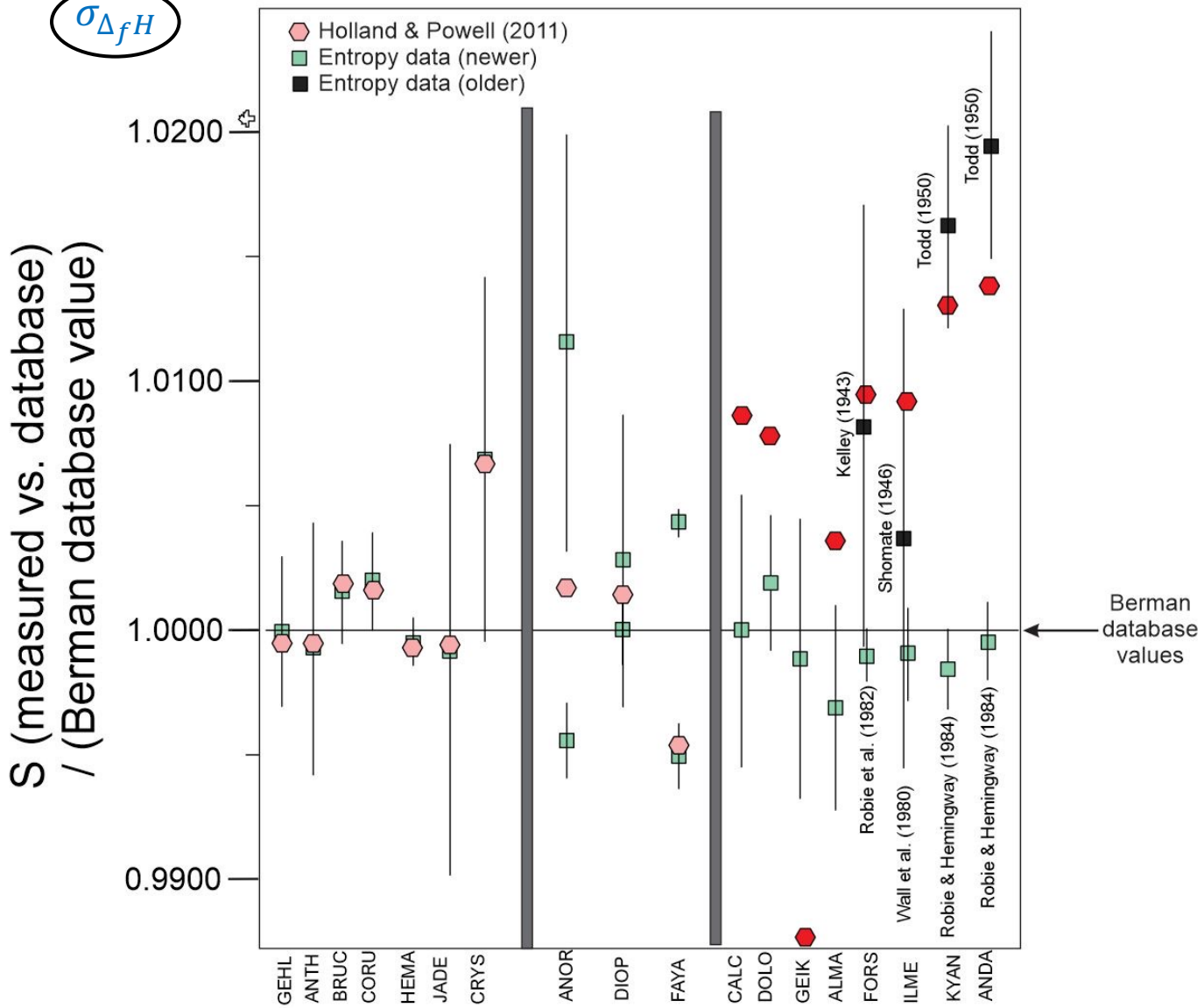
Berman

$$\Delta_f G^{P,T} = \Delta_f H^{P_0,T_0} - T S^{P_0,T_0} + \int_{T_0}^{T} Cp\,\mathrm{d}T - T\int_{T_0}^{T} \frac{Cp}{T}\,\mathrm{d}T + \int_{P_0}^{P} V\,\mathrm{d}P$$

Holland & Powell

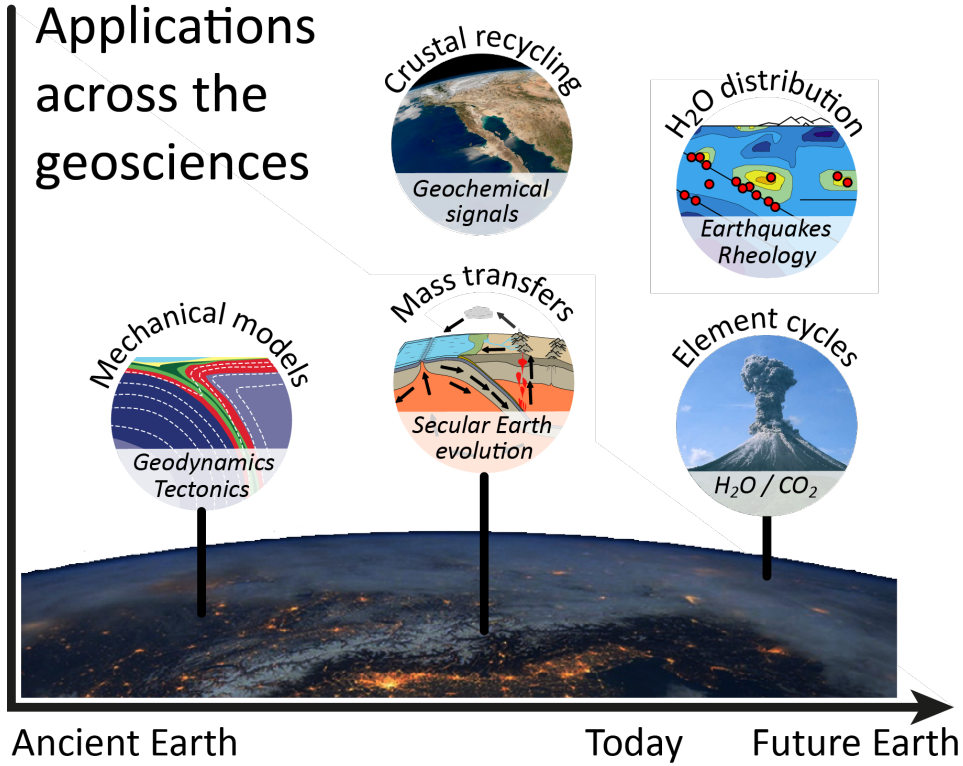
$\sigma_{\Delta_f H}$

- Entropy



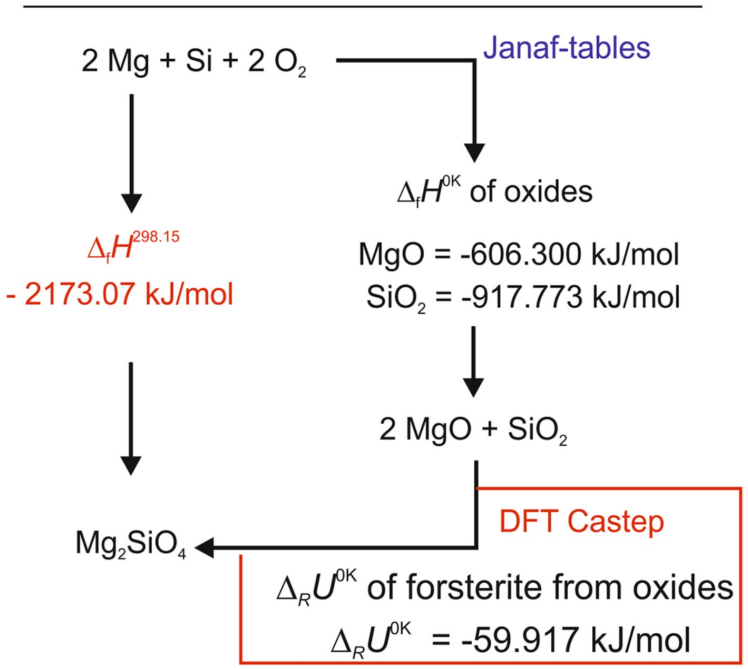
This figure was generated by Rob Berman using THERION from C. de Capitani

Perspectives



New **constraints** calculated from first principles (ab initio modeling)

Standard state properties



$$\Delta_R U^{0K} \approx \Delta_R H^{0K}$$

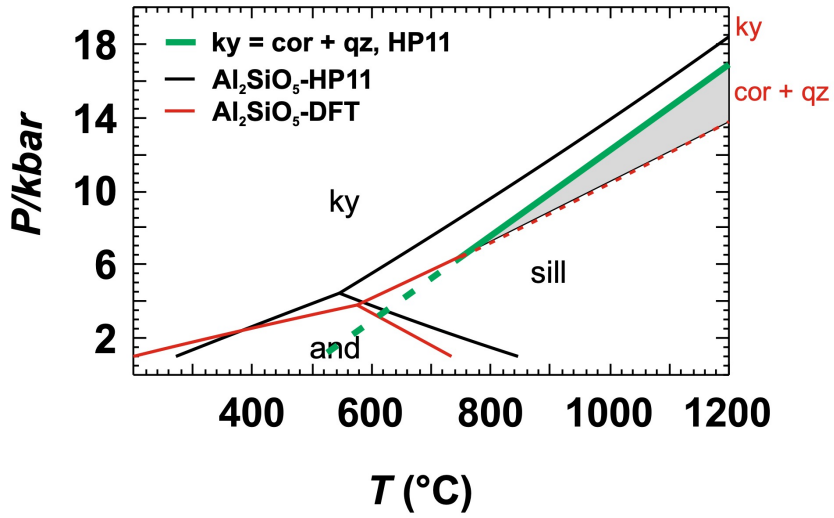
$$\Delta_f H^{0K}_{fo} = \Delta_R H^{0K} + 2\,\Delta_f H^{0K}_{MgO} + \Delta_f H^{0K}_{SiO2}$$

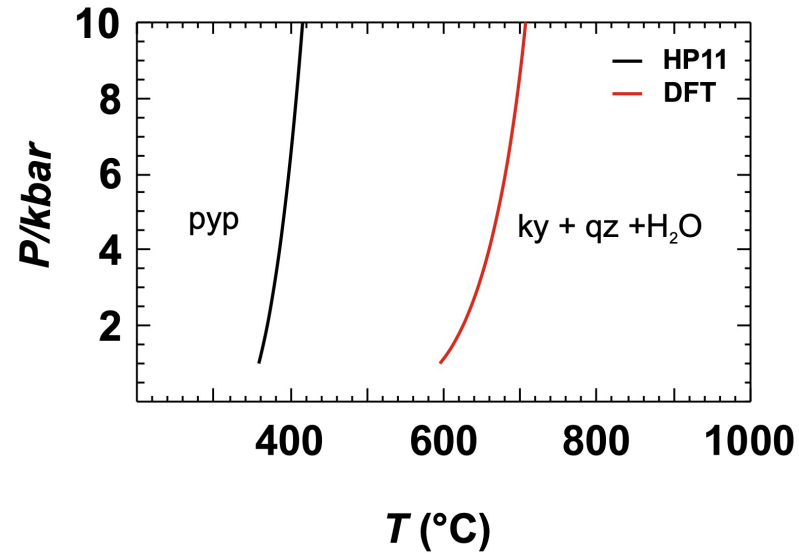
$$\Delta_f H^{0K}_{fo} = -2190.29 \text{ kJ/mol}$$

$$\Delta_f H^{298.15}_{fo} = -2173.07 \text{ kJ/mol}$$

H&P 2011: $\Delta_f H^{298.15} = 2172.57$ kJ/mol

B87: $\Delta_f H^{298.15} = -2174.41$ kJ/mol



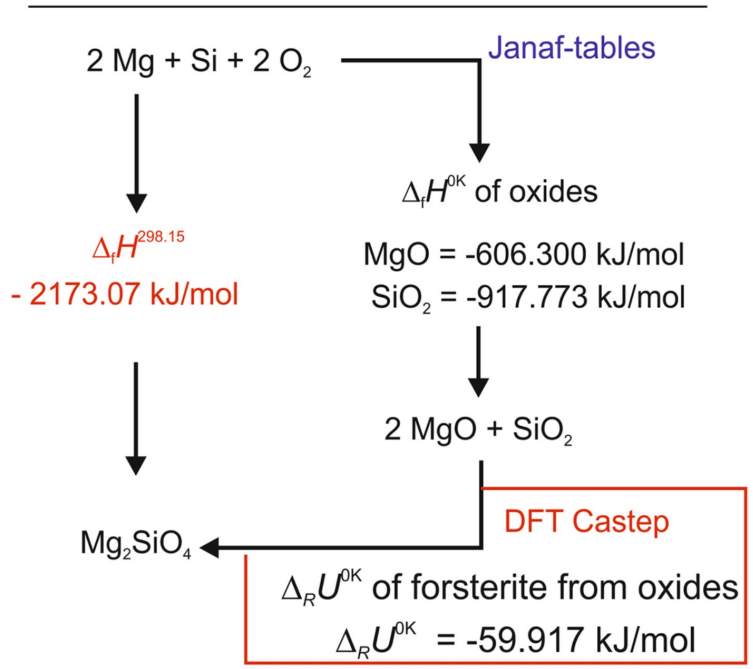


Challenge: this approximation is not valid for complex minerals

Benisek & Dachs (2018)

New **constraints** calculated from first principles (ab initio modeling)

Standard state properties



$$\Delta_R U^{0K} \approx \Delta_R H^{0K}$$

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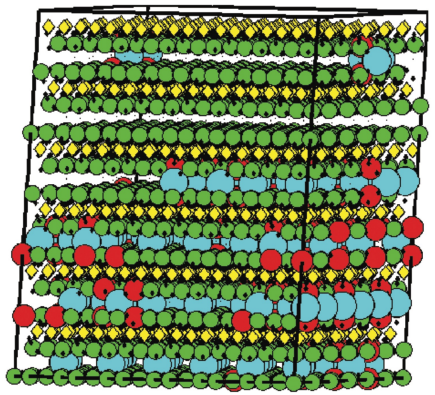
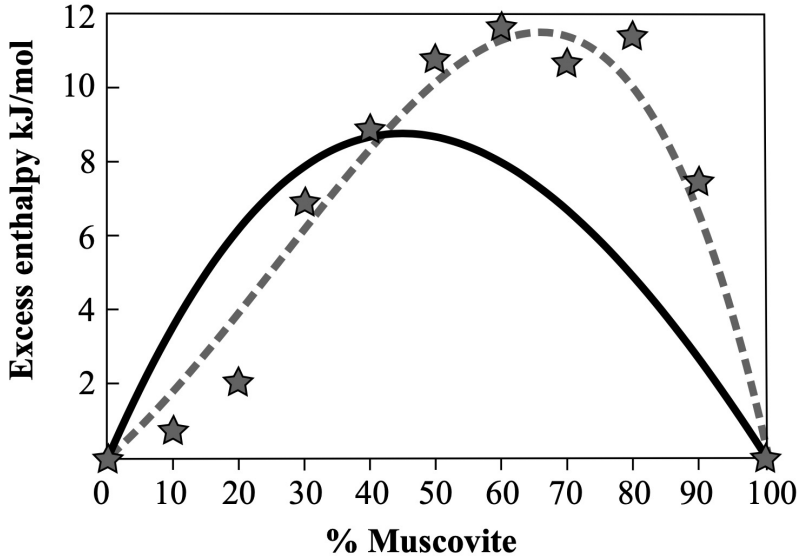
Benisek & Dachs (2018)

Excess functions



Example of structure of a supercell (for Ms30) at the end of the Monte Carlo Simulation



Dubacq et al. (2011) AM

A fantastic job was done but we need more primary data

- Ab initio modeling
- More experimental work
- Acknowledge experimental work

Encourage experiments

Change citation policy

We might need to derive a new generation of databases

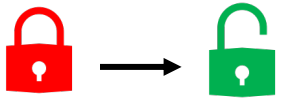
- Derive standard state properties and activity models together to ensure internal consistency
- Use BAYES to derive robust values and uncertainties
- Provide an open-source tool that can be used when new data become available

Optimization and minimization routines

Community-approved working group?

We definitively need to test more the existing databases

- Develop a database of experimental data with uncertainties
- Provide an open-source tool to easily test any database against experimental data
- Encourage users to perform more tests



Educate users

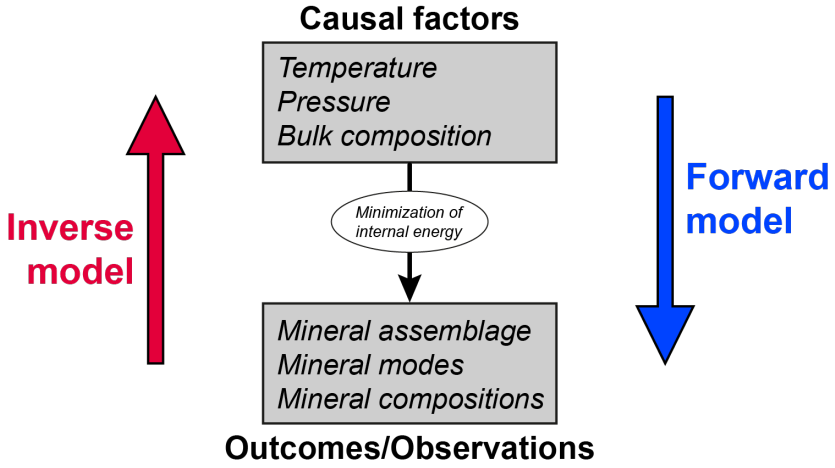
If (and only if) a database satisfies the primary constraints, we can think of

- using thermodynamic models for thermobarometry

*** *THERMOCALC (Waters)* ***

*** *Perple_X (Caddick)* ***

*** *Theriak-Domino (Tinkham)* ***



- applying the models to more complex situations

*** *Best practices in phase equilibrium modeling (Waters)* ***

*** *Reactive bulk composition: Bingo-Antidote (Lanari)* ***

- while asking ourself some important questions

*** *Influence of kinetics (Pattison)* ***

*** *How good are the models at reproducing natural patterns? (Forshaw)* ***

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and many uncited papers from fantastic groups worldwide who produced experimental data on which each user of a thermodynamic database depend …