PHASE EQUILIBRIUM MODELING
APPROACHES AND PITFALLS

Part 6: Reactive bulk composition and Bingo-Antidote

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SFMC

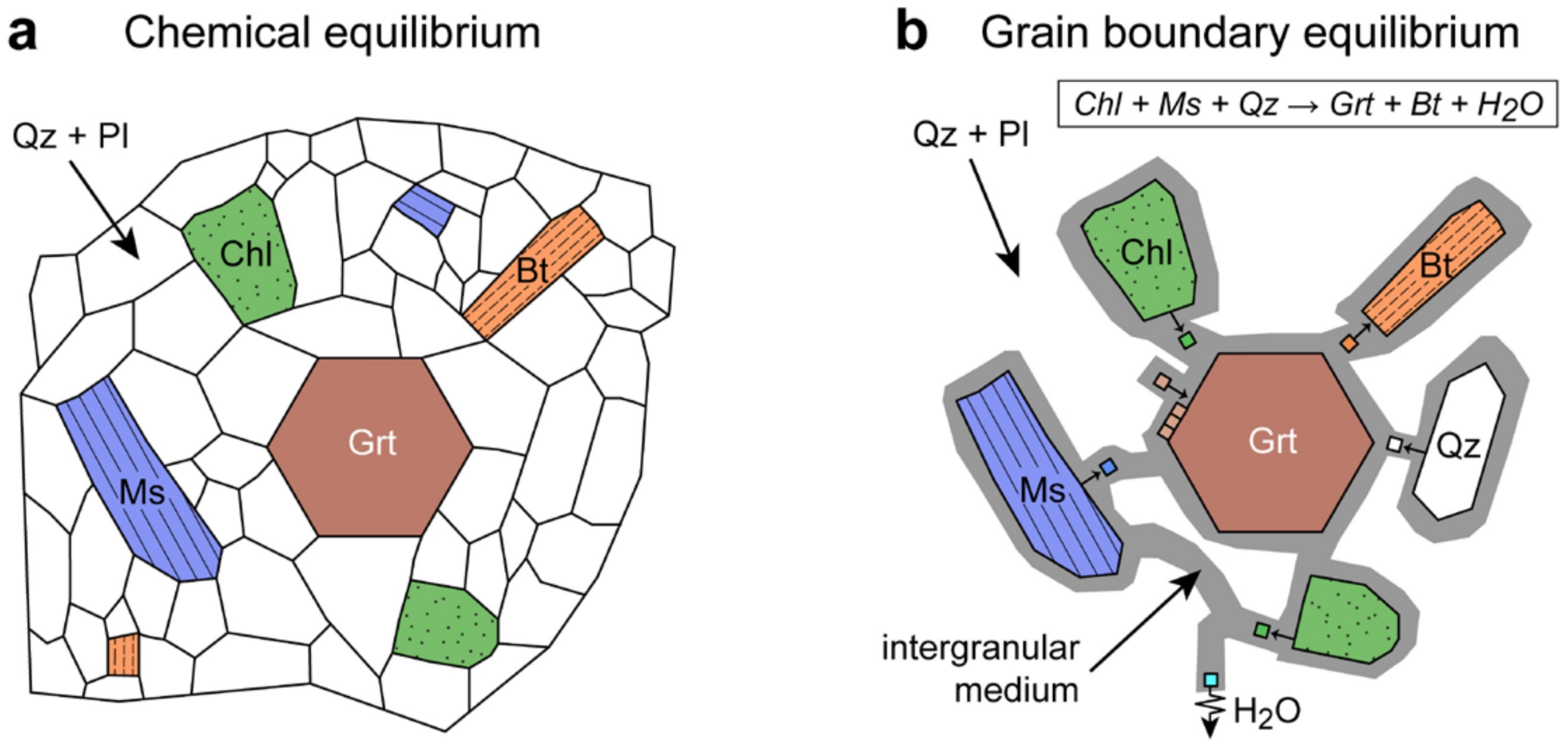
MINERALOGICAL SOCIETY OF AMERICA · MINERALOGY · PETROLOGY · CRYSTALLOGRAPHY · MCMXIX

Virtual workshop, May 10th to 14th 2021

Objectives of this lecture

- Discuss the concept of reactive bulk composition and explain why it matters for forward models
- Present a selection of strategies available to approximate the reactive bulk composition (e.g. garnet growth; domainal reactions)
- Introduce an alternative modeling strategy for thermobarometry based on iterative thermodynamic models

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



► **Chemical equilibrium model**:

All mineral phases are homogeneous in composition and coexist in equilibrium at the *P*–*T* conditions of interest

► **Grain boundary equilibrium model** :

Equilibrium control: transport rates are faster than the rates of surface processes (dissolution, precipitation)

The composition of all crystallizing phases will be identical (spatially) and only dictated by P–T–X_{bulk}

Lanari & Engi (2017), RiMG

PHASE EQUILIBRIUM MODELING

AN INTRODUCTION TO PETROLOGICAL MODELLING

Part 6

Introduction

- **Basic definitions**
- Determination of local bulk composition(s)
- Quantitative compositional mapping

Reactive bulk composition

Iterative thermodynamic modeling (ITM)

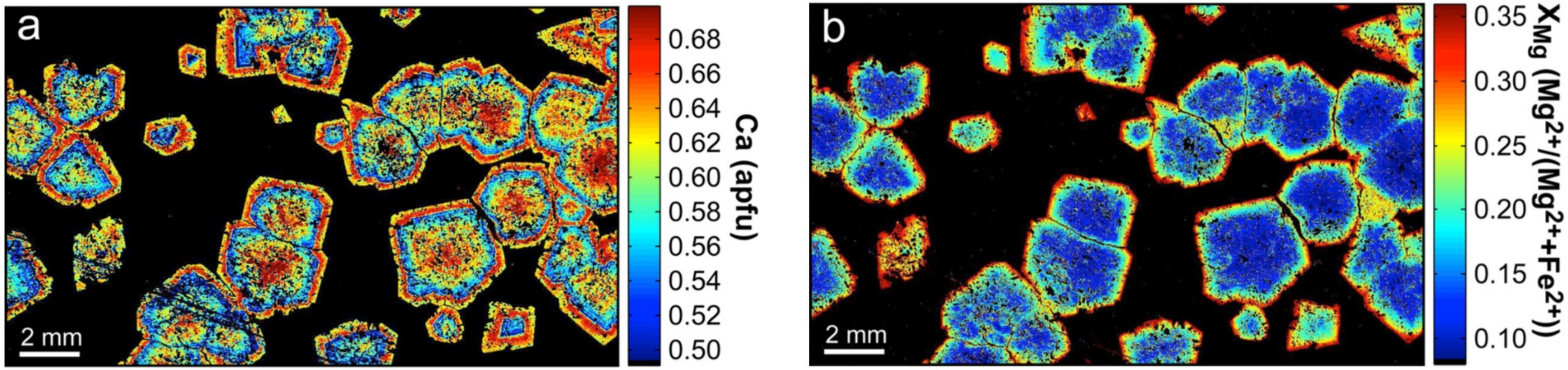
Bingo-Antidote

Summary and perspectives

Example 1: garnet in eclogite (T_{max} = 550 °C)

Grain boundary equilibrium	*close*	👍
Re-equilibration by diffusion	*limited*	👍
Global equilibrium at peak	*no*	👎

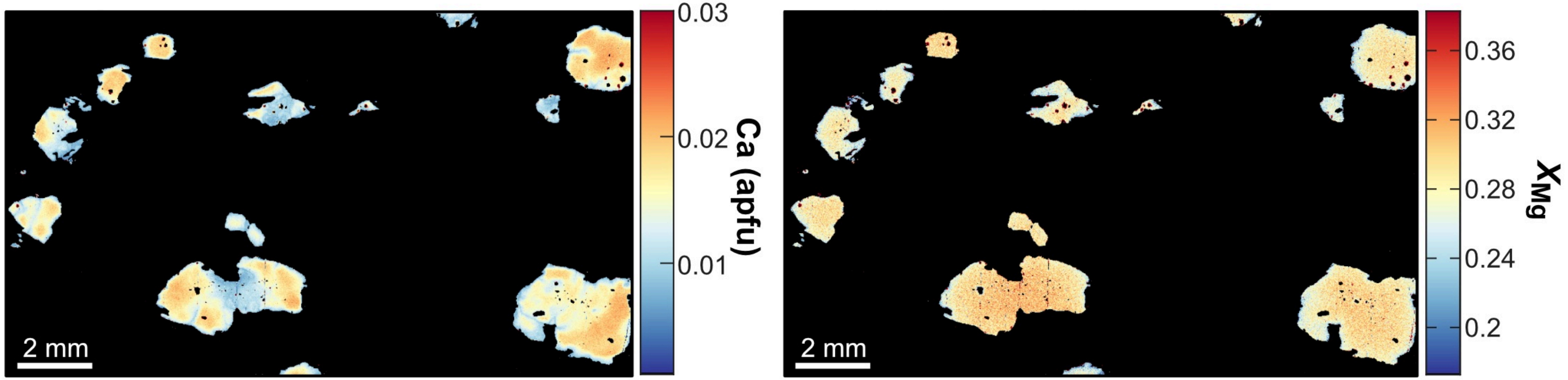
Lanari & Engi (2017), RiMG



Example 2: garnet in granulite (T_{max} = 850 °C)

Grain boundary equilibrium	*???*	👎
Re-equilibration by diffusion	*close*	👍
Global equilibrium at peak	*maybe*	👍

Lanari & Duesterhoeft (2019), JPet



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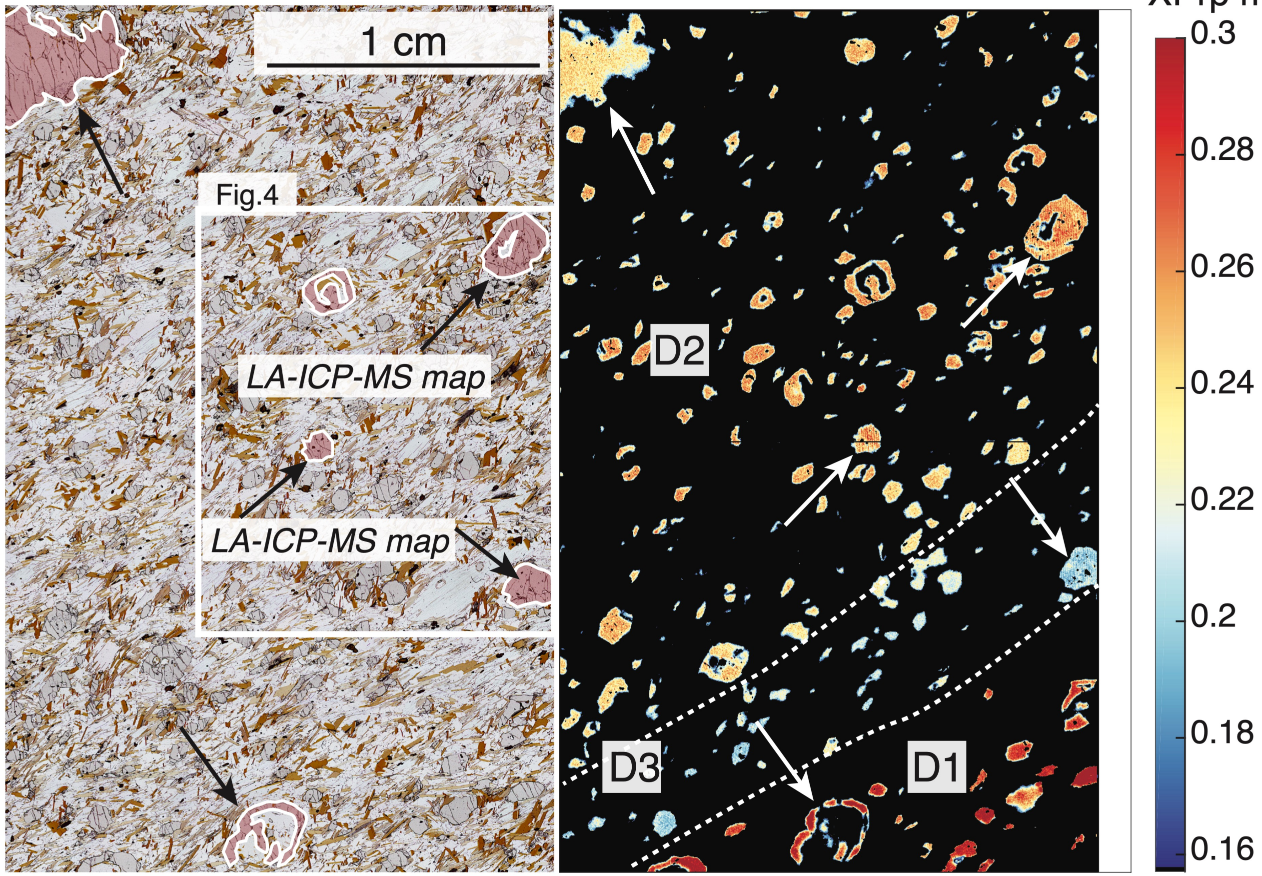
Example 3: garnet in HP metasediments (T_{max} = 780 °C)

Grain boundary equilibrium	*???*	👎
Re-equilibration by diffusion	*complex*	👎
Global equilibrium at peak	*local?*	👎

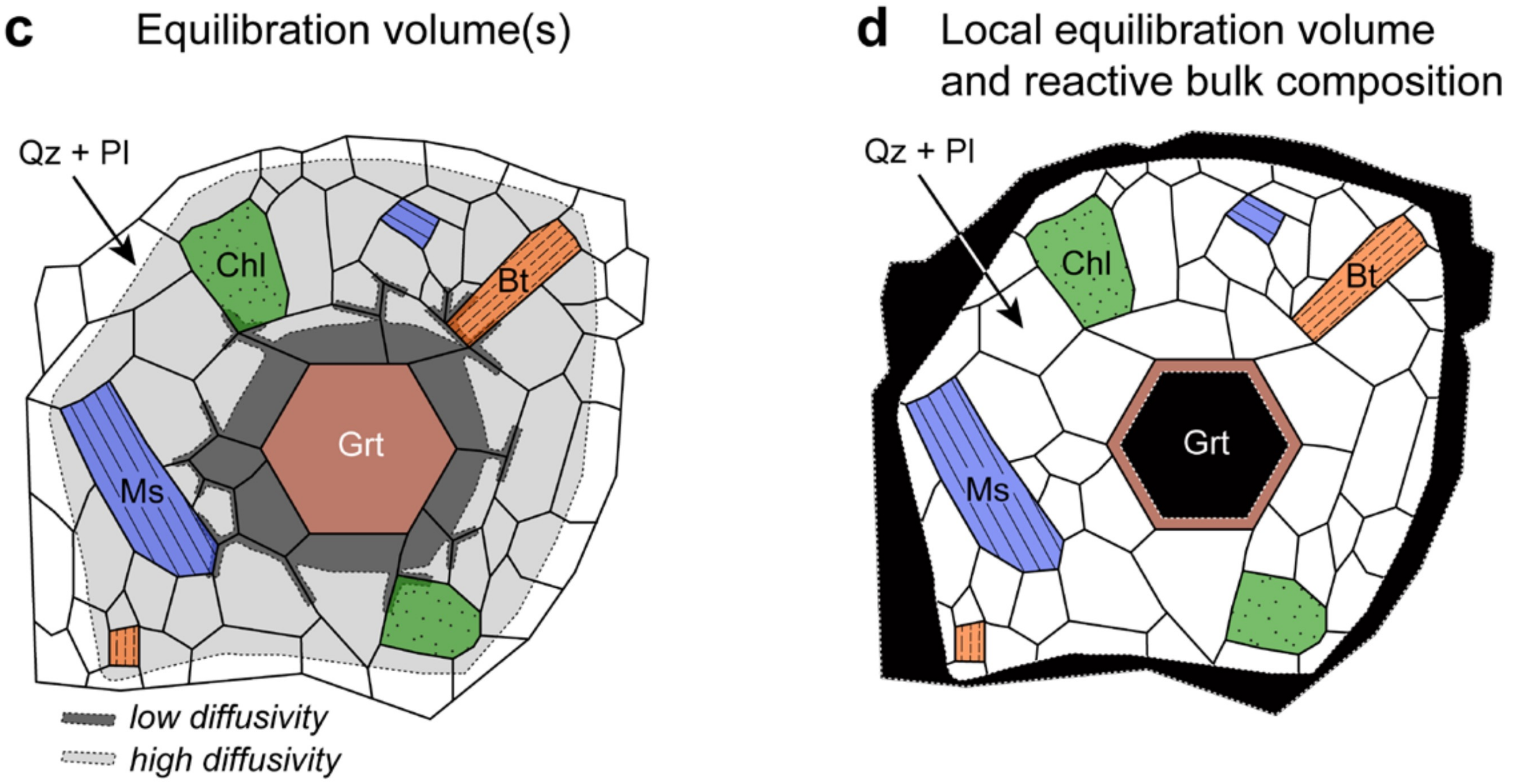
Piccoli et al. (submitted), JMG



→ The preserved garnet composition does not reflect large scale chemical equilibrium

Other examples: extreme cases of smaller equilibrium scales for some elements

*** *More examples in "THE INFLUENCE OF KINETICS" (Pattison & Forshaw)* ***



► **Equilibration volume in rocks**:

Two equilibrium volumes are shown, one for an element (dark gray) with low diffusivity, a second one (light gray) assuming fast transport

► **Local equilibration volume**:

It involves only the rim of the zoned minerals (here garnet) and a homogenous domain (matrix) of a section. The **reactive bulk composition** is the composition of the local equilibrium volume

Lanari & Engi (2017), RiMG

▶ Reactive (effective) bulk composition

Composition of the (presumed) equilibration volume at a specific stage of the evolution.

It may exclude certain refractory or inert minerals that are observed in a domain but shielded from reactions.

Conceptual quantities for the model

▶ Bulk rock composition

Average chemical composition of a whole-rock sample analyzed, for example, by X-ray fluorescence spectrometry (XRF)

▶ Local bulk composition (LBC)

Average chemical composition of a specific region or domain in a rock

Measured quantities

- How do we measure local bulk compositions?
- Can local bulk composition be used as an approximation of the reactive bulk composition?

Phase Equilibrium Modeling

An introduction to petrological modelling

Part 6

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Reactive bulk composition

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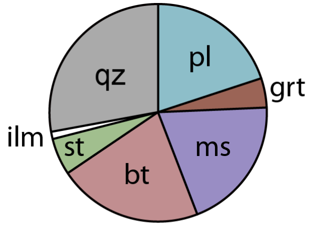
Summary and perspectives

A **simple approach** for determining LBC is to combine mineral modes and mineral compositions:

$$X^i_{\mathrm{LBC}} = w_{\mathrm{Phase}_1} X^i_{\mathrm{Phase}_1} + w_{\mathrm{Phase}_2} X^i_{\mathrm{Phase}_2} + \ldots + w_{\mathrm{Phase}_n} X^i_{\mathrm{Phase}_n}$$

with w_{Phase_1} and $X^i_{\mathrm{Phase}_1}$ the weight fraction and oxide wt%



Mineral modes from BSE images or X-ray maps

	X^i_{Grt}	X^i_{Bt}	X^i_{Pl}
SiO_2	37.6	36.4	65.2
Al_2O_3	21.4	19.8	21.9
FeO	23.0	15.3	0.01
MnO	8.76	0.05	0.01
MgO	1.05	11.1	0.01
CaO	9.72	0.02	2.22
Na_2O	0.03	0.21	9.62
K_2O	0.01	8.92	0.10

Table: mineral compositions expressed in wt% of oxides

Replacing the weight fractions by volume fractions:

$$X^i_{\mathrm{LBC}} = \frac{\rho_{\mathrm{Phase}_1}}{\rho_{\mathrm{mixture}}} v_{\mathrm{Phase}_1} X^i_{\mathrm{Phase}_1} + \frac{\rho_{\mathrm{Phase}_2}}{\rho_{\mathrm{mixture}}} v_{\mathrm{Phase}_2} X^i_{\mathrm{Phase}_2} + \ldots + \frac{\rho_{\mathrm{Phase}_n}}{\rho_{\mathrm{mixture}}} v_{\mathrm{Phase}_n} X^i_{\mathrm{Phase}_n}$$

with ρ_{mixture} the average density of the system.

$$X^i_{\mathrm{LBC}} = \sum_{j=1}^{n} \frac{\rho_j}{\rho_{\mathrm{mixture}}} v_j X^i_j$$

LBC is obtained by summing the composition of each constituting mineral phase:

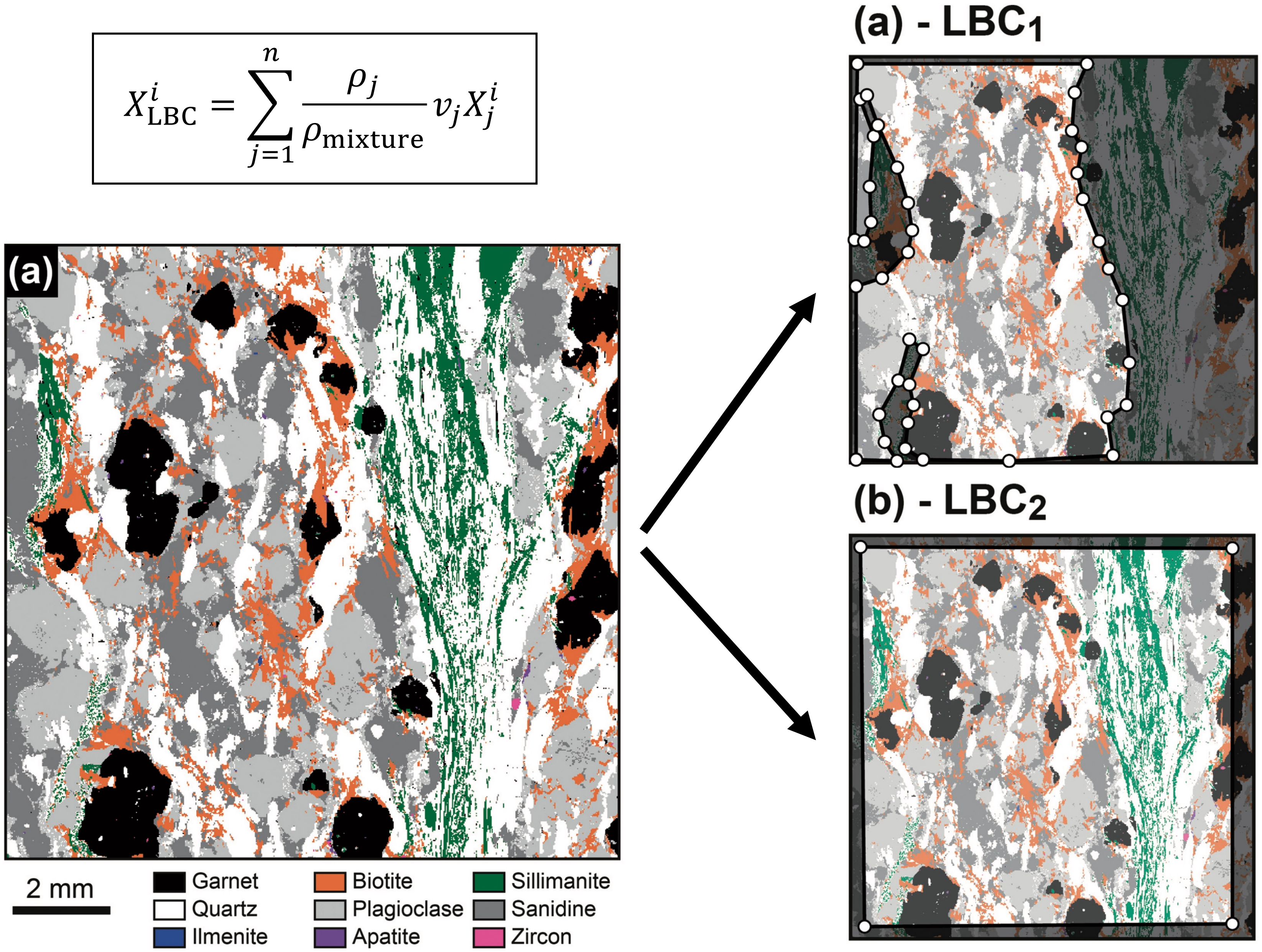
Lanari & Engi (2017), RiMG

Limits if based on BSE images and mineral compositions

- Minerals with different compositions that cannot be distinguished from each other
- Mineral zoning not always visible

A **general and more flexible approach** based on compositional maps:

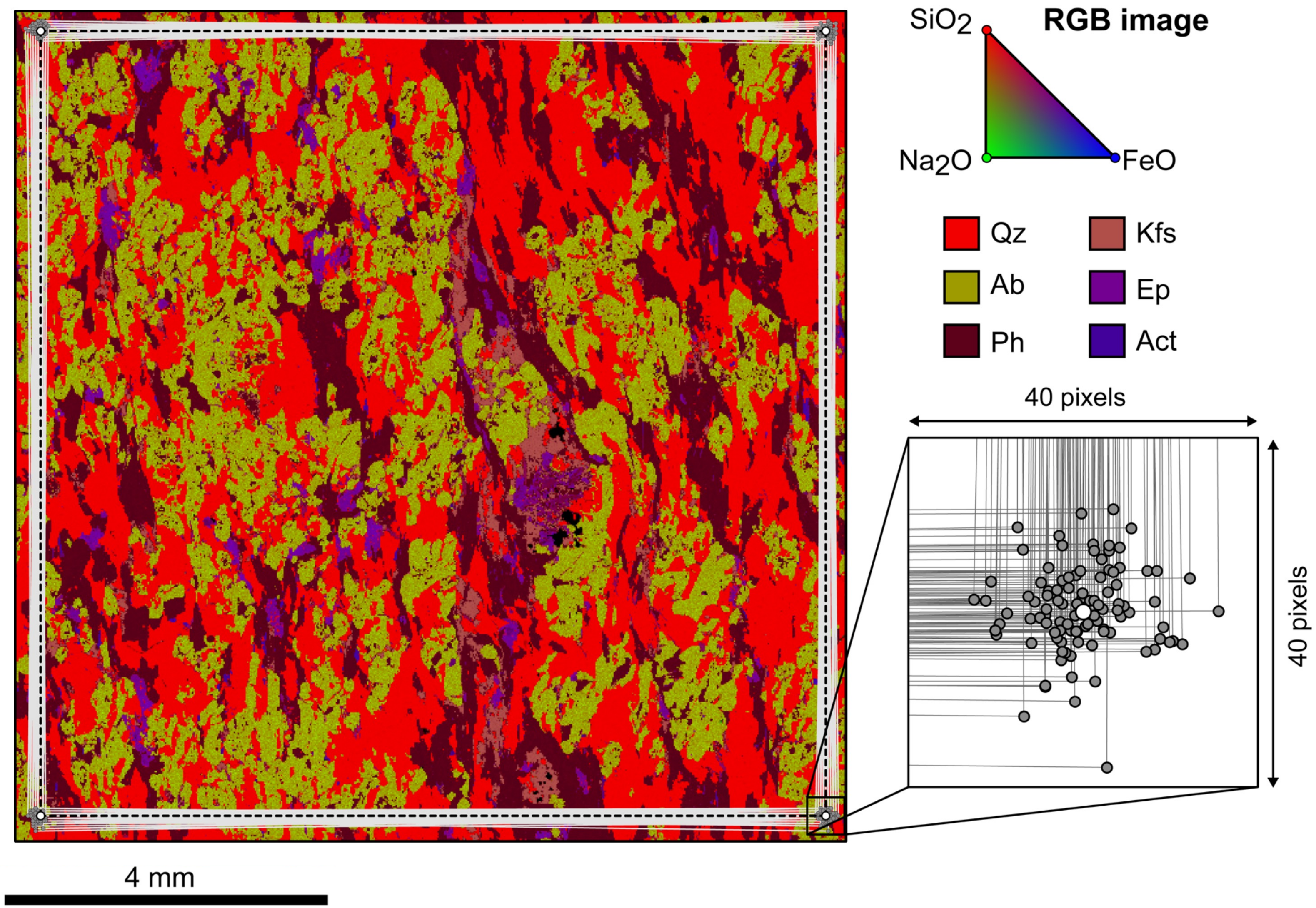
$$X^i_{\mathrm{LBC}} = \sum_{j=1}^{n} \frac{\rho_j}{\rho_{\mathrm{mixture}}} v_j X^i_j$$



Lanari & Duesterhoeft (2019), JPet

A **general and more flexible approach** based on compositional maps:

A Monte-Carlo approach to address arbitrariness



Lanari & Engi (2017), RiMG

A **general and more flexible approach** based on compositional maps:

Uncertainty in the estimation of LBC

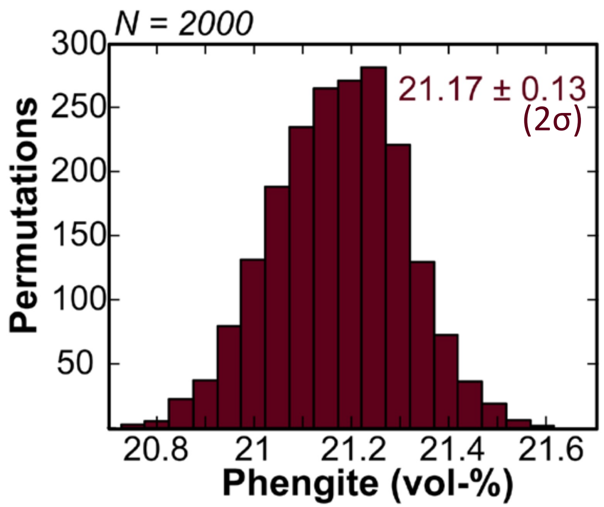
	Mean	Stdev. (2σ)	Unc. (%)
SiO_2	75.420	0.057	0.076
Al_2O_3	13.230	0.033	0.249
FeO	1.230	0.006	0.488
MgO	0.940	0.004	0.426
CaO	0.810	0.008	0.942
Na_2O	3.360	0.018	0.522
K_2O	3.090	0.017	0.551
Total	98.08		

Lanari & Engi (2017), RiMG

How sensitive are the results of a forward model?

In this example at 425 °C and 1.26 GPa

Modeled mineral modes

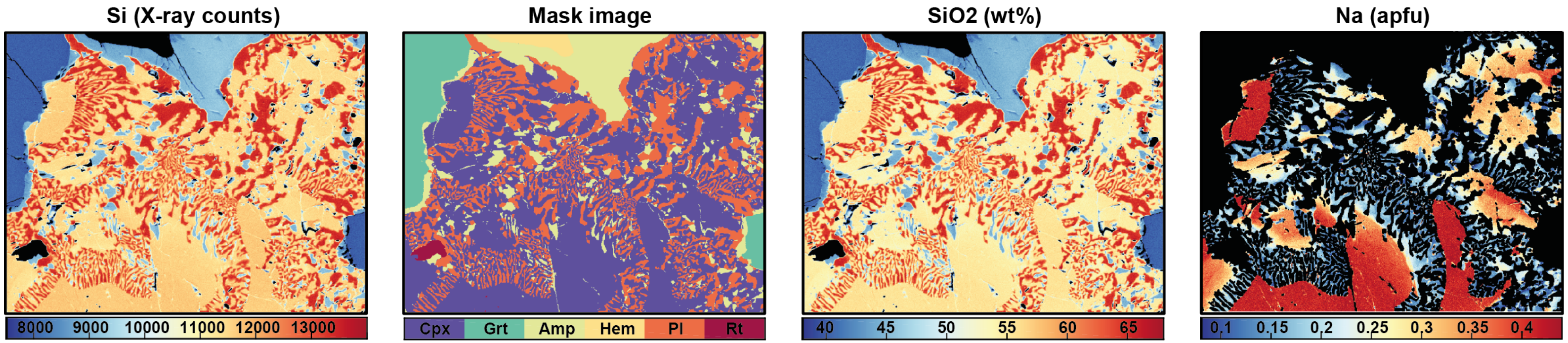


Modeled mineral composition

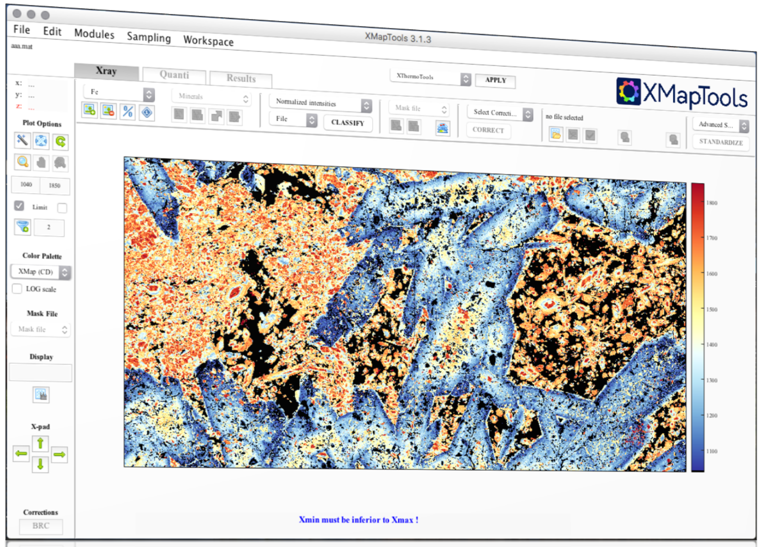
Si^{4+} = 3.481 ± 0.002 atoms per formula unit (apfu, 2σ)

Note: the consequences of choosing a smaller domain are discussed in the section "Iterative thermodynamic modeling (ITM)"

Quantitative compositional mapping using electron microprobe micro-analysis (EPMA)



Compositional maps modified from Lanari et al. (2013), Geol



XMapTools

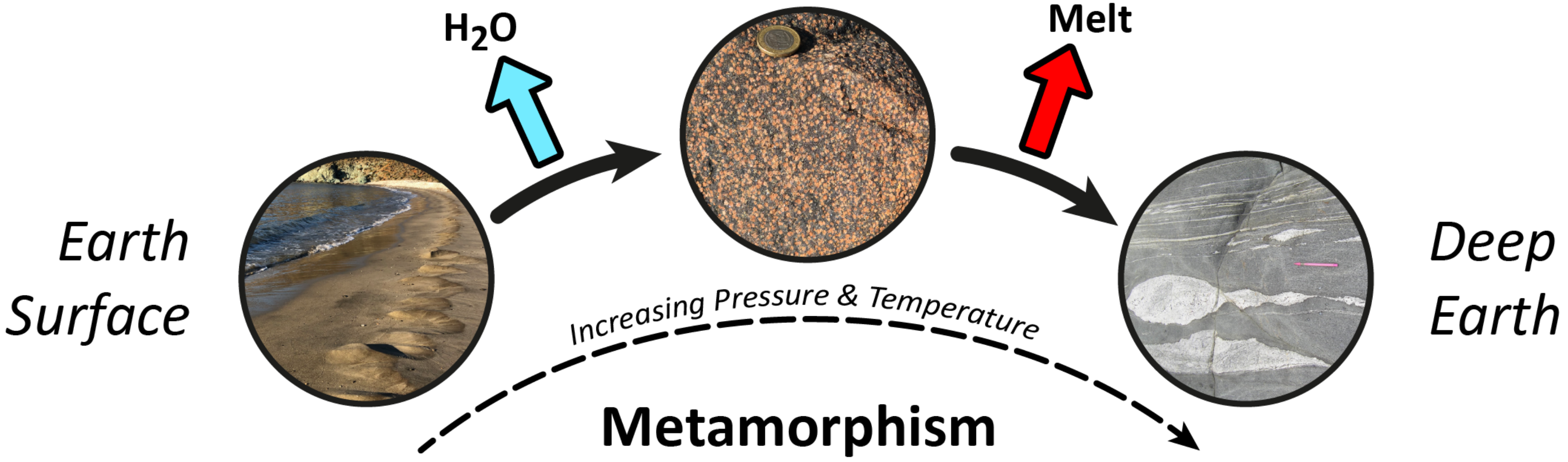
Lanari et al. (2014; 2019)

EPMA
X-ray maps
240'000 pixels
15 elements
10-40 h

Data processing
1-2 h max
Maps of structural formula
Local bulk composition

**** Friday's discussion topic "XMapTools" ****

Reactive bulk composition



▶ Fractionation by extracting components from the system (aqueous fluid, melts)

Basic tools (manual)

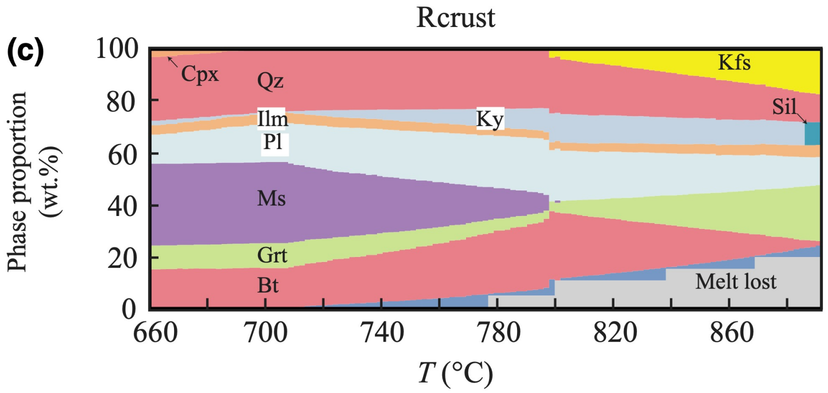
Theriak-Domino   Perple_X   THERMOCALC

e.g. Yakymchuk et al. (2017), RiMG

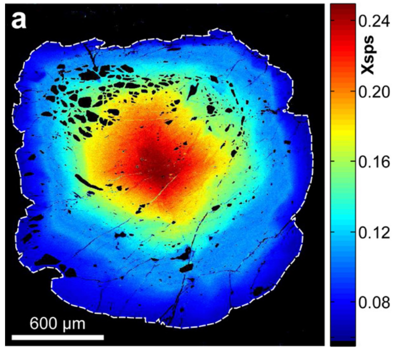
Advanced tools

Rcrust

Mayne et al. (2016), JMG



▶ Fractionation by isolating components in the system (minerals)



"Fractionation effects become significant as soon as porphyroblasts represent >2 vol% in pelitic systems and > 4 vol% in mafic systems"

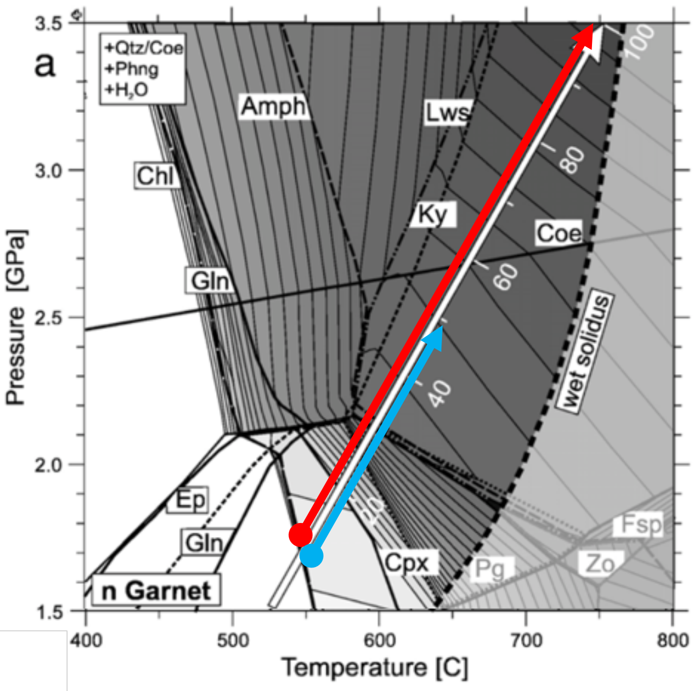
Lanari & Engi (2017), RiMG

Note: The processes of diffusion, resorption and replacement work against fractionation!

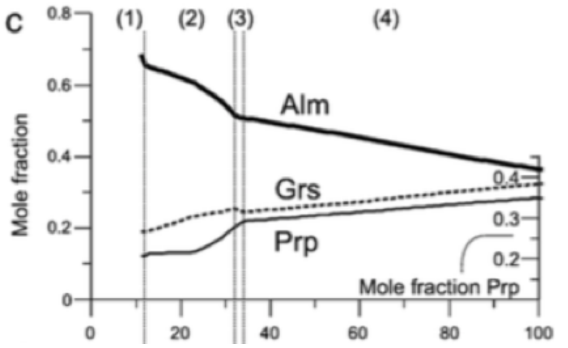
Although the effects of **garnet fractionation** on phase diagrams are recognized and quantified since more than three decades (e.g. Spear 1988, 1991; Stuwe 1997; Evans 2004; Gaidies et al. 2008), fractionation is often neglected or simply ignored in modern petrological studies

Example: Garnet fractionation in Eclogite

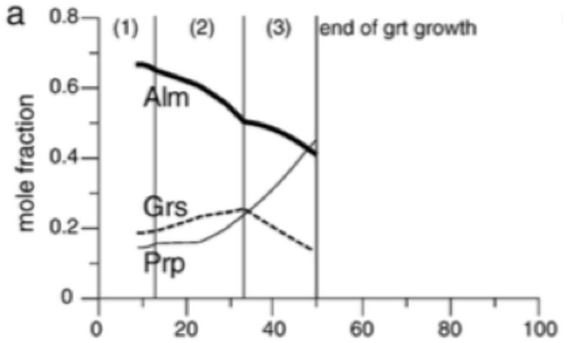
Konrad-Schmolke et al. (2008), Lithos



Case 1: no garnet fractionation

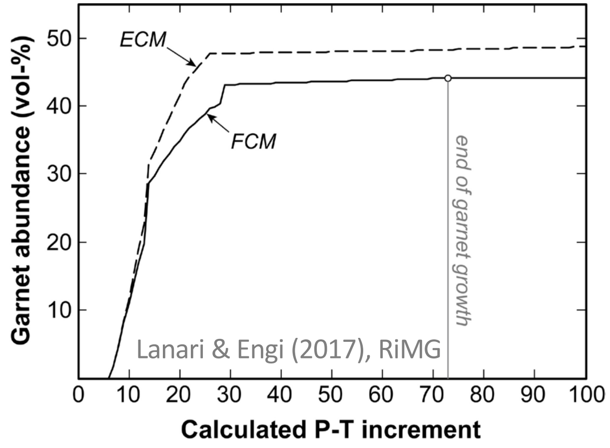


Case 2: garnet fractionation



Fractionation affects:

- Mineral compositions
- Mineral modes



Lanari & Engi (2017), RiMG

Approximation of a reactive bulk composition and modeling strategies

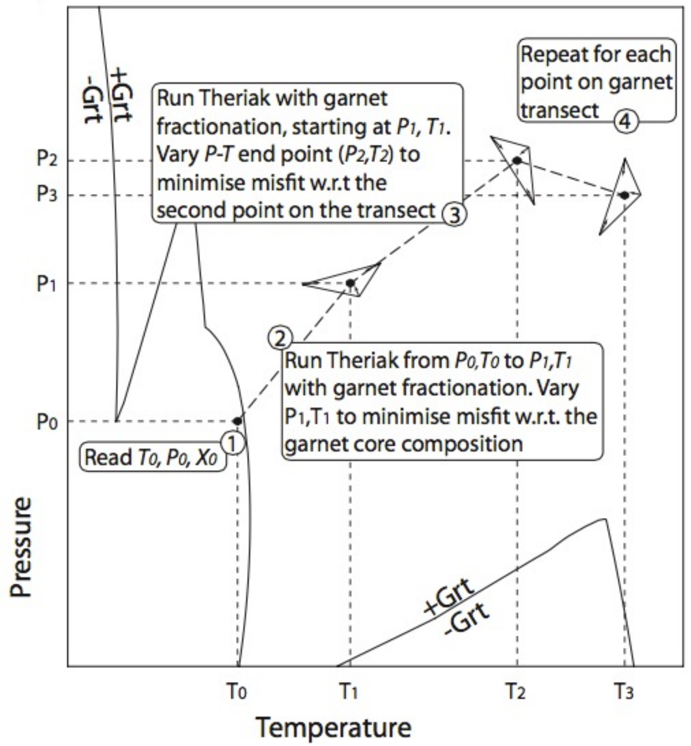
- Assuming Rayleigh fractionation of Mn between garnet and matrix (e.g. Evans 2004)

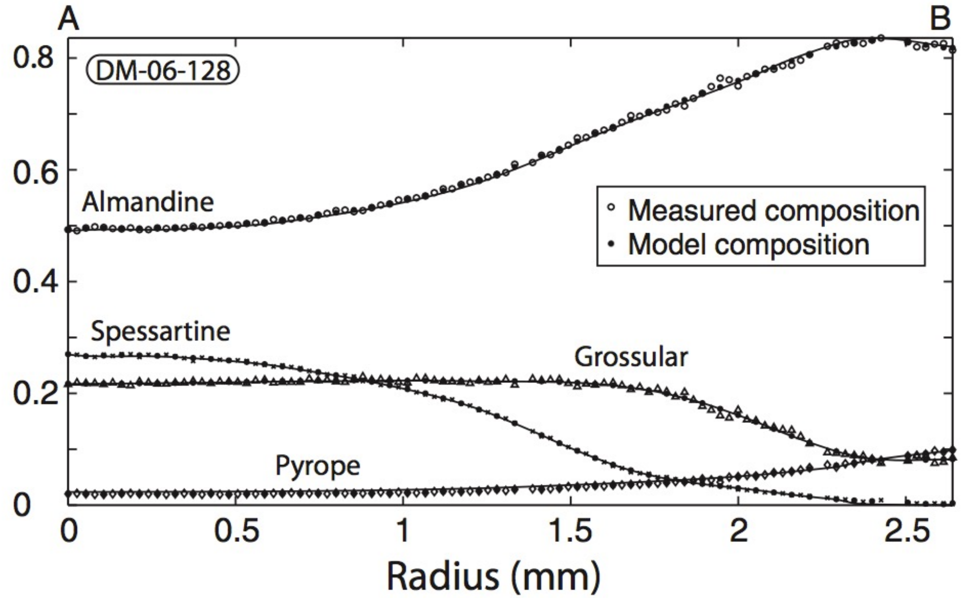
$$X_{\mathrm{grt}}^{\mathrm{MnO}} = X_{\mathrm{bulk}}^{\mathrm{MnO}} K_{\mathrm{d}} \left(1 - w_{\mathrm{grt}}\right)^{K_{\mathrm{d}}}$$

- Progressive fractionation and update of the reactive bulk composition for stage *n*

$$X_{\mathrm{RBC}}^{n} = \frac{X_{\mathrm{RBC}}^{n-1} - w_{\mathrm{grt}}^{n-1} X_{\mathrm{grt}}^{n-1}}{1 - w_{\mathrm{grt}}^{n-1}}$$

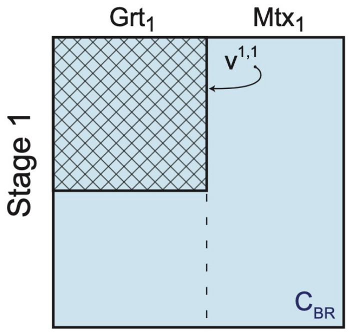
- Fixed *P–T* trajectory (+ diffusion): Theria_G — Gaidies et al. (2008)
- Optimized *P–T* trajectory: Iterative optimization — Moynihan & Pattison (2013)





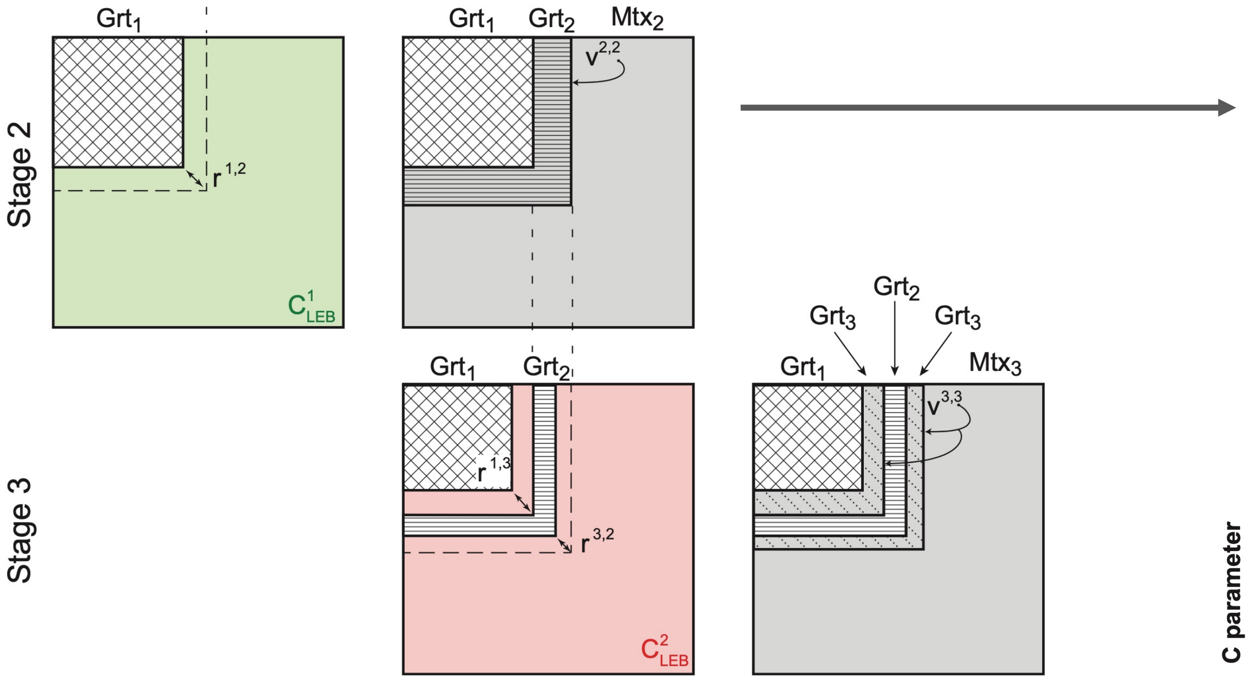
Lanari et al. (2017), EJM

Stage 1: optimization of *P–T*

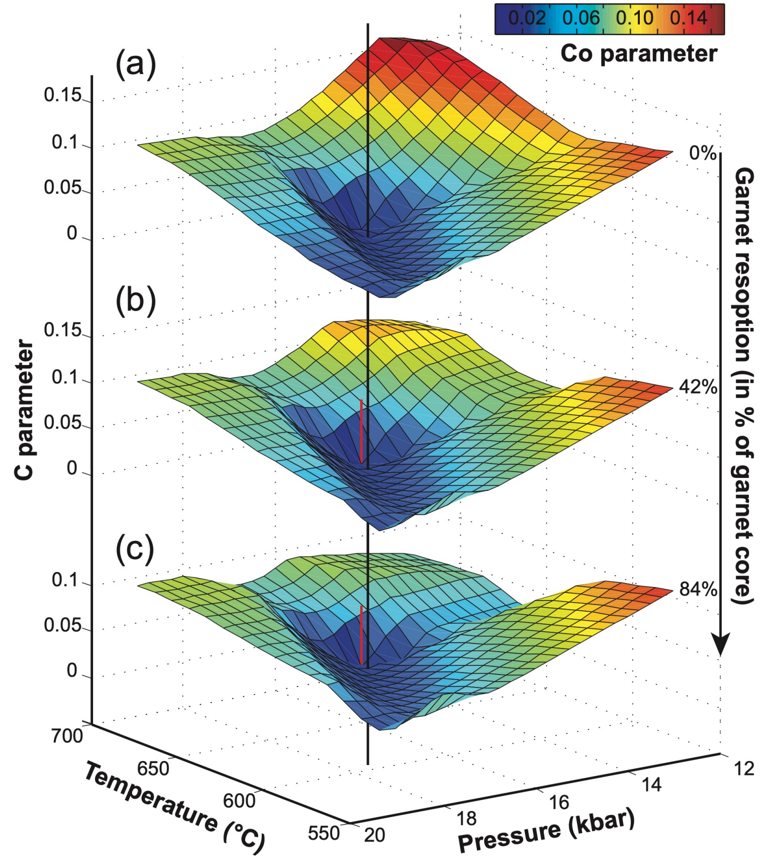


$$\text{Misfit: } L_0 = \sqrt{\sum_{k=1}^{m} \frac{\left(f_k^{\text{measured}} - f_k^{\text{model}}\right)^2}{\omega_k}}$$

Stage 2: optimization of *P–T–r*^{1,2}

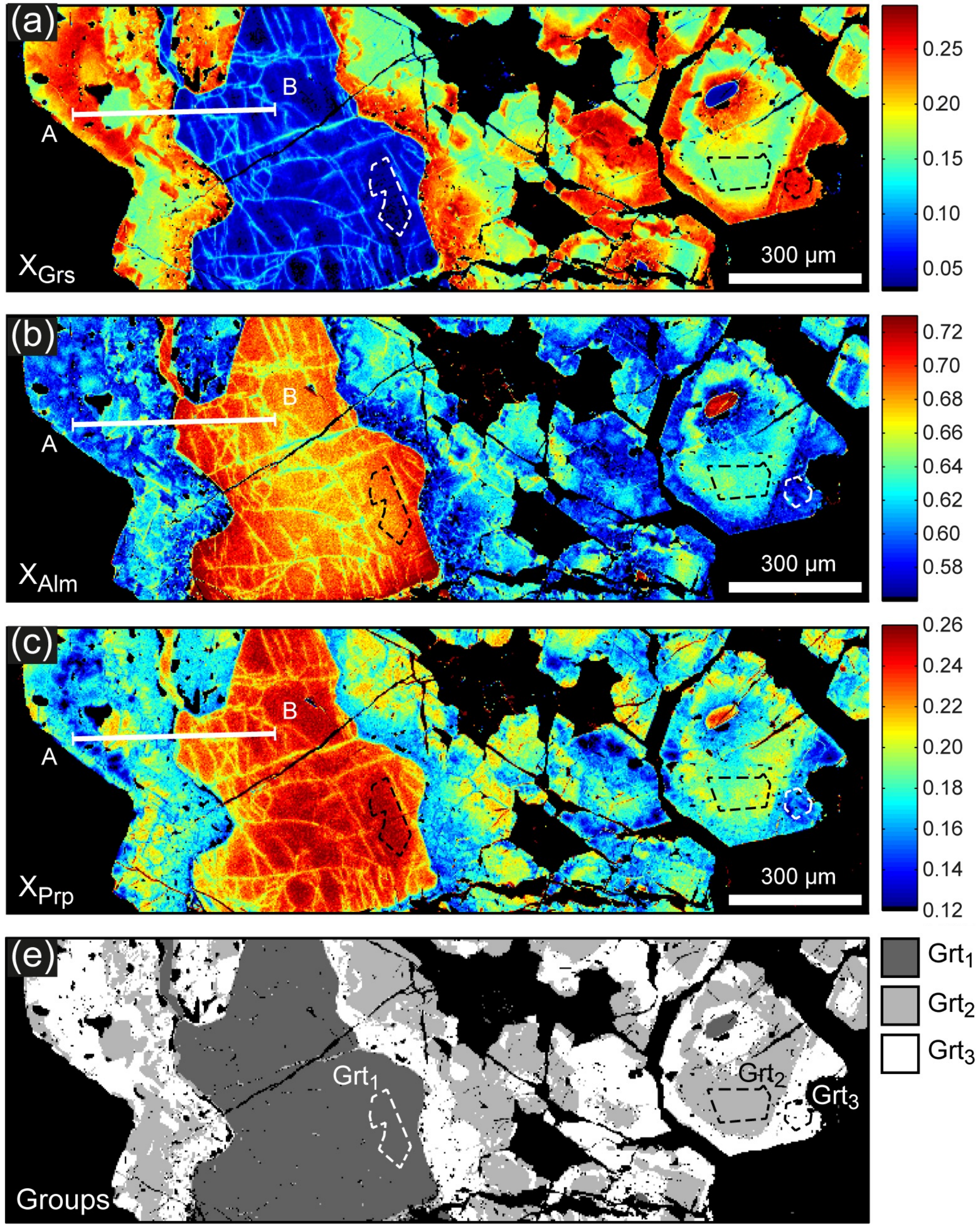


Stage 3: optimization of *P–T–r*^{1,3}*–r*^{3,2}

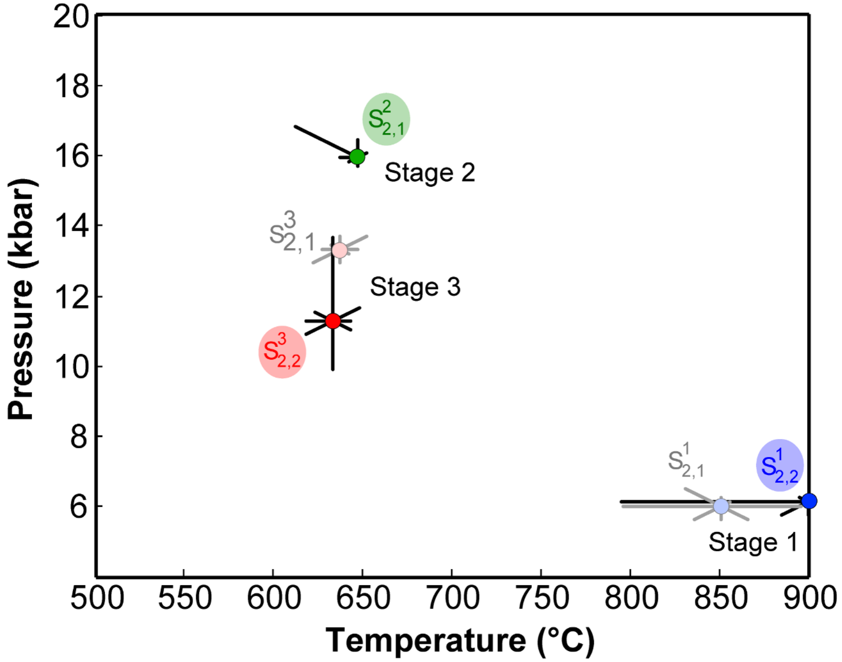


A reactive bulk composition is optimized at each stage!

Application example (Sesia Zone, Western Alps, Italy)



Growth conditions of each stage



- Stage 1: Granulite (Permian - 280 Ma)
- Stage 2: Eclogite (Alpine - 65 Ma)
- Stage 3: BS - Eclogite (Alpine - <65 Ma)

Lanari et al. (2017), EJM

PHASE EQUILIBRIUM MODELING

AN INTRODUCTION TO PETROLOGICAL MODELLING

Part 6

Introduction

Reactive bulk composition

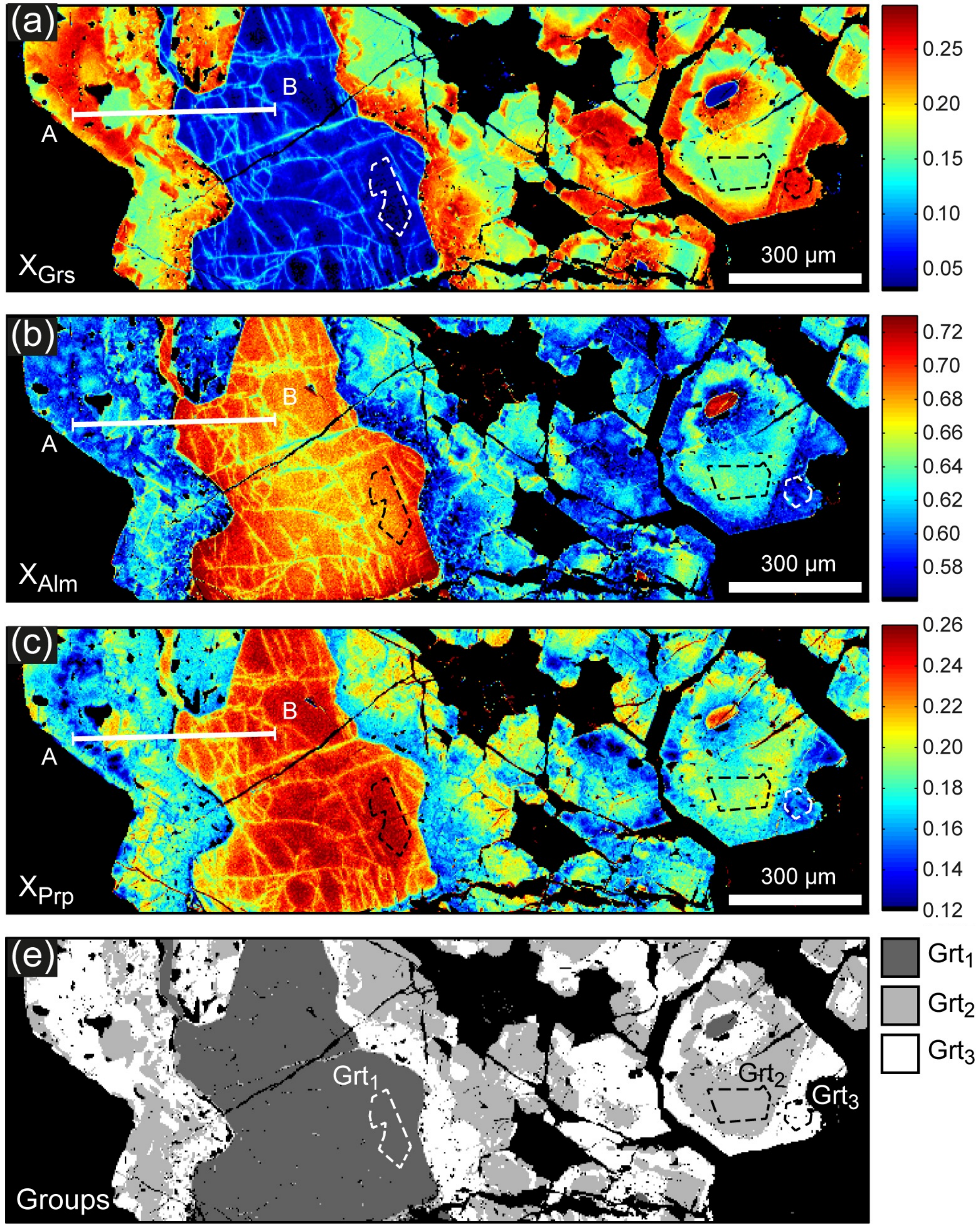
- Fractionation effects
- Mineral fractionation
- **Dynamic bulk composition**

Iterative thermodynamic modeling (ITM)

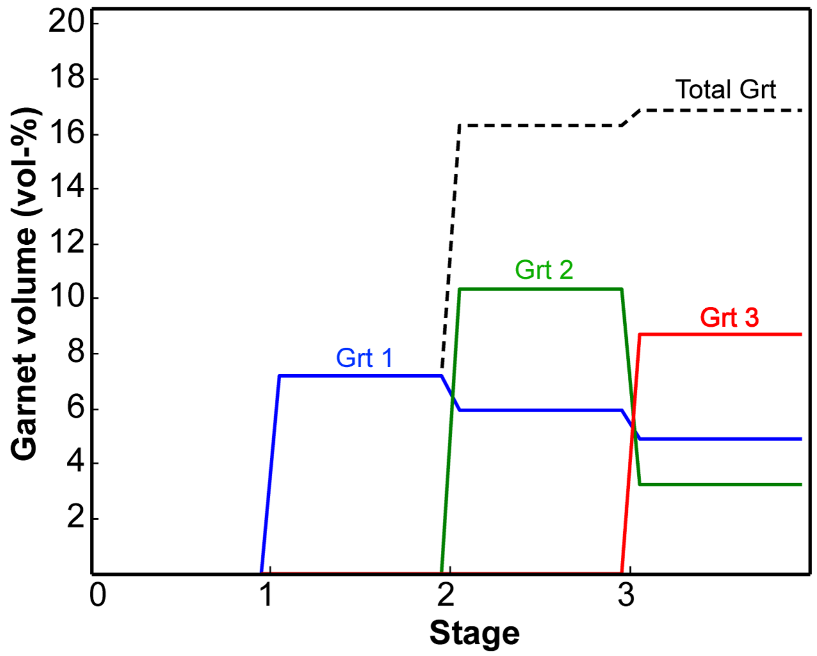
Bingo-Antidote

Summary and perspectives

Application example (Sesia Zone, Western Alps, Italy)



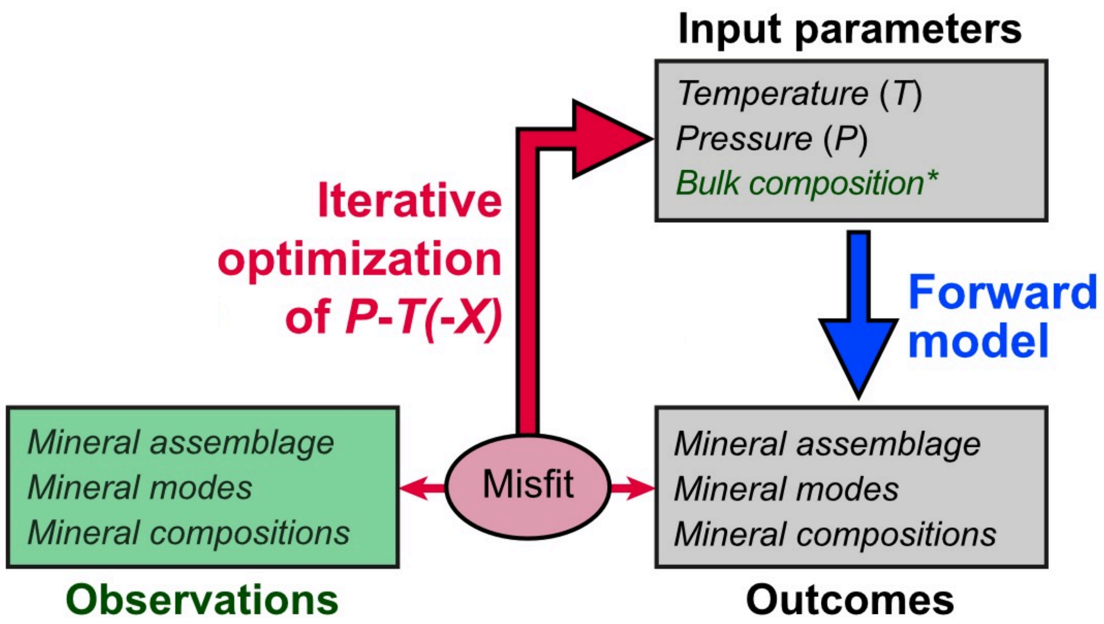
Predicted garnet growth and resorption



- Stage 1: Granulite (Permian - 280 Ma)
- Stage 2: Eclogite (Alpine - 65 Ma)
- Stage 3: BS - Eclogite (Alpine - <65 Ma)

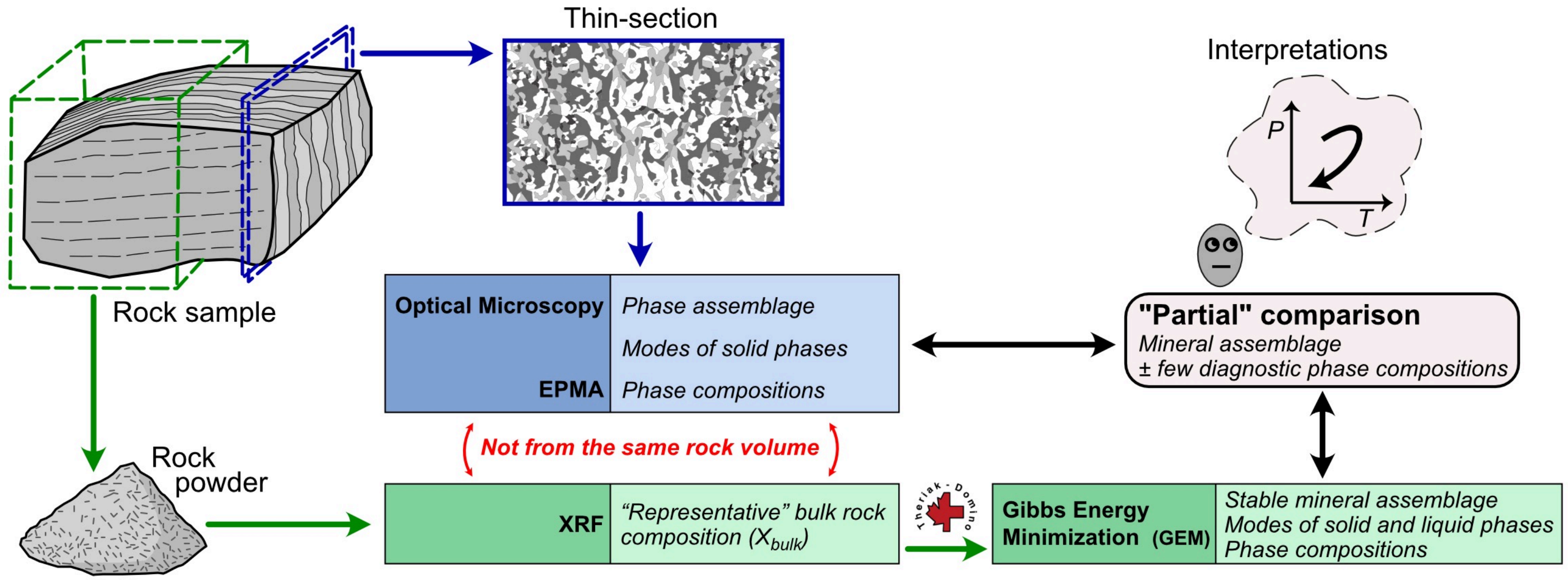
Lanari et al. (2017), EJM

Iterative thermodynamic models

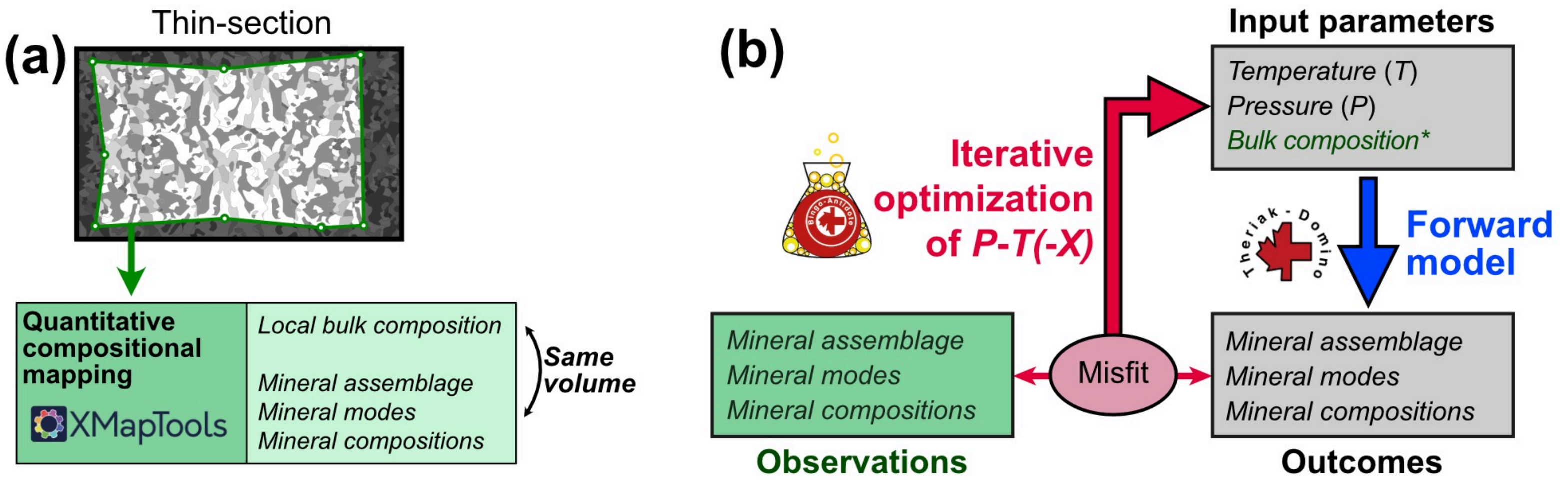


Duesterhoeft & Lanari (2020), JMG

► General strategy for forward thermodynamic models



► Alternative strategy for iterative thermodynamic models (ITM)



Duesterhoeft & Lanari (2020), JMG

Mineral assemblage *Mineral modes* *Mineral compositions*	← Misfit →	*Mineral assemblage* *Mineral modes* *Mineral compositions*
Observations		**Outcomes**

Scoring strategy based on model quality factors

- ✓ Assemblage — Q_{asm}
- ✓ Mineral modes — Q_{vol}
- ✓ Mineral compositions — Q_{cmp}

→ Q_{total} — *Can be used as misfit*

Q_{asm}

THER	XMAP
a	a
b	b
c	c
-	-
-	-
Q_{asm} = 100%	

THER	XMAP
a	a
b	b
c	c
-	d
-	e
Q_{asm} = 60%	

Q_{vol}

THER	XMAP
80%	60%
10%	30%
10%	10%
-	-
-	-
Q_{vol} = 81%	

THER	XMAP
80%	59%
10%	29%
10%	9%
-	2%
-	1%
Q_{vol} = 81%	

Q_{cmp}

Perfect match within uncertainty → 100

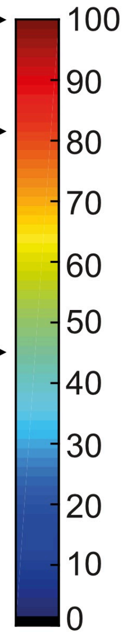
Significant differences (> 10 %) in some elements → 80

	Obs.	*Mod.*
Al	1.73 ± 0.08	**1.78**
Fe	1.01 ± 0.05	**0.99**
Mg	1.27 ± 0.08	**1.49**
Ti	0.11 ± 0.02	**0.12**

Critical differences (> 20 %) for most elements → 45

	Obs.	*Mod.*
Al	1.73 ± 0.08	**1.27**
Fe	1.01 ± 0.05	**1.13**
Mg	1.27 ± 0.08	**1.65**
Ti	0.11 ± 0.02	**0.08**

Example for biotite

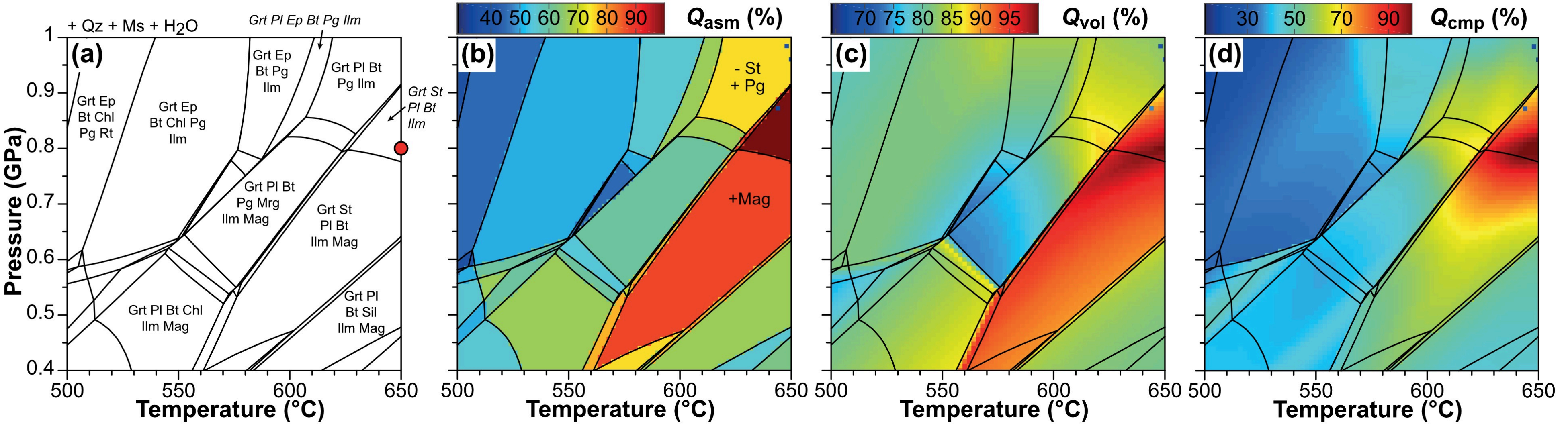


Note that Q_{vol} and Q_{cmp} are only calculated only for the matching phases

Lanari & Hermann (2021), JMG

Pressure-Temperature maps of model quality factors

In this example for an average pelite composition. Pseudo-observations are set as the model outcome at 650 °C and 0.8 GPa



Global evaluation Q_{total}

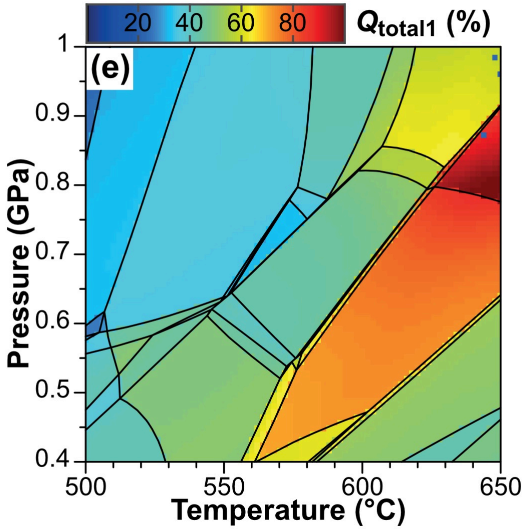
$$Q_{total1} = \frac{Q_{asm} + Q_{vol} \times Q_{asm} + Q_{cmp} \times Q_{asm}}{3}$$

Duesterhoeft & Lanari (2020), JMG

Adaptative scheme

$$Q_{total2} = w_{asm} \cdot Q_{asm} + w_{vol} \cdot Q_{vol} + w_{cmp} \cdot Q_{cmp}$$

with w_{asm} w_{asm} and w_{asm} weighting parameters



Phase Equilibrium Modeling

An introduction to petrological modelling

Part 6

Introduction

Reactive bulk composition

Iterative thermodynamic modeling (ITM)

- Strategy
- Model quality factors
- Is it relevant to use a local bulk composition?

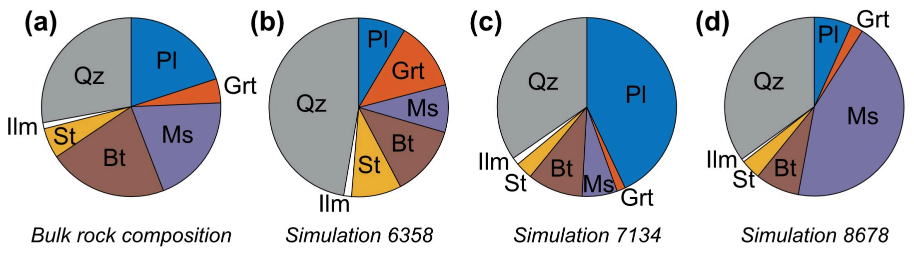
Bingo-Antidote

Summary and perspectives

Monte Carlo simulation

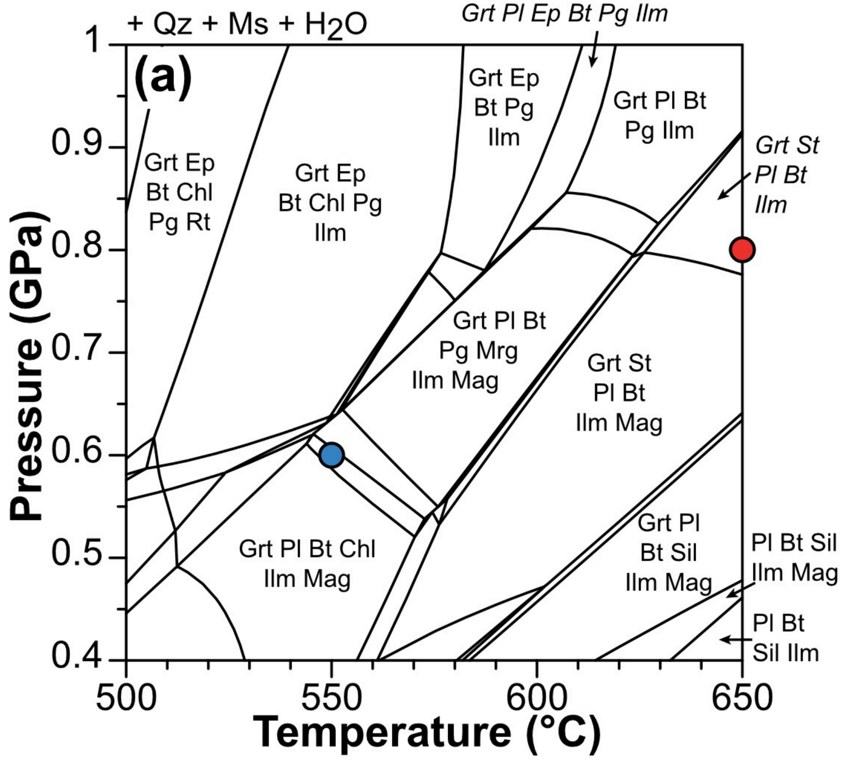
Lanari & Hermann (2021), JMG

Fixed mineral compositions	+	Variable modes (N=10,000)	=	Variable LBC (N=10,000)
from the model		*Simulated*		*Input of GEM*



10,000 simulations for each scenario

Fixed *P–T* (650 °C, 0.8 Gpa)



Equilibrium scenario

All mineral compositions are taken as the model outcomes at 650 °C and 0.8 Gpa (X_{ab} = 0.71) 🔴

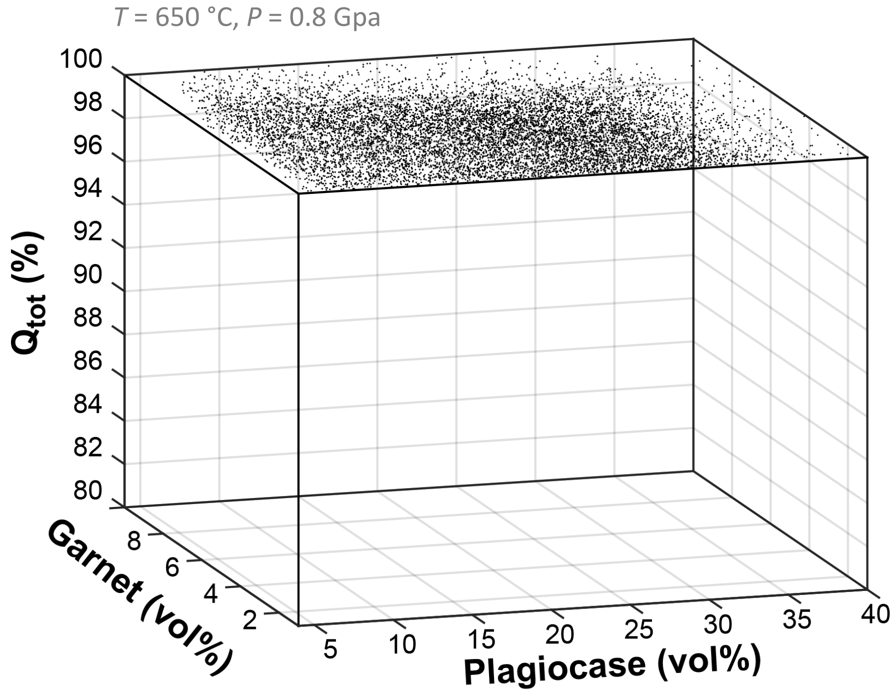
Disequilibrium scenario

Mineral compositions are taken as the model outcomes at 650 °C and 0.8 Gpa except for plagioclase for which a “wrong” composition is used (X_{ab} = 0.64) 🔵

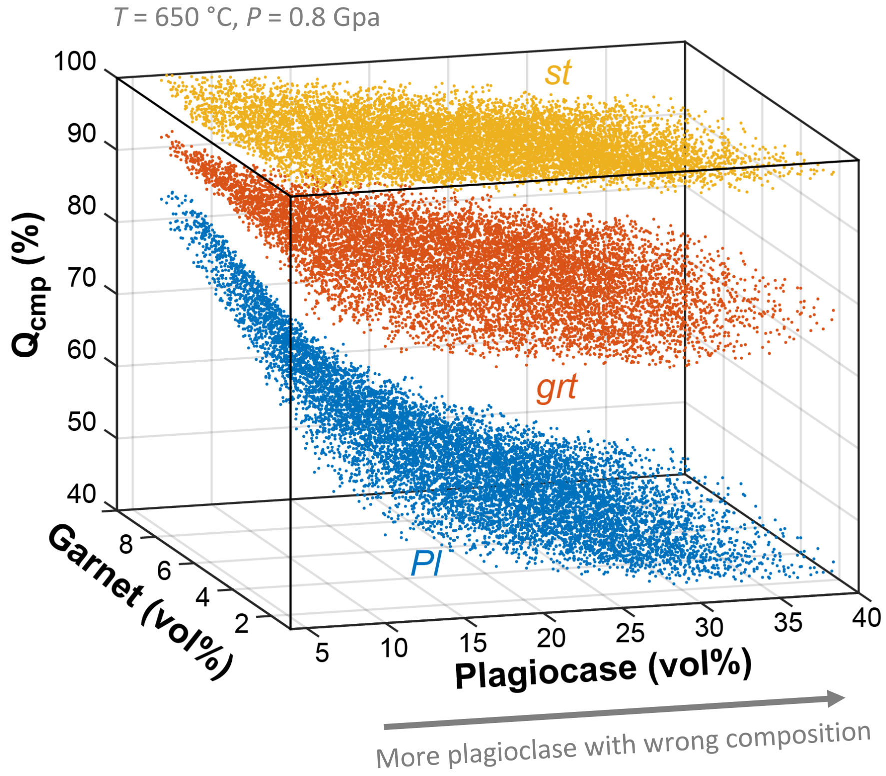
How are the LBC affecting the model outcomes at 650 °C and 0.8 Gpa?

Lanari & Hermann (2021), JMG

Equilibrium scenario



Disequilibrium scenario



The Investigation of well equilibrated samples can be performed using the bulk rock composition determined by XRF or any local bulk composition

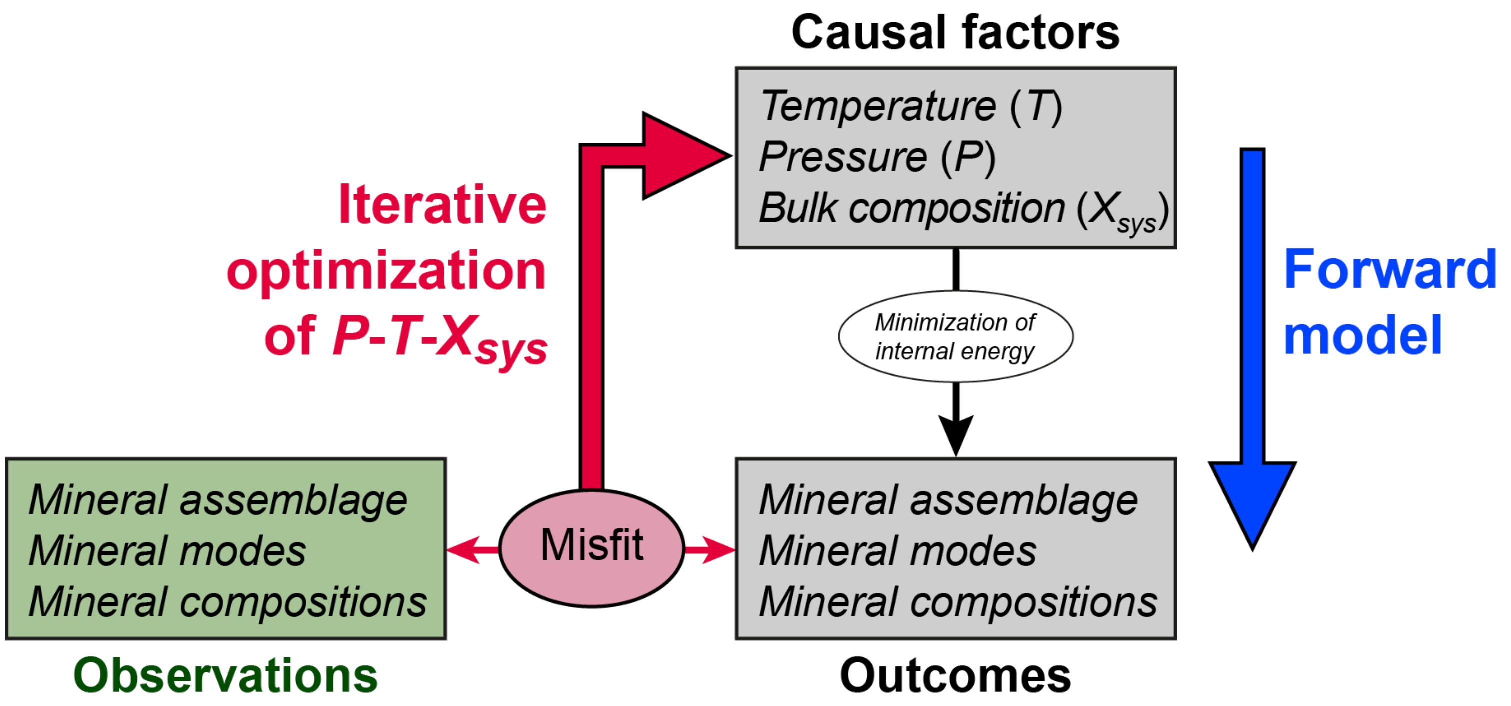
The response of different domains should be investigated using a robust statistical approach to identify which mineral or part of a mineral are (or are not) in the equilibration volume

Warning: phase diagrams are different!

*** e.g. *"BEST PRACTICES" (Waters)* ***

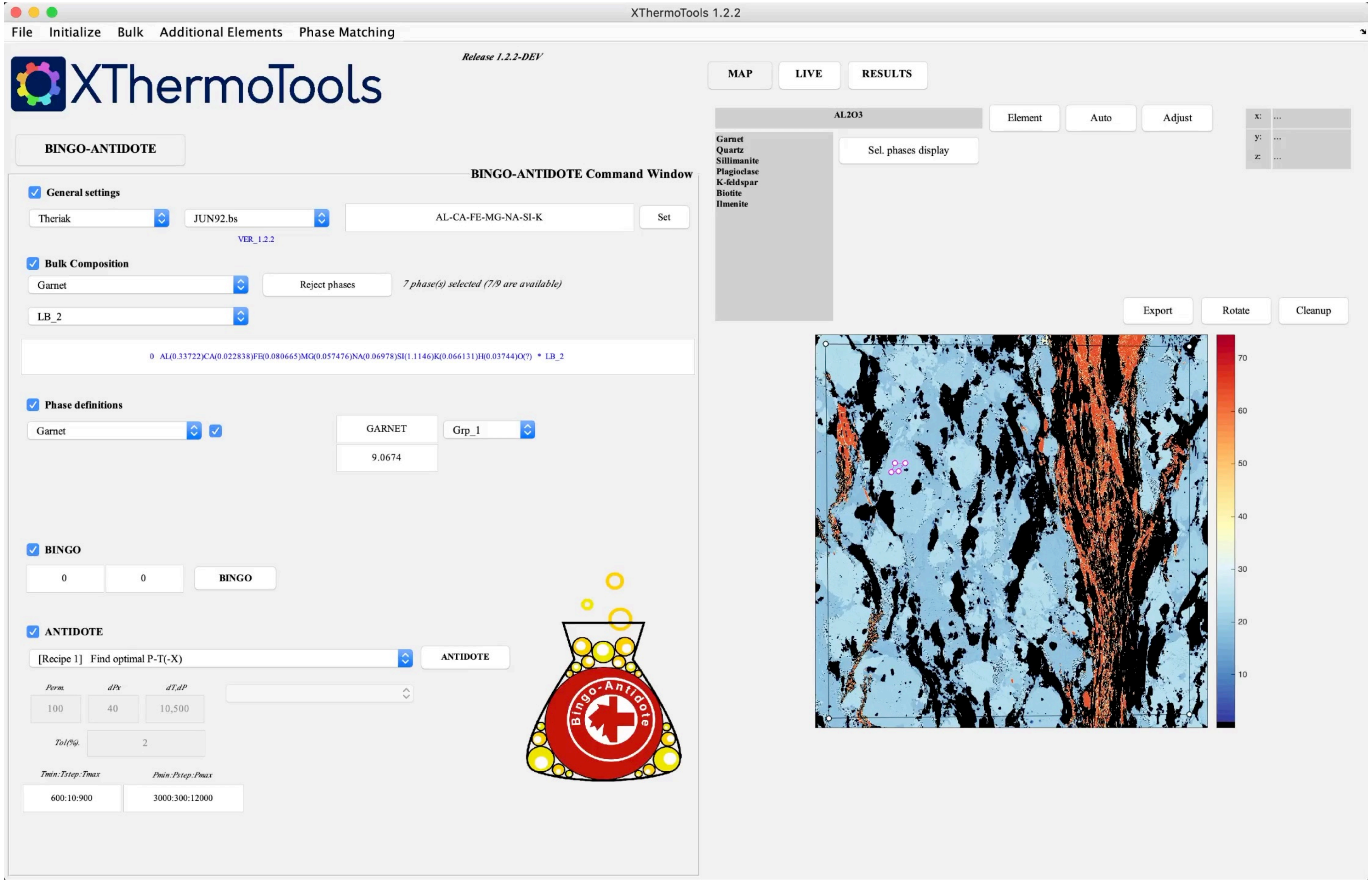
Bingo-Antidote

A **software solution** for iterative thermodynamic modeling



- **BINGO** uses Theriak to minimize the Gibbs energy and calculate the model quality factors Q_{asm}, Q_{vol}, Q_{cmp} and Q_{totat} for any set of P–T–X_{syst} conditions
- **ANTIDOTE** contains a series of optimization subroutines to determine the optimal set of P–T(–X) conditions or map the objective function(s) in different dimensions

Bingo-Antidote — Evaluation at single *P*–*T* conditions (Bingo)



Phase Equilibrium Modeling

An introduction to petrological modelling

Part 6

Introduction

Reactive bulk composition

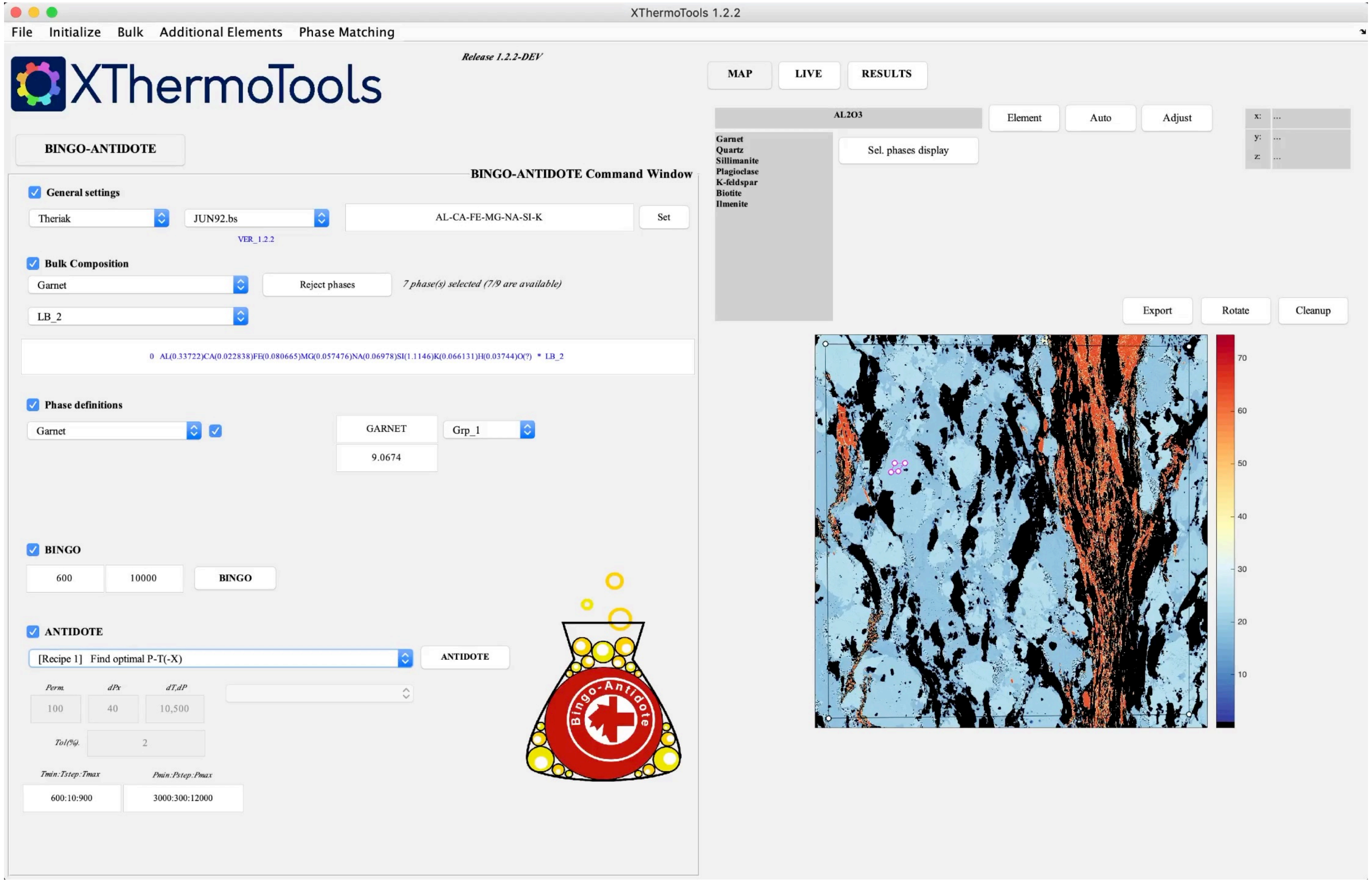
Iterative thermodynamic modeling (ITM)

Bingo-Antidote

- Program description
- Examples

Summary and perspectives

Bingo-Antidote — Optimization of *P–T* conditions (Antidote)



Bingo-Antidote — Output part 1: Q_{asm} and Q_{vol}

```
------------------------------------------------------
   >>> New BINGO Run: 10-May-2021 07:47:38  <<<

Bulk        1  AL(0.33722)CA(0.022838)FE(0.080665)MG(0.057476)NA(0.06978)SI(1.1146)K(0.066131)H(0.03744)O(?)  *  LB_2
Database    JUN92.bs
P(bar)      7000
T(C)        733


##### Evaluation criterion (1) ASSEMBLAGE #####
Phases:      GARNET    FSP2      FSP2_Kfs  BIOTITE   B-QUARTZ  SILLIMANITE
THER:        1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
XMAP:        1.000000  1.000000  1.000000  1.000000  1.000000  1.000000

--------------------------------
n =         6
m =         6
l =         6
Qasm =      100.00
--------------------------------


##### Evaluation criterion (2) VOLUME FRACTIONS #####
Phases:      GARNET    FSP2      FSP2_Kfs  BIOTITE   B-QUARTZ  SILLIMANITE
THER:        0.093010  0.235869  0.165864  0.080922  0.350362  0.073972
XMAP:        0.090674  0.222942  0.167373  0.085637  0.351800  0.081573
abs(D):      0.002336  0.012927  0.001509  0.004715  0.001438  0.007601

-----------------------------
Qvol =      98.48
-----------------------------
```

Bingo-Antidote — Output part 2: Q_{cmp}

Evaluation criterion (3) PHASE COMPOSITIONS

-

GARNET

Els:	CA	MG	FE	MN*
THER:	0.107950	0.807239	2.084811	0.000000
XMAP:	0.139156	0.847686	2.002418	0.000000
UNC:	0.021363	0.083308	0.109730	0.000000
DIFFab:	0.031206	0.040447	0.082393	0.000000
QUALs:	0.898423	1.000000	1.000000	0.000000

Qcmp = 96.6141 %

-

BIOTITE

Els:	SI	AL	TI*	FE	MG
THER:	3.000000	1.000000	0.000000	1.152073	1.847927
XMAP:	2.864768	1.678142	0.000000	1.057982	1.187051
UNC:	0.068303	0.060722	0.000000	0.040829	0.069665
DIFFab:	0.135232	0.678142	0.000000	0.094091	0.660876
QUALs:	0.417905	0.000000	0.000000	0.521724	0.000000

Qcmp = 23.4907 %

Bingo-Antidote — Output part 3: summary

Phase	GARNET	FSP2	FSP2_K	BIOTIT	B-QUAR	SILLIM
Evaluated	Yes	Yes	Yes	Yes	Yes	Yes
Qual (%)	96.61	88.45	98.84	23.49	100.00	100.00
v_norm	0.09	0.24	0.17	0.08	0.35	0.07

Qcmp = 90.58

CHEMICAL POTENTIAL OF COMPONENTS

Oxide	mu (J)
CAO	-808839
H2O	-379004
FEO	-363989
K2O	-933067
NA2O	-864173
MGO	-684447
SIO2	-965676
O2	-638807
AL2O3	-1762130

STABLE ASSEMBLAGE (THERIAK)

Phase (solids)	Volume (%)	Density (kg.m^3)
GARNET	9.30	4036
FSP2	23.59	2621
FSP2_Kfs	16.59	2550
BIOTITE	8.09	2953
B-QUARTZ	35.04	2556
SILLIMANITE	7.40	3238

Bingo-Antidote a set of tools to explore and test

TABLE 2 List of recipes available in ANTIDOTE 1.1 (reference, name, description)

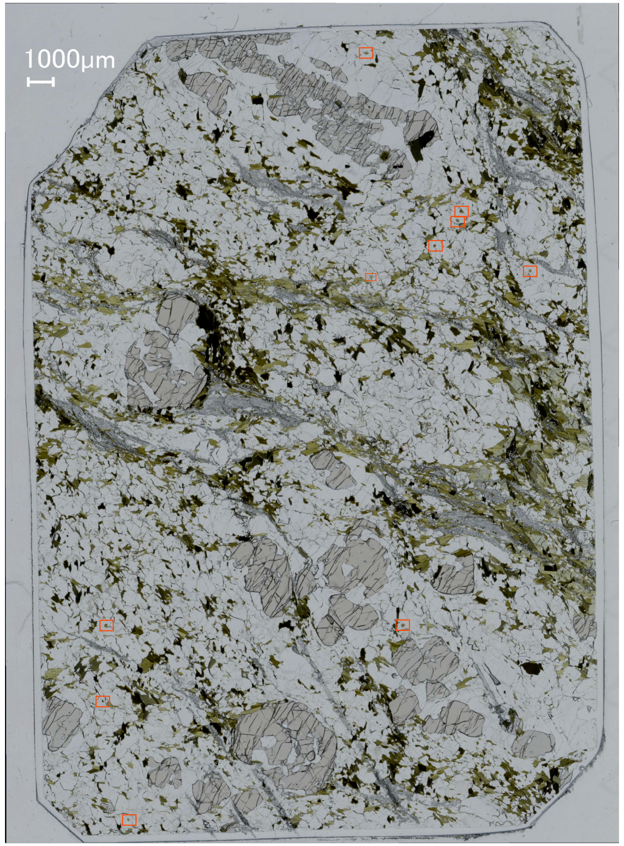
Global inversion and optimal *P–T–X* conditions		
#1	Find optimal *P–T*(–*X*)	Search routine performing a global optimization of *P*, *T*, possibly including the molar amounts of some components of the bulk composition such H, C or O and activity variables of fluids and gases: a_{H_2O}, a_{CO_2}, $f(O_2)$
#2	*P–T* map of *Q* factors	Mapping function for mapping the quality factor functions (Q_{asm}, Q_{vol}, Q_{cmp}, Q_{cmp} of individual phases and Q_{total}) in the *P–T* space
#3	*P–T* uncertainty	Search routine evaluating the local shape of the objective function ($-Q_{total}$, see text) and calculating an uncertainty envelope
Single-phase thermobarometry		
#4	Find optimal *P–T* (single phase)	Search routine performing single-phase thermobarometry via *P–T* optimization
#5	*P–T* map (single phase)	Mapping function generating Q_{cmp} maps for single phase
#6	*P–T* uncertainty (single phase)	Search routine for calculating an uncertainty envelope
Sensitivity tests on the results of GEM		
#7	Bulk sensitivity	Evaluation of the model sensitivity to the bulk composition at fixed *P–T* by randomly changing the domain shape
#8	*P–T* sensitivity	Evaluation of the model sensitivity to *P–T* conditions under fixed bulk composition by randomly changing *P–T*
#9	*P–T*-bulk sensitivity	Evaluation of the model sensitivity to the bulk composition and *P–T* conditions by randomly changing the domain shape and the *P–T* conditions
Textural investigation		
#10	Floating window (fixed *P–T*, variable bulk)	Model evaluation at fixed *P–T* for variable LBC calculated along a path using a rectangular floating window and a moving average scheme
#11	Scanning window (find optimal *P–T*, variable bulk)	Search routine applied to a scanning window to quantify how local heterogeneities in compositions can affect the optimal *P–T* conditions
#12	Growing window (find optimal *P–T*, variable bulk)	Search routine applied to a growing window for the quantification of size-related effects on the model quality
#13	Chemical potential mapping (fixed *P–T*)	Mapping of chemical potential landscapes
Optimization of compositional and activity variables		
#14	Scanning H (fixed *P–T*)	Optimization of compositional variables at fixed *P–T*
#15	Scanning C (fixed *P–T*)	
#16	Scanning O (fixed *P–T*)	

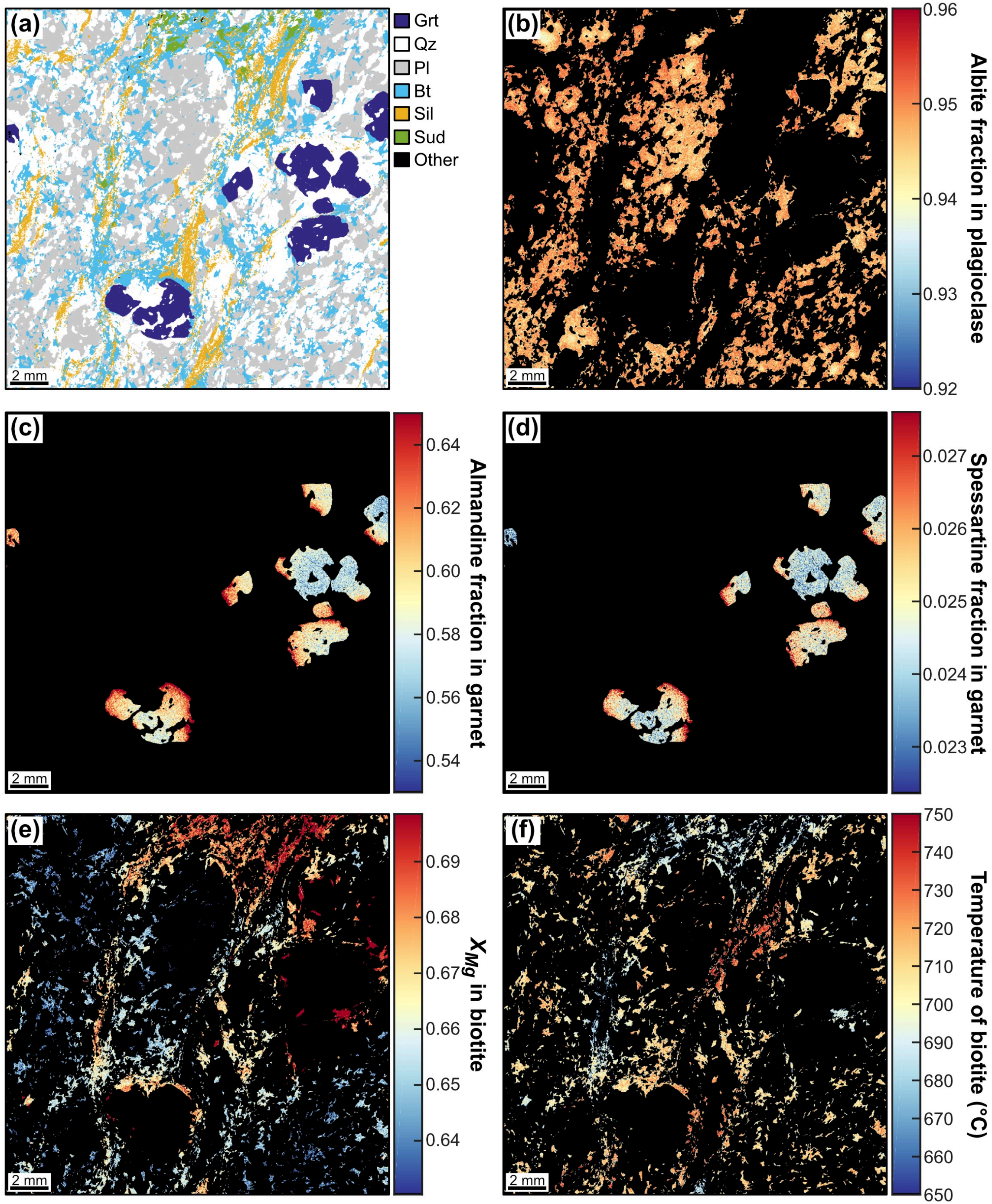
Duesterhoeft & Lanari (2020), JMG

Example

West Guilford (Ontario, Canada)

Metapelitic rock consisting of Grt+Bt+Sil+St+Pl+Qz





Duesterhoeft & Lanari (2020), JMG

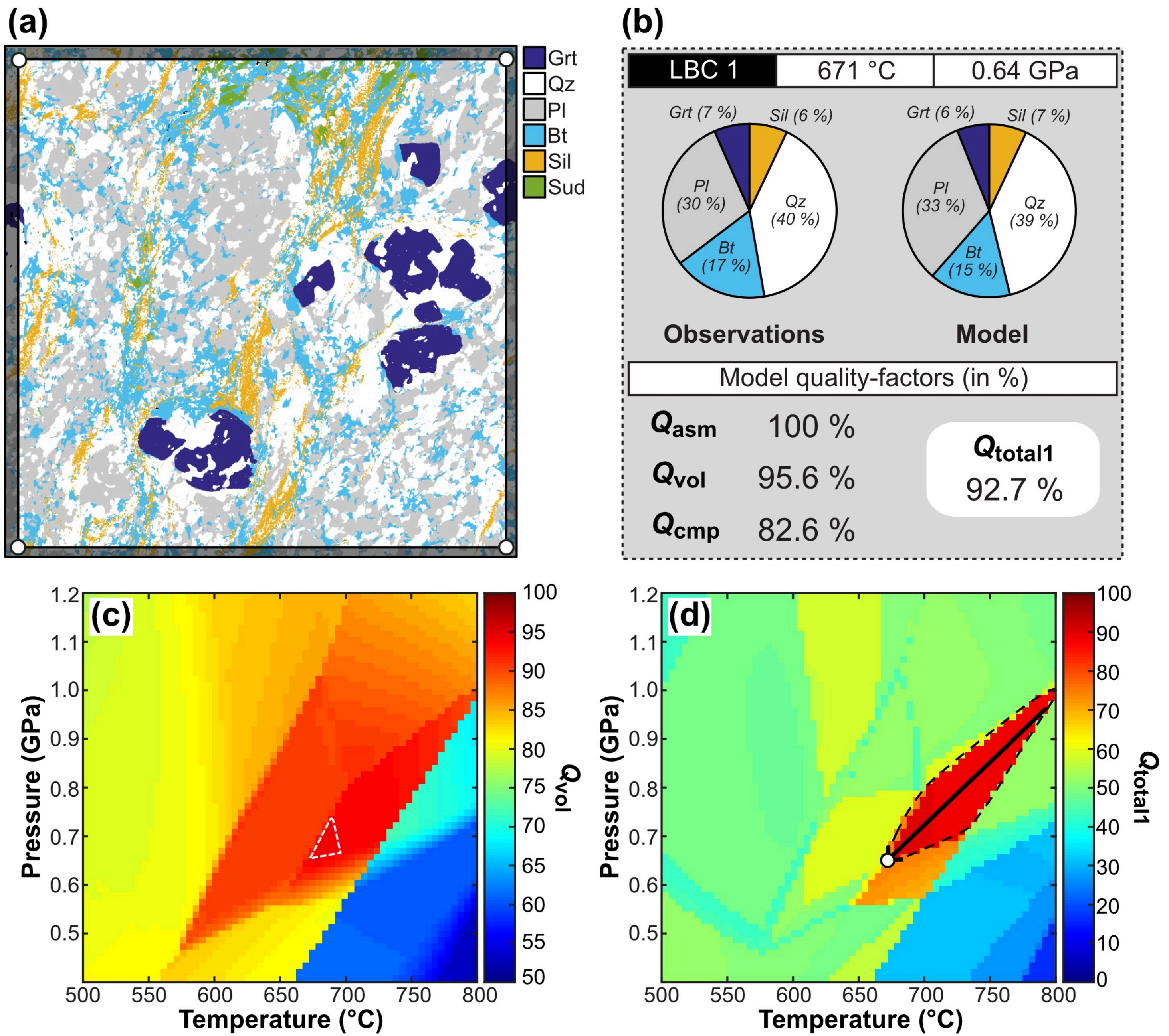
Example

Thermodynamic database: JUN92.bs (updated from Berman 1988)

- Estimation of "optimal" *P–T* conditions

Existing results:

0.72 ± 0.05 Gpa (GASP)
Anovitz & Essene (1989)



Duesterhoeft & Lanari (2020), JMG

Example

- Comparison of results obtained with different databases

Q_{cmp} values of minerals

Perfect match within uncertainty →

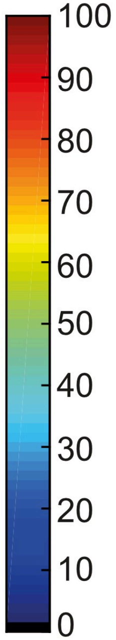
Significant differences (> 10 %) in some elements →

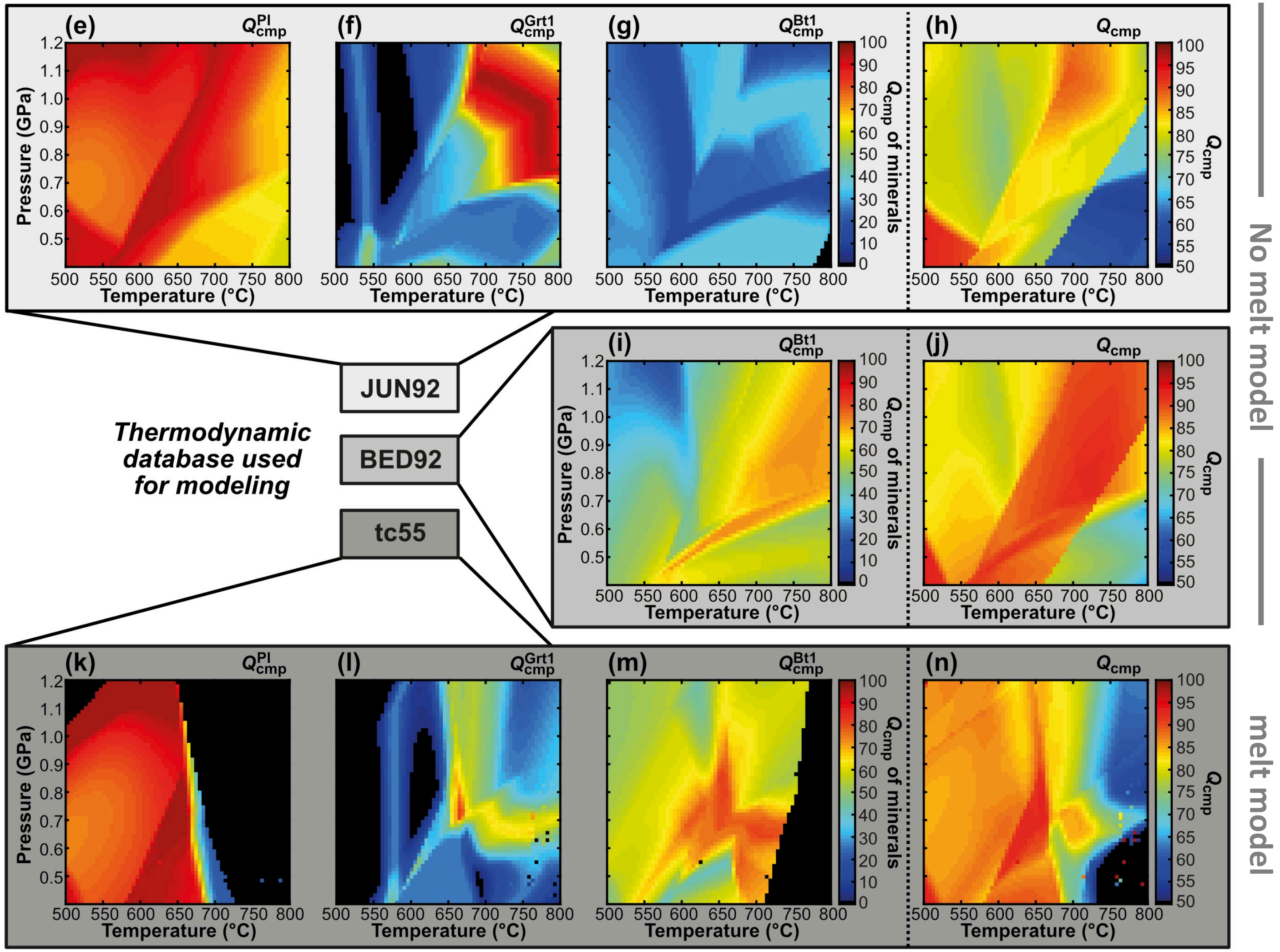
	Obs.	*Mod.*
Al	1.73 ± 0.08	1.78
Fe	1.01 ± 0.05	0.99
Mg	1.27 ± 0.08	1.49
Ti	0.11 ± 0.02	0.12

Critical differences (> 20 %) for most elements →

	Obs.	*Mod.*
Al	1.73 ± 0.08	1.27
Fe	1.01 ± 0.05	1.13
Mg	1.27 ± 0.08	1.65
Ti	0.11 ± 0.02	0.08

Example for biotite



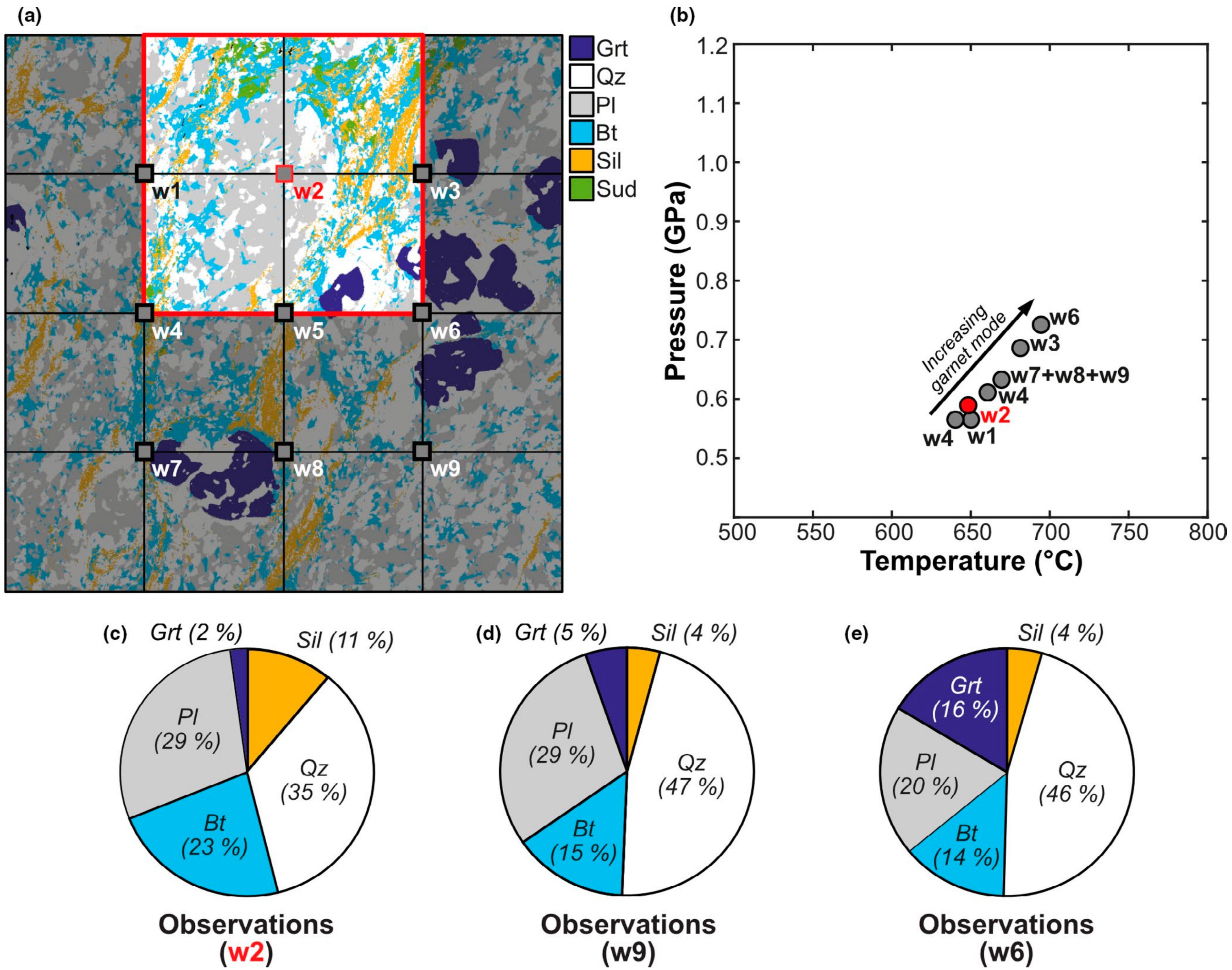


- ▶ Peak conditions: identical with all databases
- ▶ Mineral formation conditions: slight differences between databases

Example

Thermodynamic database: JUN92.bs (updated from Berman 1988)

- Automated Textural investigation



Duesterhoeft & Lanari (2020), JMG

PHASE EQUILIBRIUM MODELING

AN INTRODUCTION TO PETROLOGICAL MODELLING

Part 6

Introduction

Reactive bulk composition

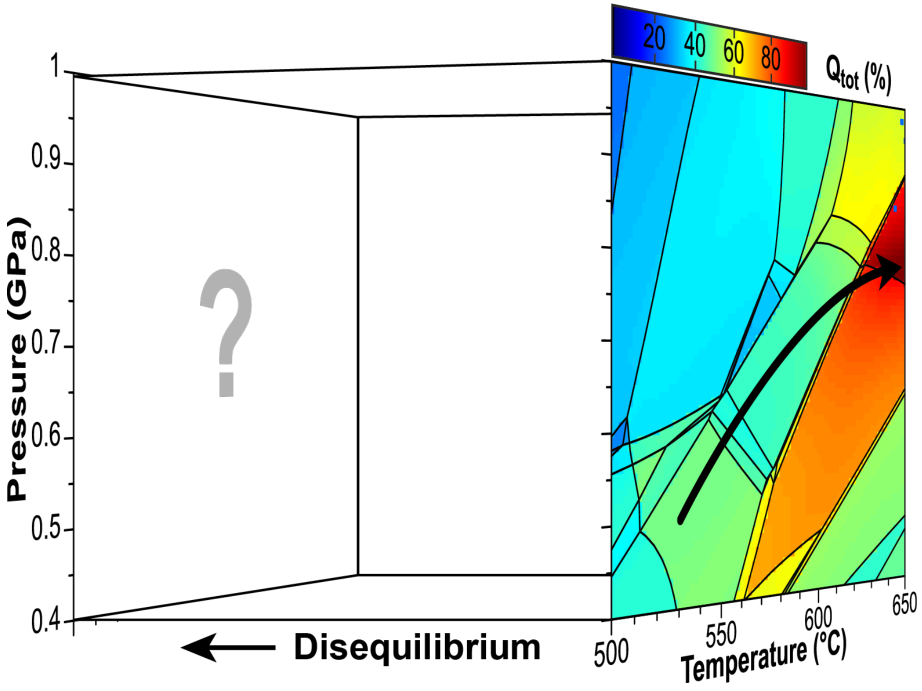
Iterative thermodynamic modeling (ITM)

Bingo-Antidote

Summary and perspectives

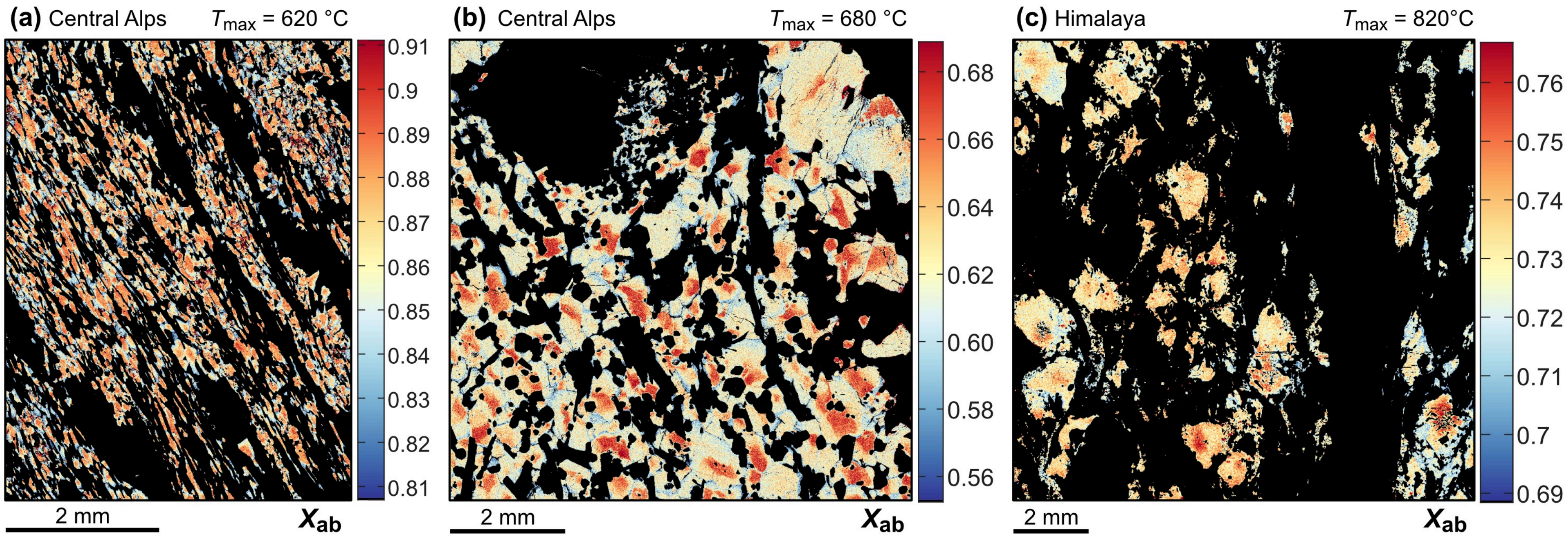
- Disequilibrium features in metamorphic rocks
- Test of databases with natural samples

Summary and perspectives



Challenges: partial re-equilibration

Apparently, plagioclase is often in a "disequilibrium scenario"



Lanari & Hermann (2021), JMG — Lanari & Dietrich (unpublished data) — Lanari & Duesterhoeft (2019), JPeT

As are also garnet, white mica, epidote, amphibole, etc.

e.g. Tracy (1982), RIMG

For plagioclase: it is possible to exclude the unreacted core and quantify the differences if iterative models are used. Remember that the presence of a metastable plagioclase affects the position of garnet isopleths.

➡ Bingo-Antidote provides a set of tools to explore and test

Summary

- Fraction effects (presence of zoned minerals or metastable relics; extraction of melt) can affect isopleth thermobarometry. In this case, a reactive bulk composition must be used
- Local bulk compositions can be used as reactive bulk compositions in ITM for thermobarometry
- It is recommended to investigate several domains in rocks potentially affected by partial re-equilibration at peak conditions
- Based on ITM, we can apply equilibrium thermodynamics to complex natural rocks in a more meaningful way

Perspectives

► Why not using model quality factor to test databases? It provides an efficient and rapid

- comparison between databases
- test of specific solid solution models

*** *more tests in "ASSESSMENT AGAINST THE NATURAL RECORD" (Forshaw & Pattison)* ***

PHASE EQUILIBRIUM MODELING

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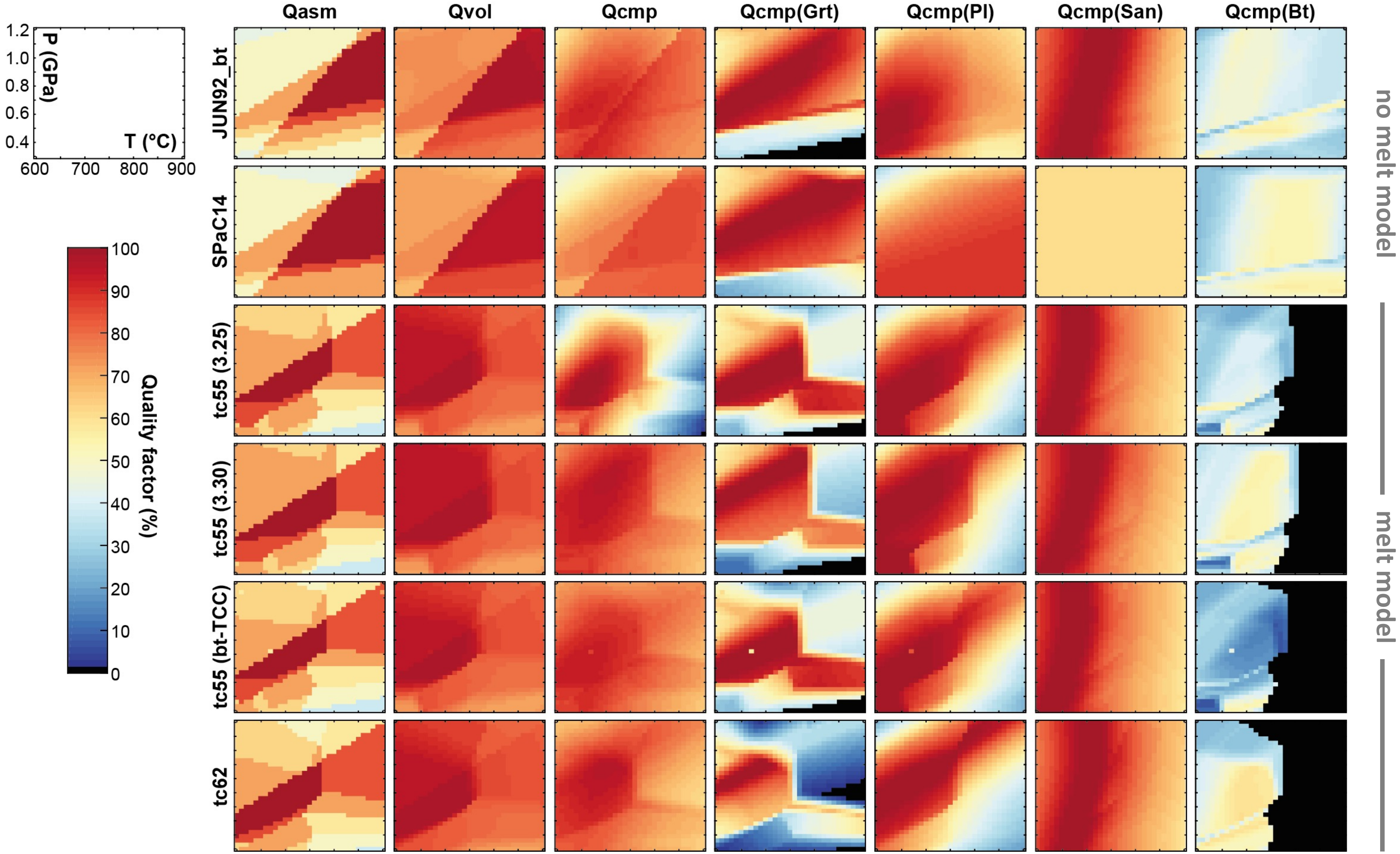
Summary and perspectives

- Disequilibrium features in metamorphic rocks
- **Test of databases with natural samples**

Improve the databases by running more tests to identify problems in solution models?



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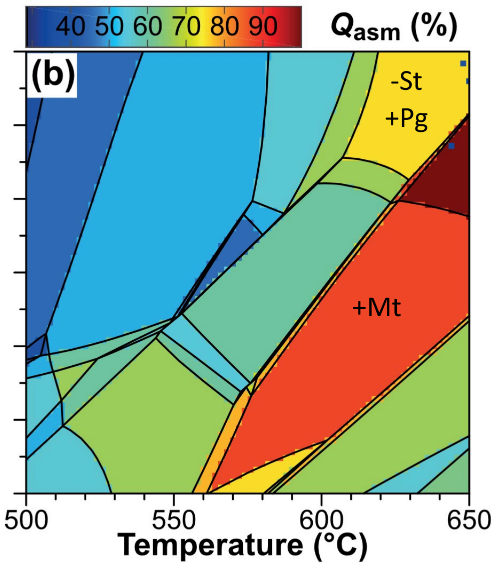
(Maps of) model quality factors: Q_{asm} Q_{vol} Q_{cmp} Q_{total}

Duesterhoeft & Lanari (2020), JMG



THER	XMAP
a	a
b	b
c	c
-	-
-	-
Qasm=100%	

THER	XMAP
a	a
b	b
c	c
-	d
-	e
Qasm=3/5=60%	

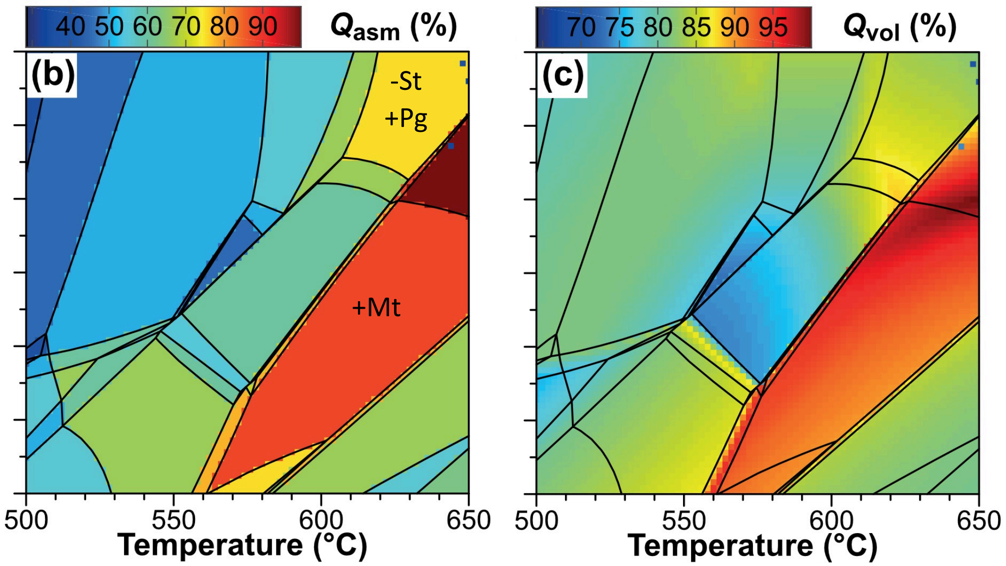
Mineral assemblage (Q_{asm})

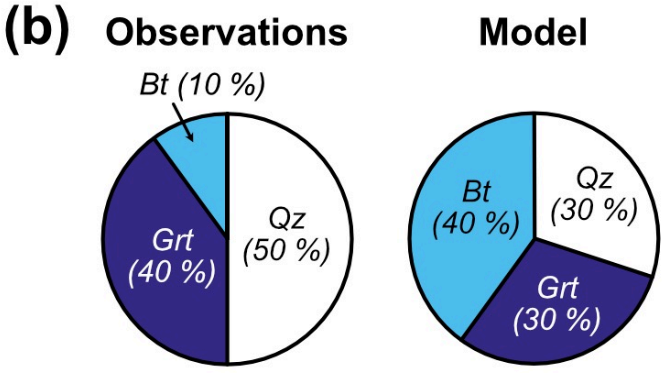
$$Q_{\mathrm{asm}} = \frac{l}{k}$$

l is the number of marching phases between model and observation
k is the total number of phases involved in model and observation

(Maps of) model quality factors: Q_{asm} Q_{vol} Q_{cmp} Q_{total}

Duesterhoeft & Lanari (2020), JMG





Q_{vol} = 72 %

Mineral modes (Q_{vol})

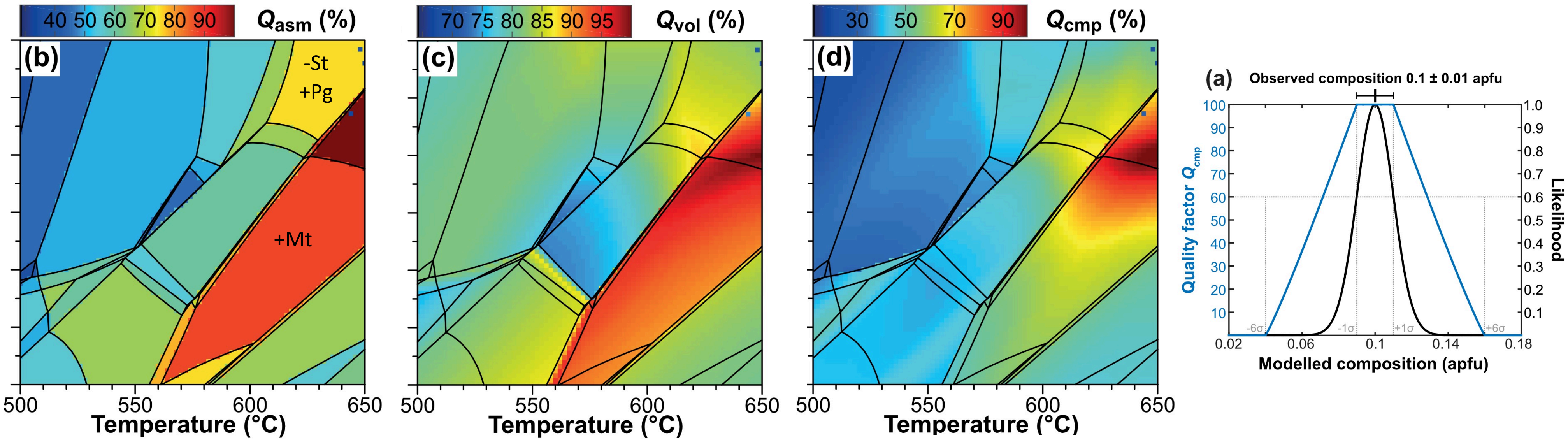
$$Q_{\mathrm{vol}} = \sqrt{\sum_{i=1}^{l} \frac{\left(v_i^{\mathrm{mod}} + v_i^{\mathrm{obs}}\right)}{2} \cdot \left(1 - \frac{\mathrm{abs}\left(v_i^{\mathrm{mod}} - v_i^{\mathrm{obs}}\right)}{v_i^{\mathrm{mod}} + v_i^{\mathrm{obs}}}\right)^2}$$

l is the number of matching phases between model and observation

v_i^{obs} and v_i^{mod} are the observed and modeled volume fractions

(Maps of) model quality factors: Q_{asm} Q_{vol} Q_{cmp} Q_{total}

Duesterhoeft & Lanari (2020), JMG



Mineral compositions ($\boldsymbol{Q}_{\mathbf{cmp}}$)

Q_{cmp} of element j in phase i

$$Q_{i,j}^{\mathrm{cmp}} = 100 \cdot \left(1 - \frac{\left(\left(\Delta_{i,j} - \sigma_{ij}\right)\right)}{6 \cdot \sigma_{ij}}\right)^{X_{i,j}^{\mathrm{model}}+1}$$

Q_{cmp} of the model

$$Q_{\mathrm{cmp}} = \sum_{i} v_i^{\mathrm{norm}} \sum_{j}^{j=l} \frac{Q_{i,j}^{\mathrm{cmp}}}{l}$$

For a phase *i*, $\Delta_{i,j}$ is the absolute difference in composition of element *j*; σ_{ij} is the relative analytical uncertainty expressed in apfu; $X_{i,j}^{\mathrm{model}}$ is the modeled composition; v_i^{norm} is the normalized volume fraction for the *l* matching phases