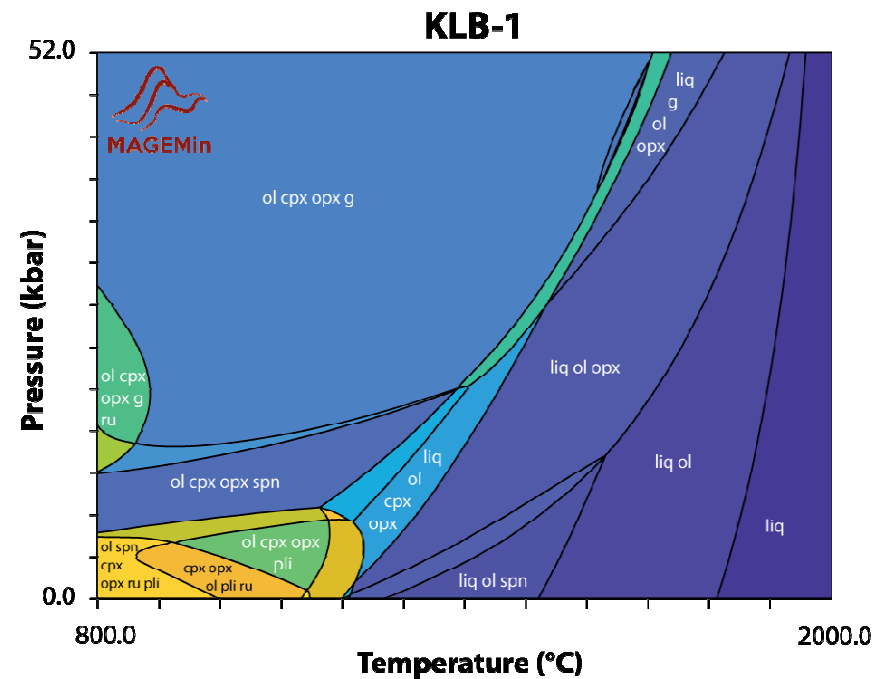


A new and efficient computational thermodynamics approach for magmatic systems

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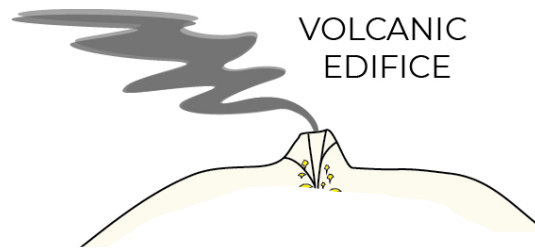


1. Johannes-Gutenberg University Mainz, Germany

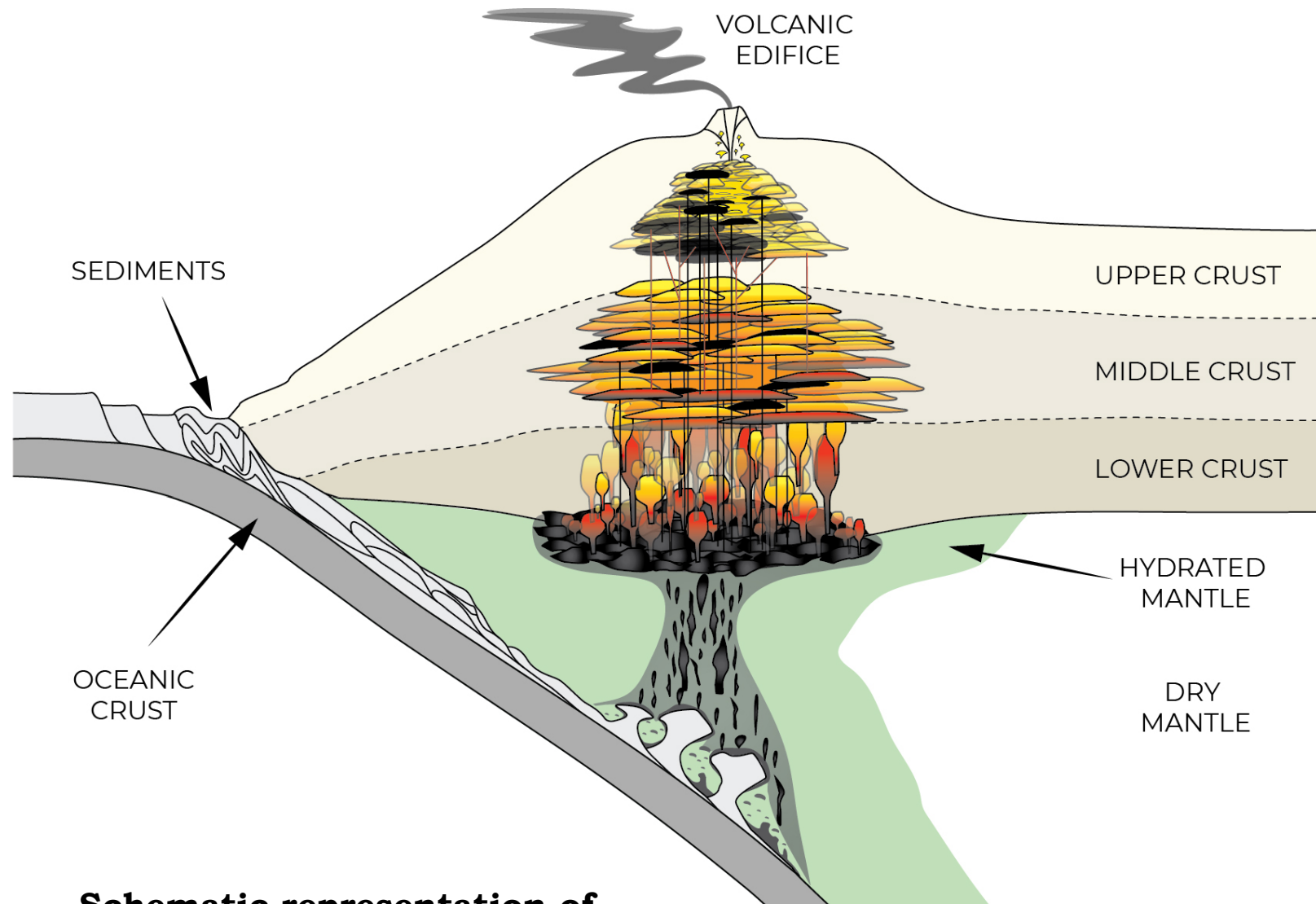
2. Melbourne University, Melbourne, Australia

3. Federal Institute of Geosciences and Natural Resources (BGR), Hannover, Germany

Introduction – The magmatic refinery



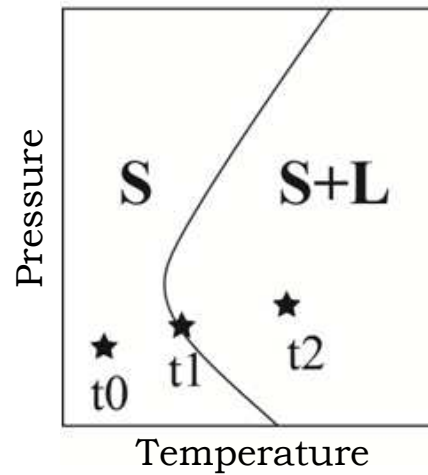
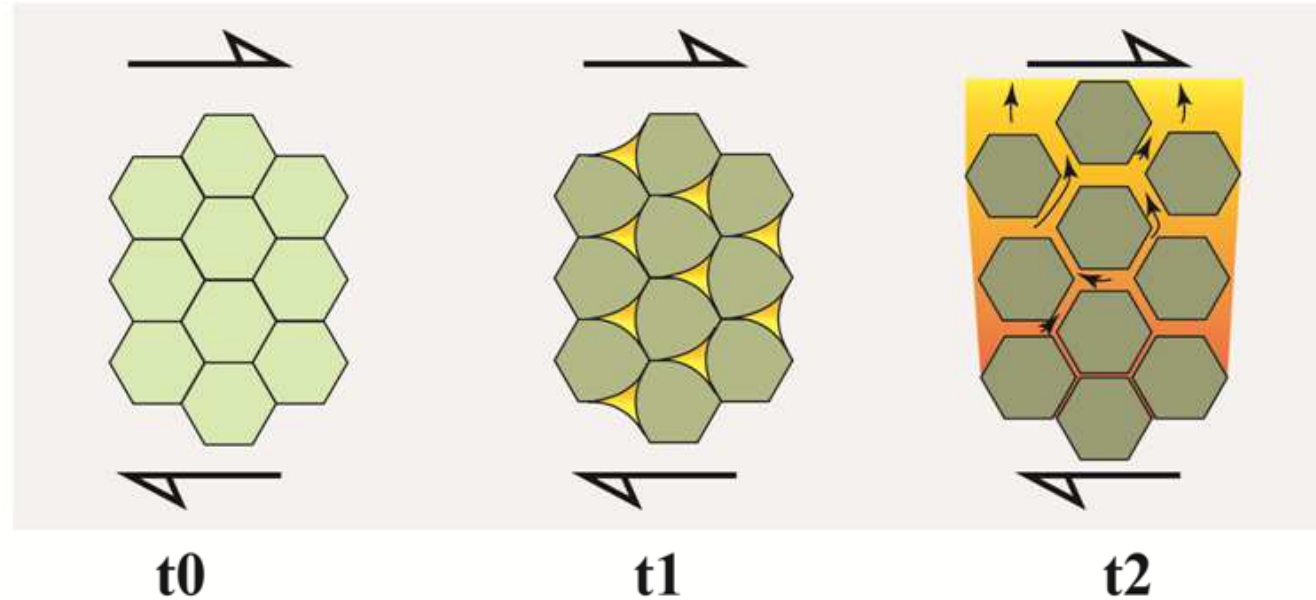
Introduction – The magmatic refinery



**Schematic representation of
the exposed Famatinian magmatic arc**
(Sierra de Valle Fértil, Argentina)

(After J. Cornet, ETH Zürich)

Introduction – Reactive magma transport model

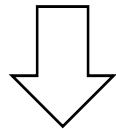


- Thermomechanical deformation
- Two-phase flow
- **Thermodynamics**

(visco-elasto-plastic)
(magma segregation)
(stable phases)

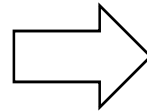
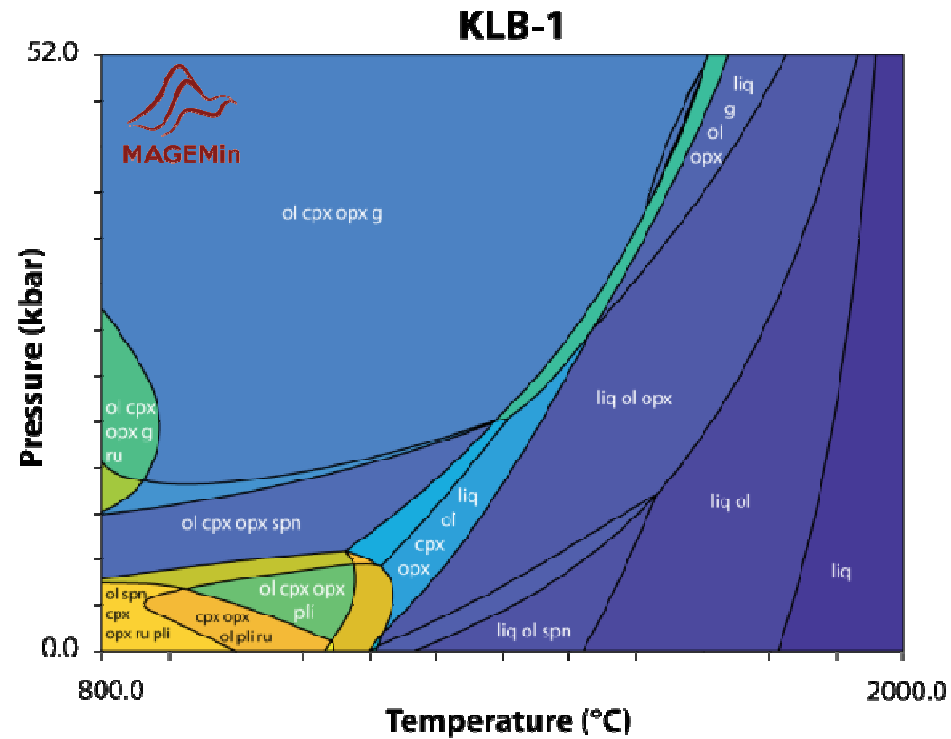
Thermodynamic equilibrium – stable phases

- Pressure
- Temperature
- Composition
- Thermodynamic database (minerals/melt)



Gibbs free energy minimization

- Perple_X
- MELTS
- Theriak-Domino

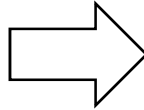


- Stable phases
- Phase fractions
- Solid/fluid/melt densities
- Seismic velocities, expansivity...

Why do we need a new minimizer?

Available Gibbs free energy Minimizer

- Perple_X
- MELTS
- Theriak-Domino



Developed to produce phase diagrams

- Not/partially parallelized
- Relatively slow and/or unstable (often 'crashes')
- Cannot be directly coupled to geodynamic simulations
- Not optimized to update solution under slight P - T - C changes
- Lot of work in adding new db

Constraints on a minimizer for magmatic modelling

- Open source and code efficient
 - Built-in database
 - Fully parallel for scalability
 - Easily callable by external software
 - Fast and stable
 - Incorporate most recent thermodynamic database
- C language
 - No input files
 - MPI
 - Executable or C-wrapper
 - Holland et al., 2018

Phase equilibria – mathematical formulation

- Chemical potential of phases (pure and solution)

$$(1) \quad \mu_i = \frac{\tilde{\mu}_i}{RT} = g_{i(l)}^{\circ} + \ln(x_{i(l)}) + g_{i(l)}^{\text{ex}},$$

- Gibbs free energy of a multicomponent multiphase system

$$(2) \quad \frac{G}{RT} = \sum_{l=1}^L n_l \sum_{i=1}^{N_l} x_{i(l)} \mu_i + \sum_{k=1}^K n_k \mu_k,$$

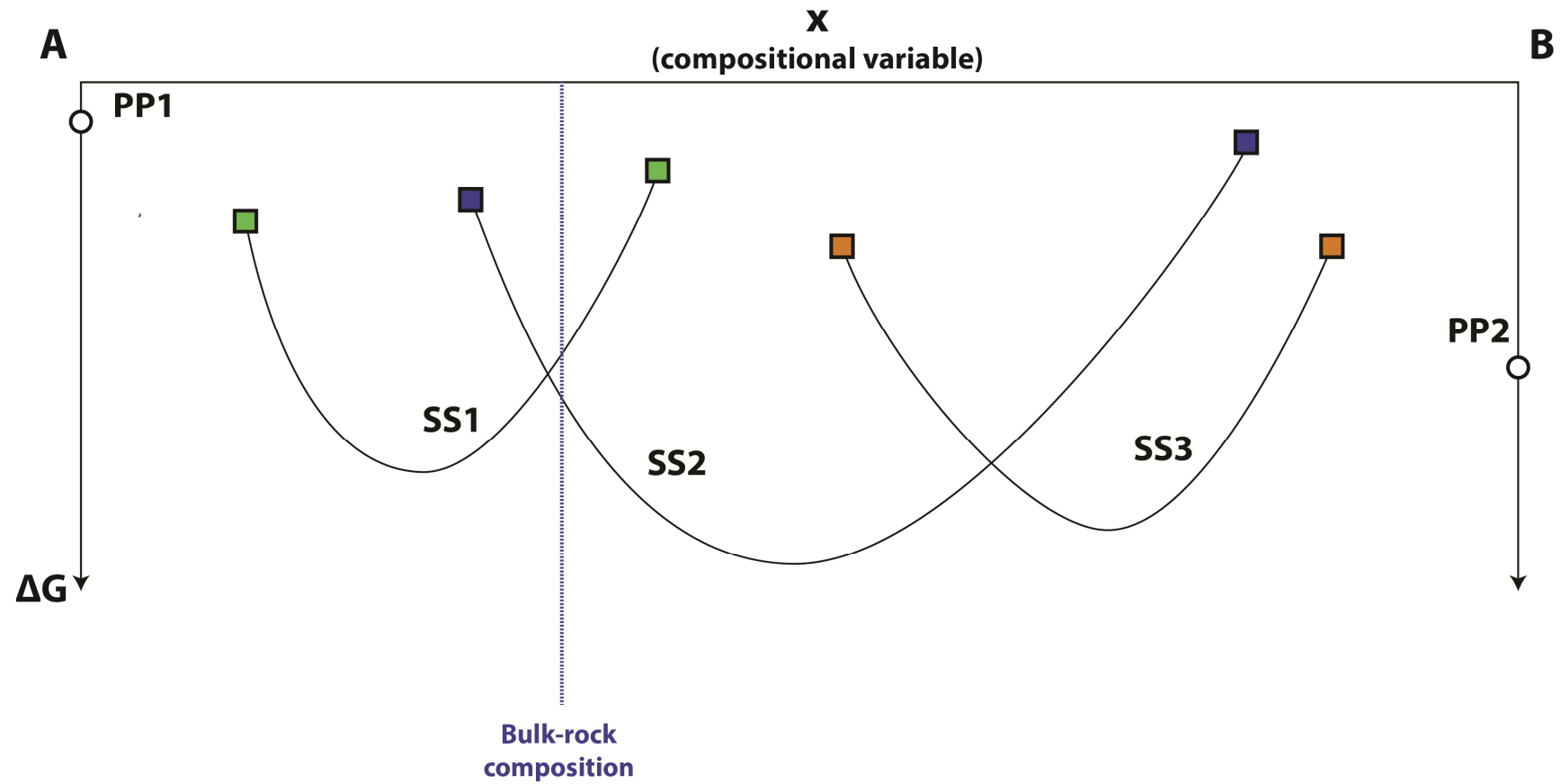
- Gibbs-Duhem equation

$$(3) \quad \mu_i = \sum_{j=1}^C a_{ij} \Gamma_j.$$

- Mass constraint

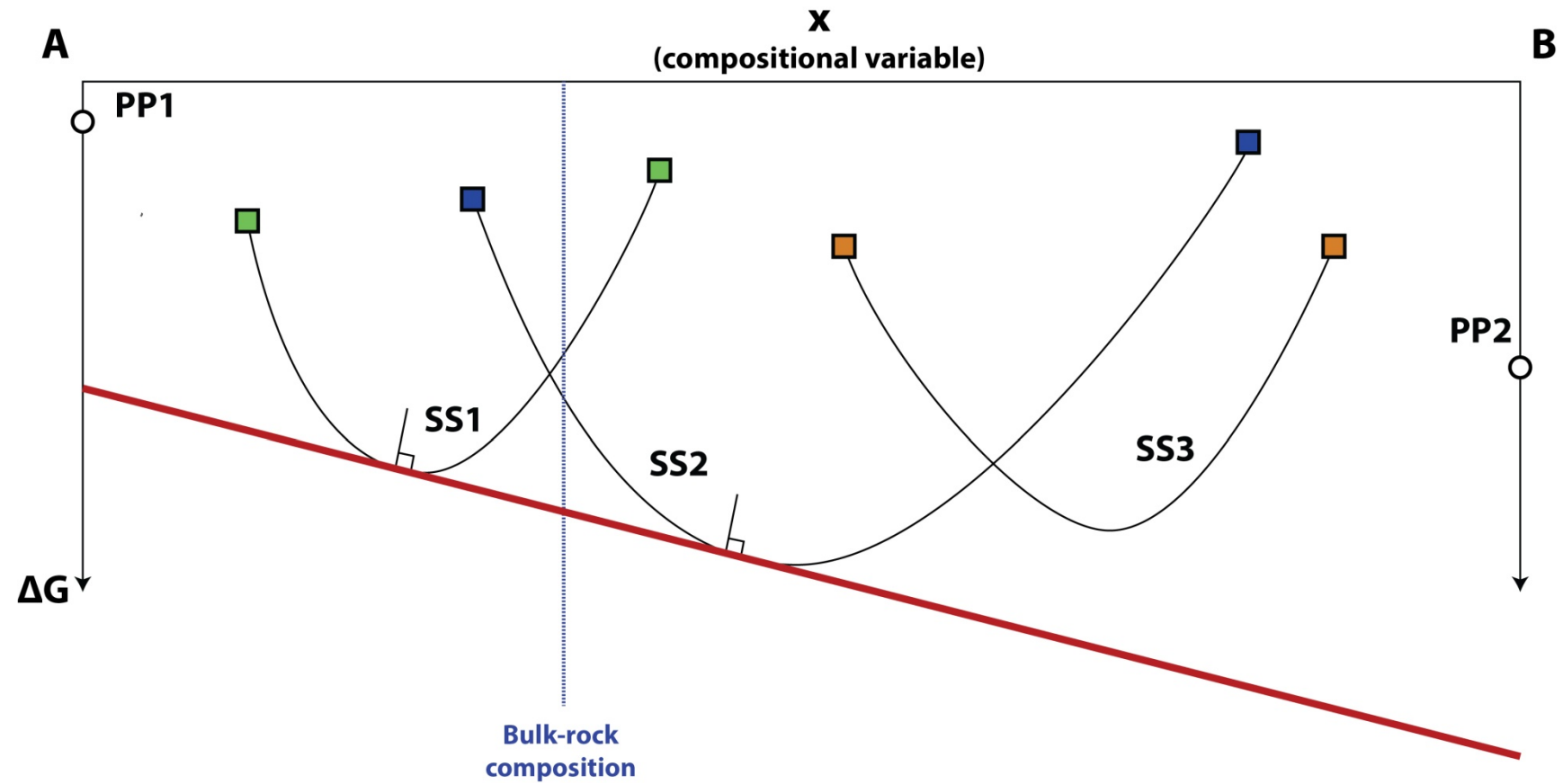
$$(4) \quad b_j = \sum_{l=1}^L n_l \sum_{i=1}^{N_l} x_{i(l)} a_{ij} + \sum_{k=1}^K n_k a_{kj},$$

Phase equilibria : an optimization problem



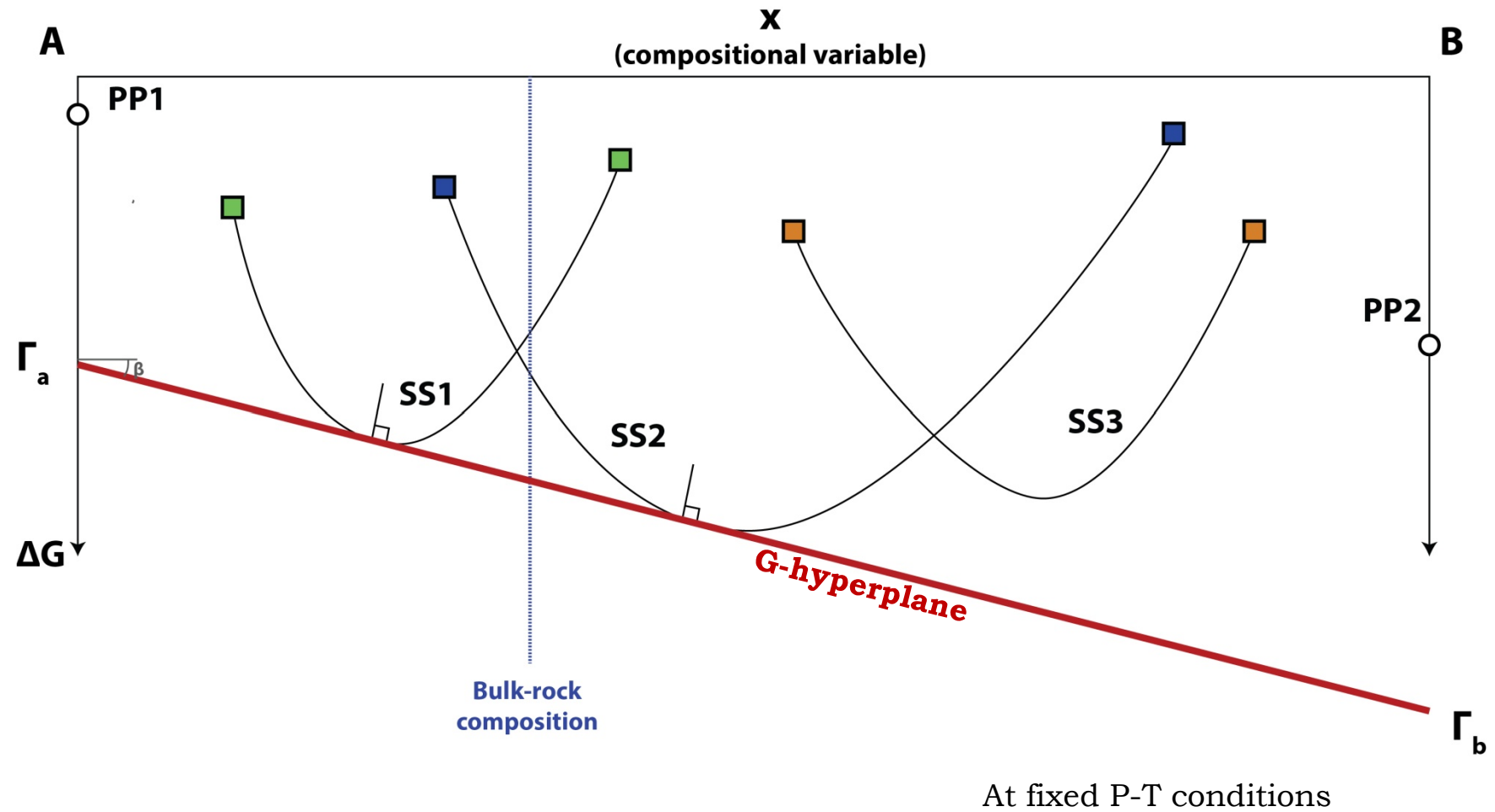
At fixed P-T conditions

Phase equilibria : an optimization problem



At fixed P-T conditions

Phase equilibria : an optimization problem



Approaches to Gibbs free energy minimization

I. Pseudocompounds (Perple_X, Connolly)

- Discretized solution space (treat each point as pure phase)
- Simplex linear programming



- Avoid local minimum
- Algorithm relatively easy to implement

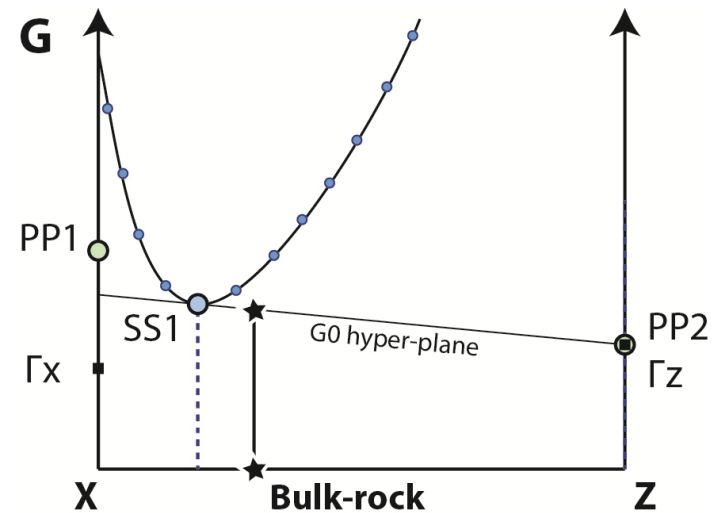
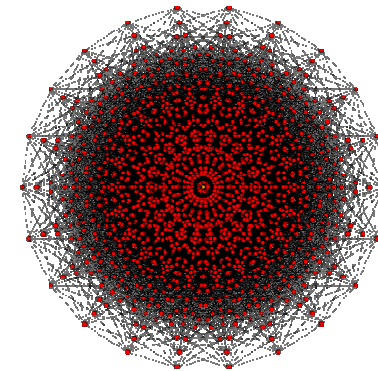


- Slow for large multicomponent systems
- Massive memory usage

e.g., Amphibole discretization in 11D (10 points/dim)

→ **100 billion** pseudocompounds!

Perple_X



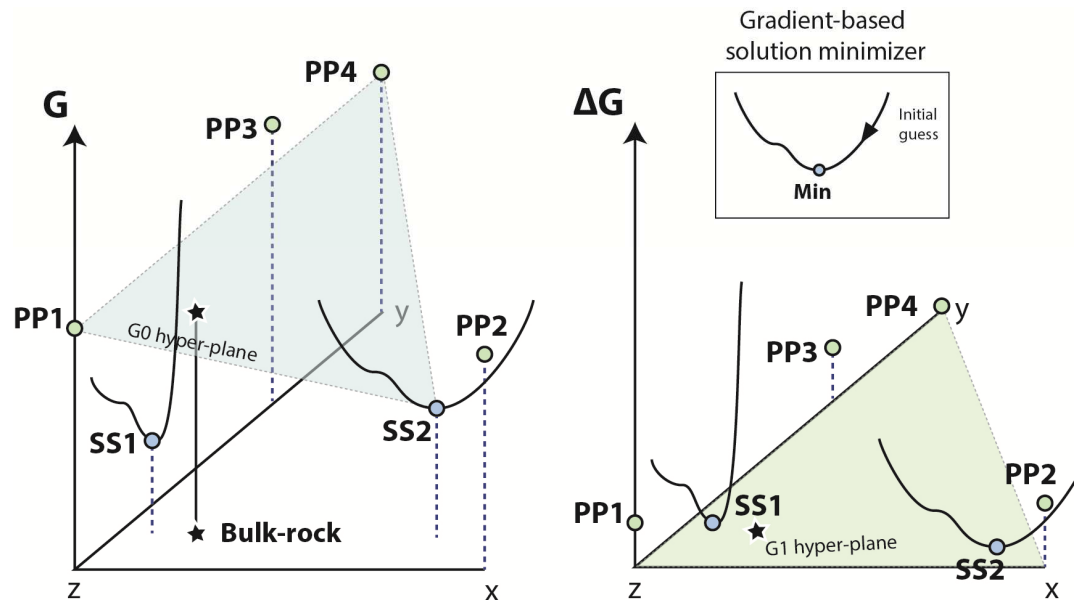
(11D hypercube, after Wikipedia)

Approaches to Gibbs free energy minimization

II. Levelling (Theriak-Domino, de Capitani)



- Consider Endmembers as pure phases
 - Simplex approach to estimate Γ
 - Minimize solution phases within Γ space
- } **ITERATE**



- Gradient based method
- Low memory usage



- Slow for complex systems
- Chemical potential Γ not coupled with mass constraint

Approaches to Gibbs free energy minimization

III. Partitioning Gibbs energy (Piro et al., 2011, 2013)

- Coupled mass balance and chemical potential
- SLE solved with Newton-Raphson method

$$\left. \begin{aligned} \mu_i &= \frac{\tilde{\mu}_i}{RT} = g_{i(l)}^\circ + \ln(x_{i(l)}) + g_{i(l)}^{\text{ex}} \\ \mu_i &= \sum_{j=1}^C a_{ij} \Gamma_j \end{aligned} \right\} x_{i(l)} = \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^\circ - g_{i(l)}^{\text{ex}} \right)$$

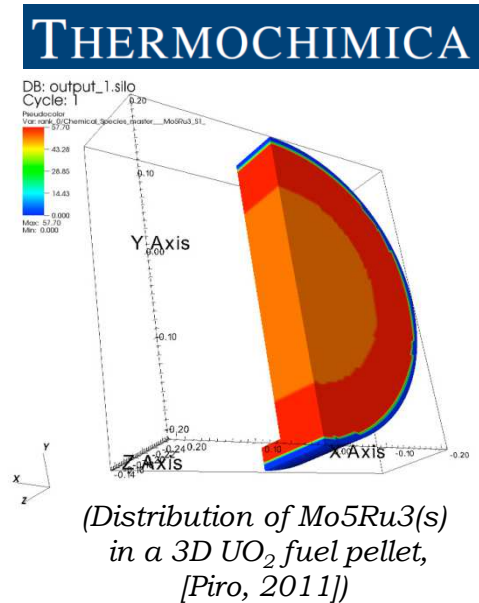
$$b_j = \sum_{l=1}^L n_l \sum_{i=1}^{N_l} \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^\circ - g_{i(l)}^{\text{ex}} \right) a_{ij} + \sum_{k=1}^K n_k a_{kj}$$



- Scales to large multicomponent systems (> 100)
- Mass balance is coupled with chemical potential
- Very efficient (developed for nuclear reactor simulations)
- Easily parallelized and memory efficient

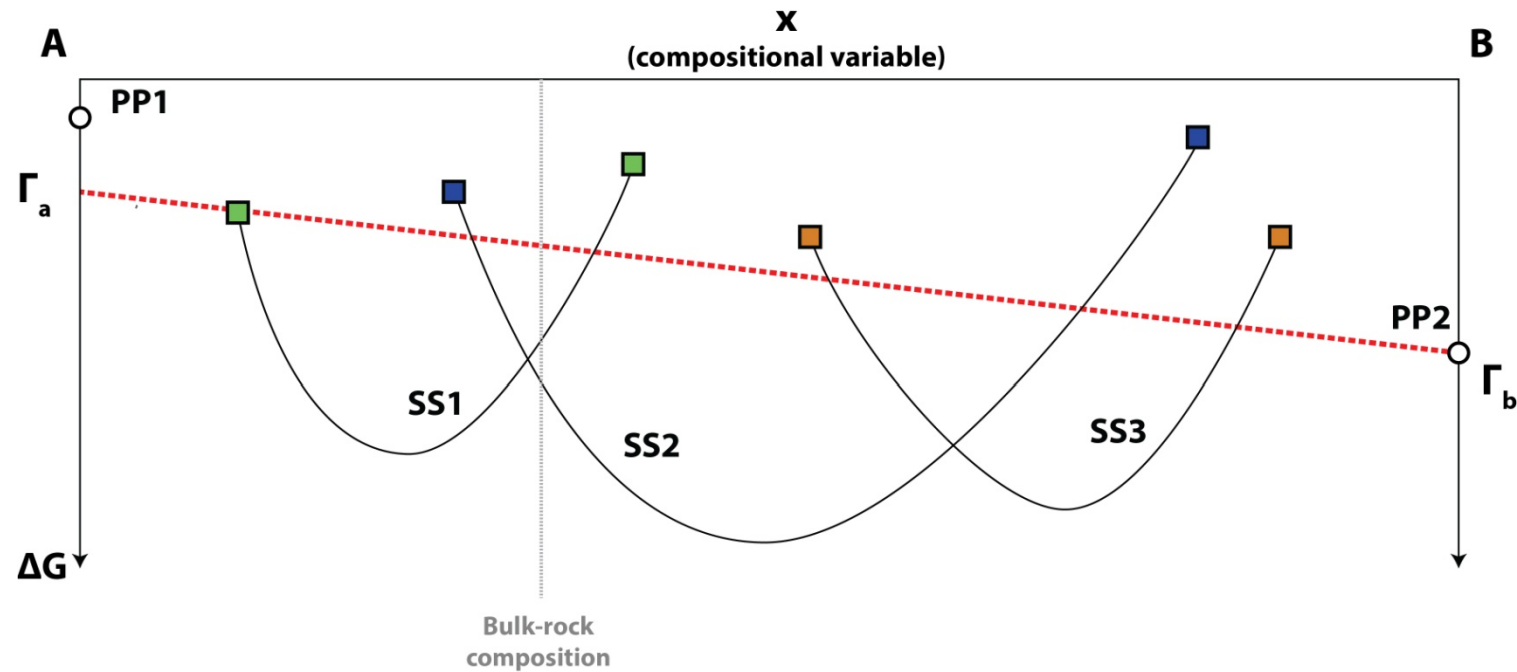


- Cannot deal with complex mineral phases (Site-Fraction based)



MAGEMin: a three step Gibbs energy minimizer

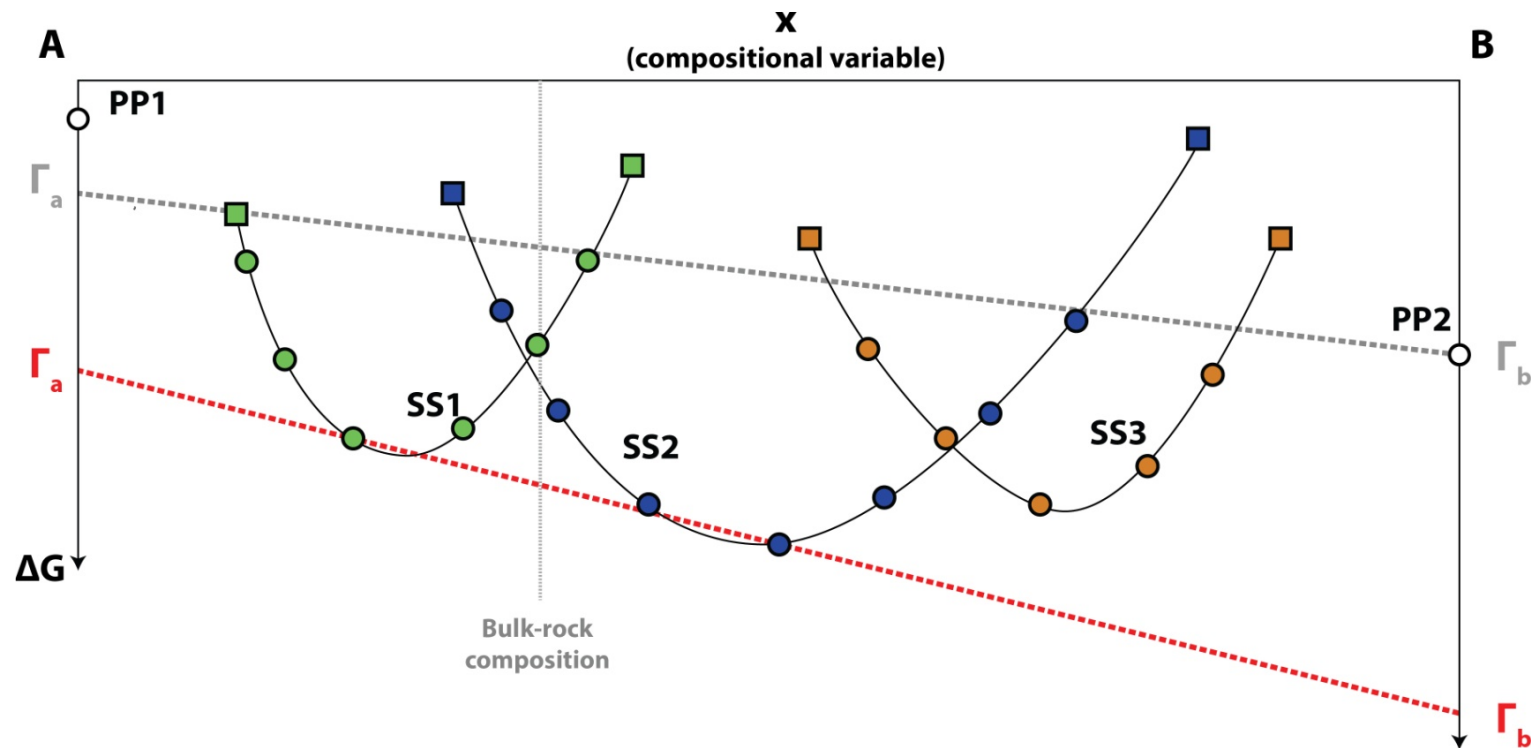
| (1) Levelling using pure phases and solution endmembers



| • Very low computational cost

MAGEMin: a three step Gibbs energy minimizer

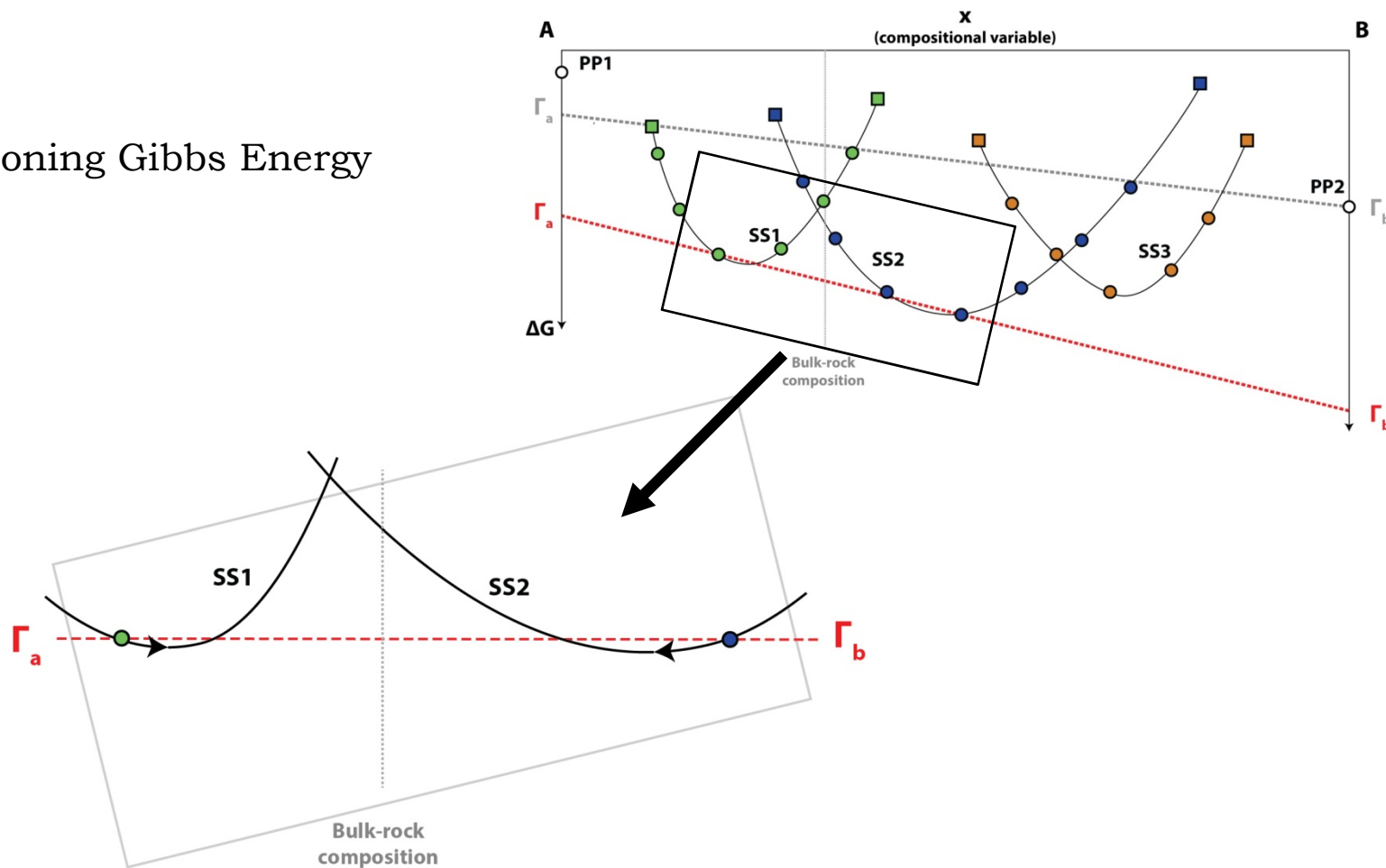
(2) Discretization under the G-hyperplane



- Discretization under the G-hyperplane guess
- Avoid local minimum and computationally cheap

MAGEMin: a three step Gibbs energy minimizer

(3) Partitioning Gibbs Energy



- Good initial guess for gradient based method
- Quick convergence to arbitrary mass residual

MAGEMin: a three step Gibbs energy minimizer

Current stage



- Fully parallel C-library with built-in database (*Holland et al., 2018*)
- Combines the best of available methods
- Low memory usage (< 2 Mb)
- Can be called from any software/geodynamic model
- Single core performance
 - ~150 ms with no initial guess
 - < 80 ms with initial guess



Ongoing development

- Taking into account solvus (e.g., amphibole)
- Code/method optimization to improve performances

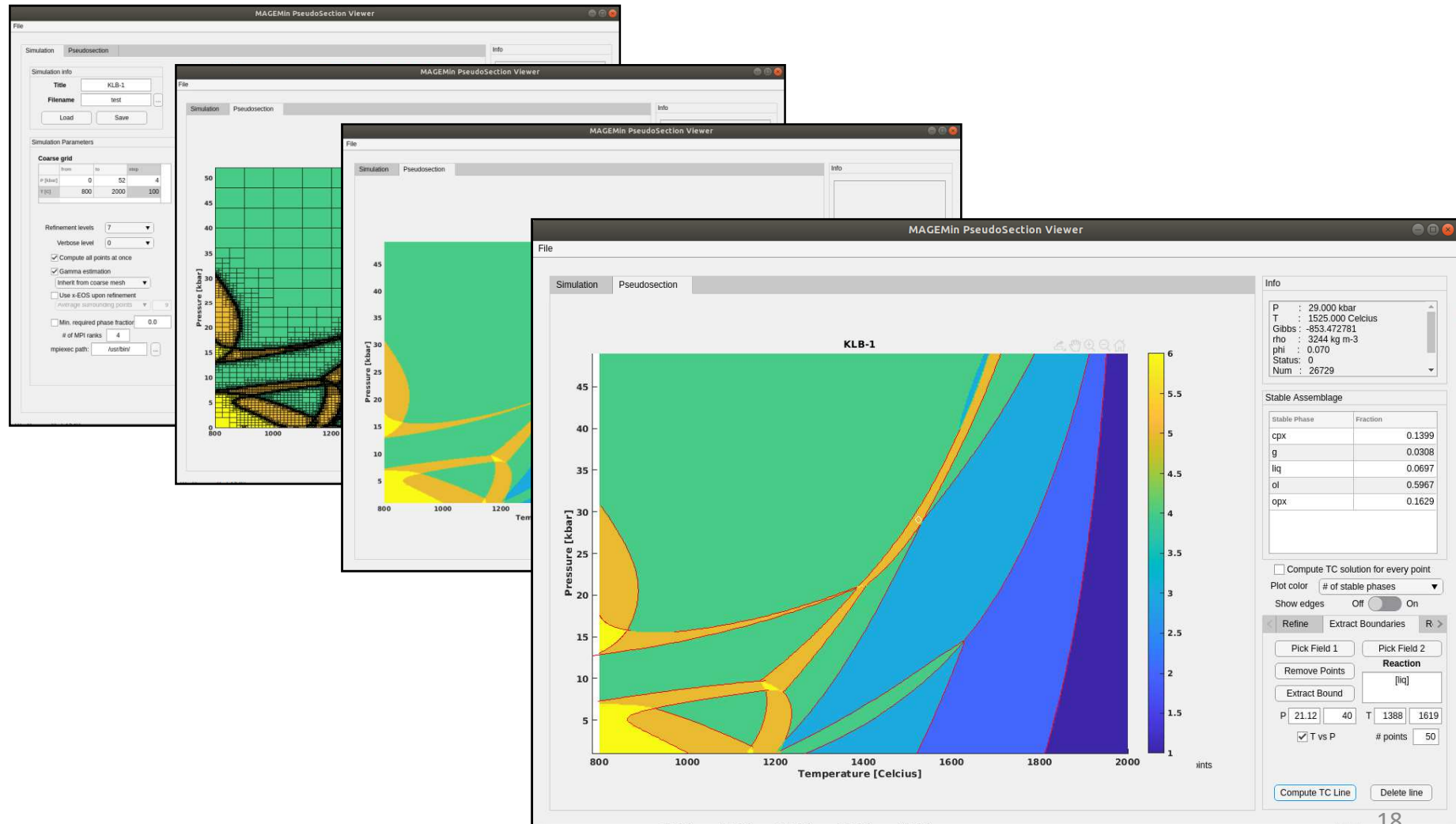
Upcoming additions (intermediate term)

- Adding other thermodynamic database

Mineral Assemblage Gibbs Energy Minimization – MAgEMin

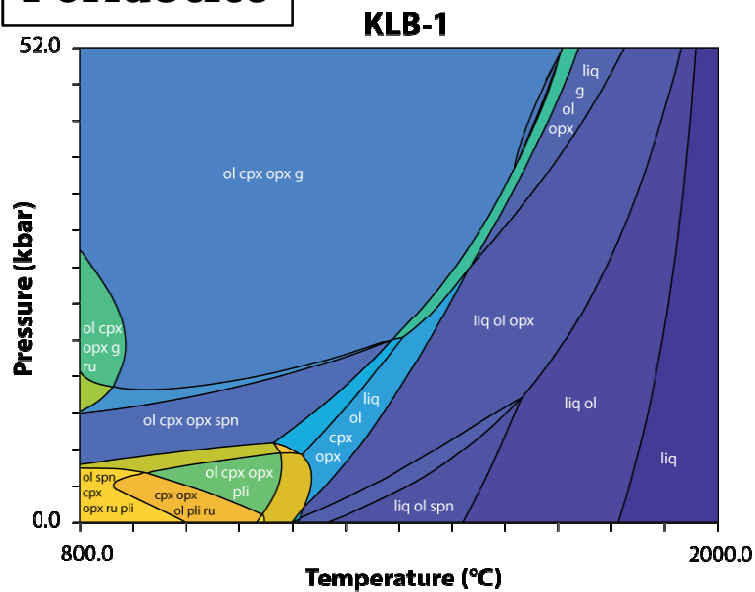


- MATLAB based Graphic User Interface
- Uses adaptive mesh refinement to compute diagrams
- Direct benchmarking with THERMOCALC

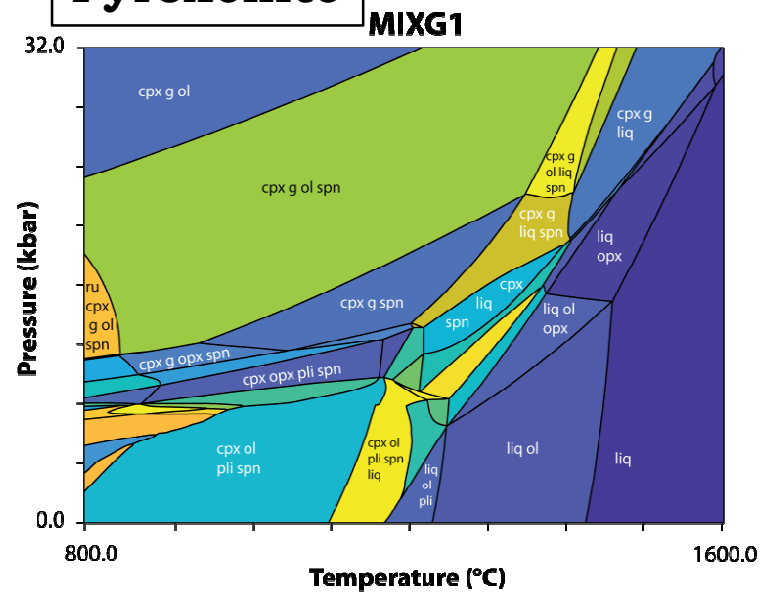


Examples of phase diagram – KNCFMASSTOCr system

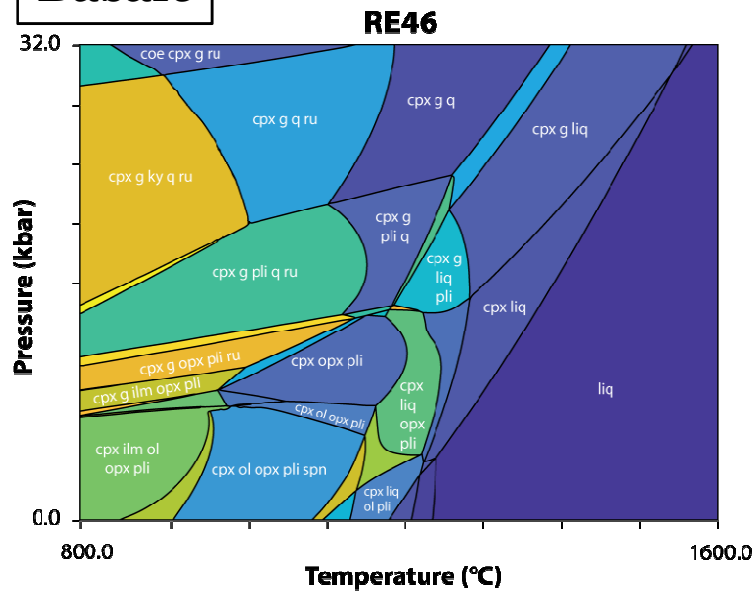
Peridotite



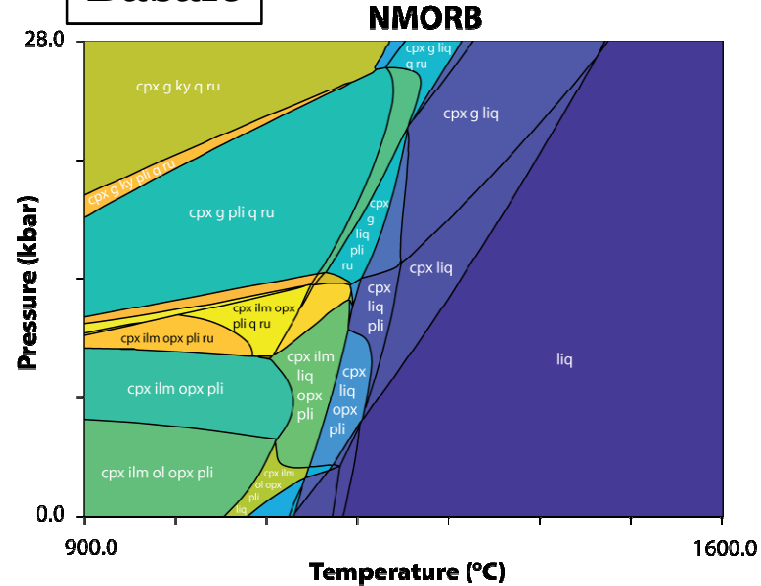
Pyroxenite



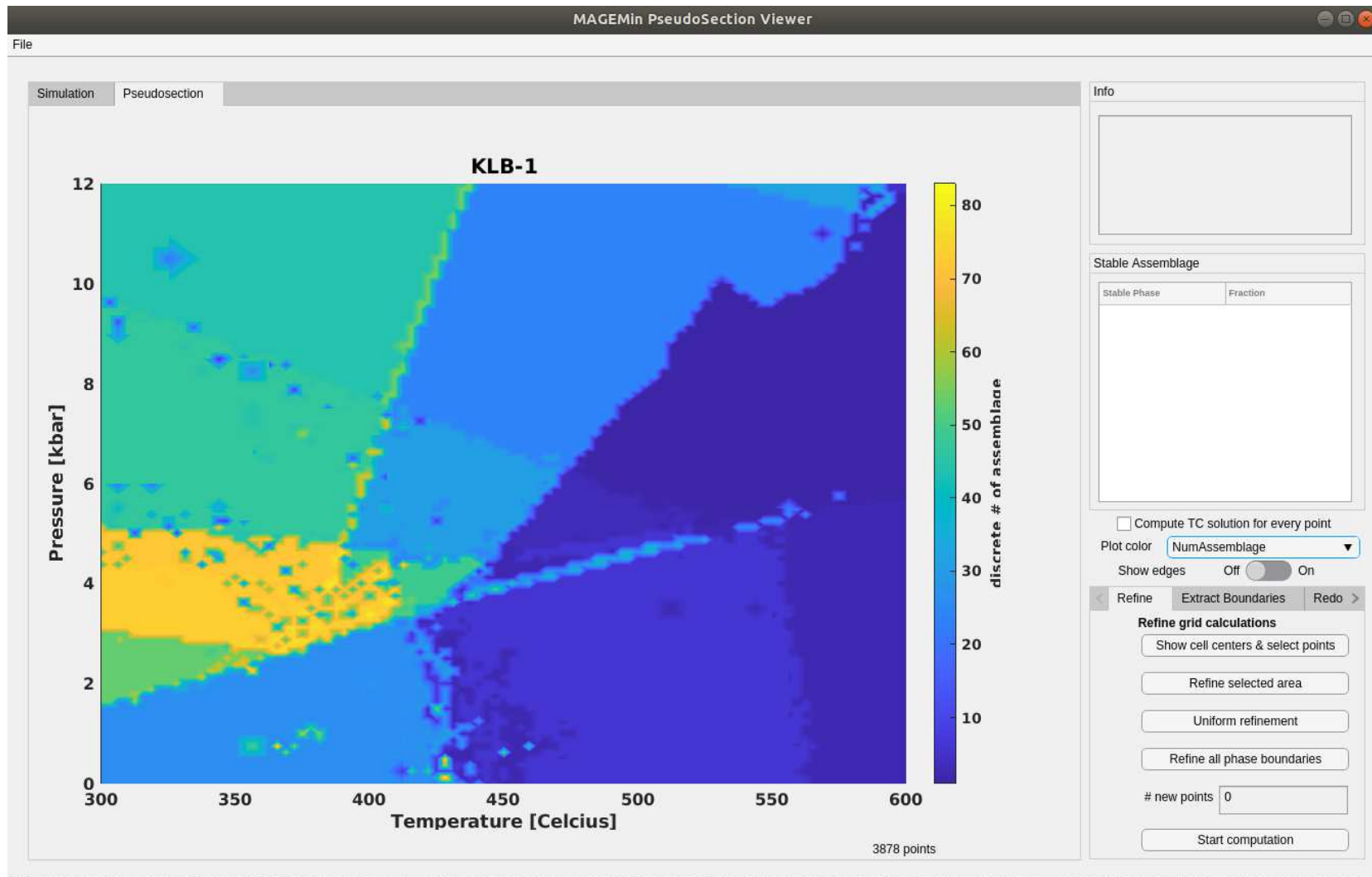
Basalt



Basalt



Low P-T issues to be resolved...





Will be released as open-source software at:

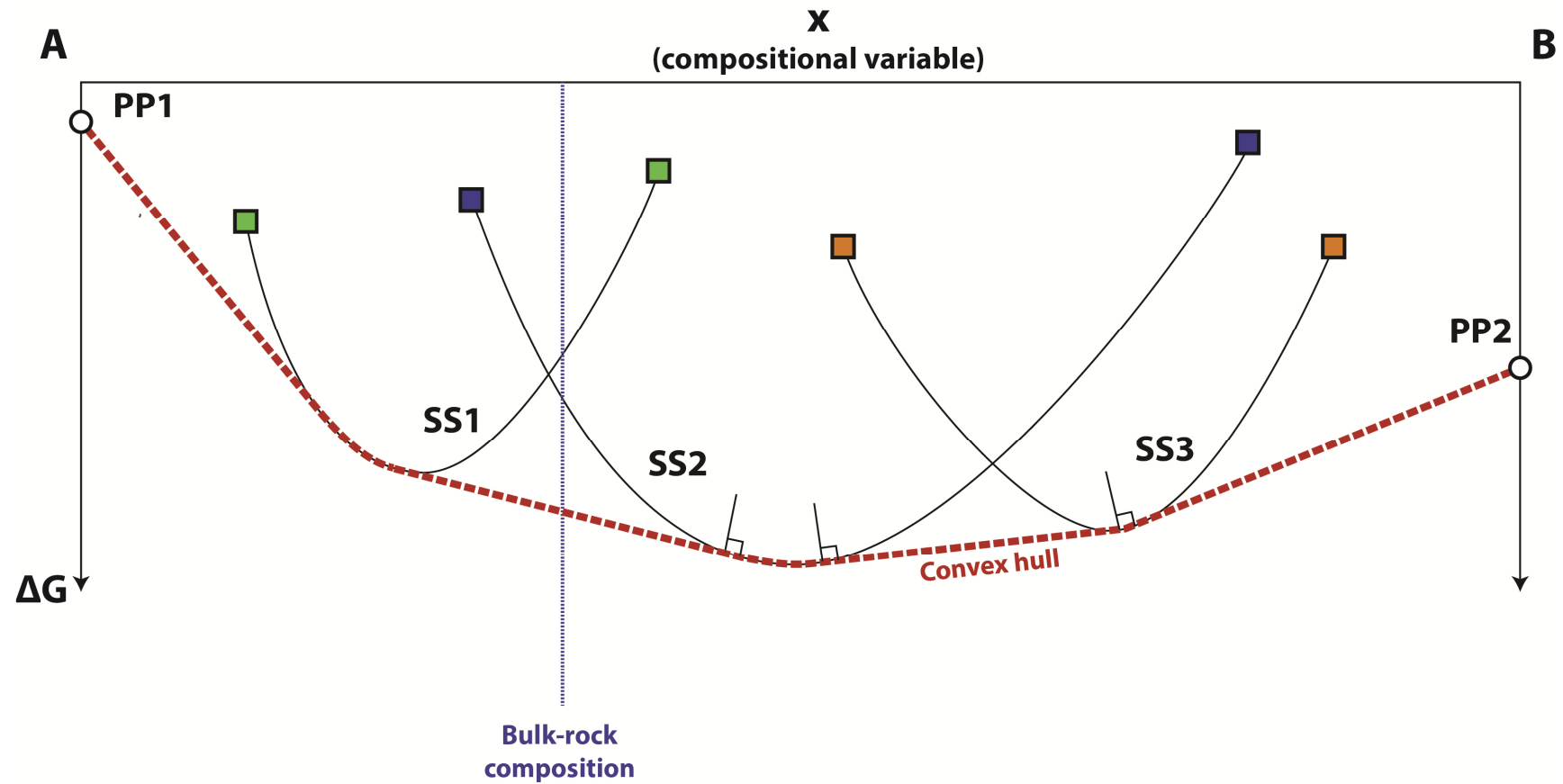
www.magemin.eu

Once ready!

Contact nriel@uni-mainz.de

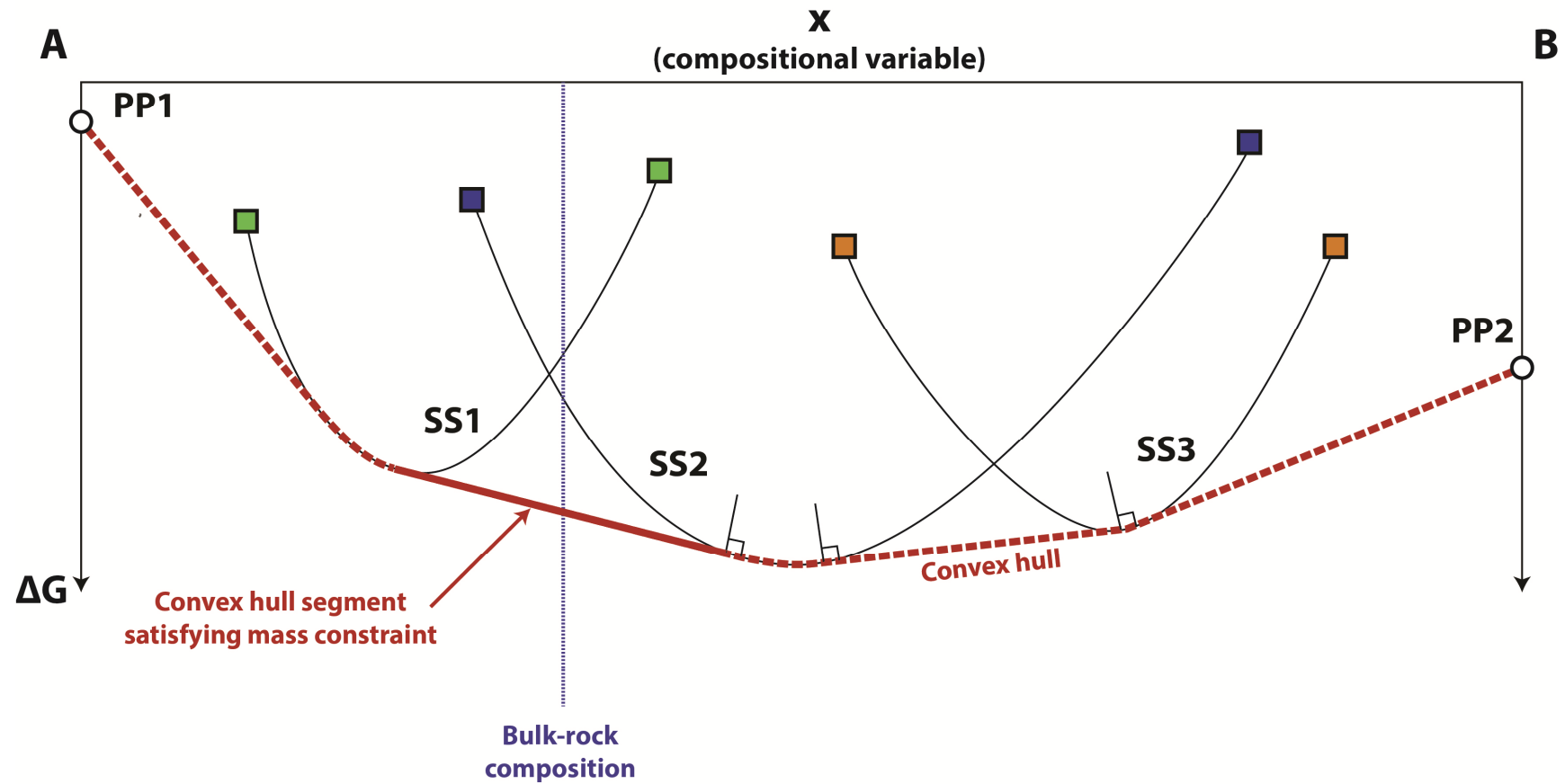
Appendix

Thermodynamic equilibrium: an optimization problem



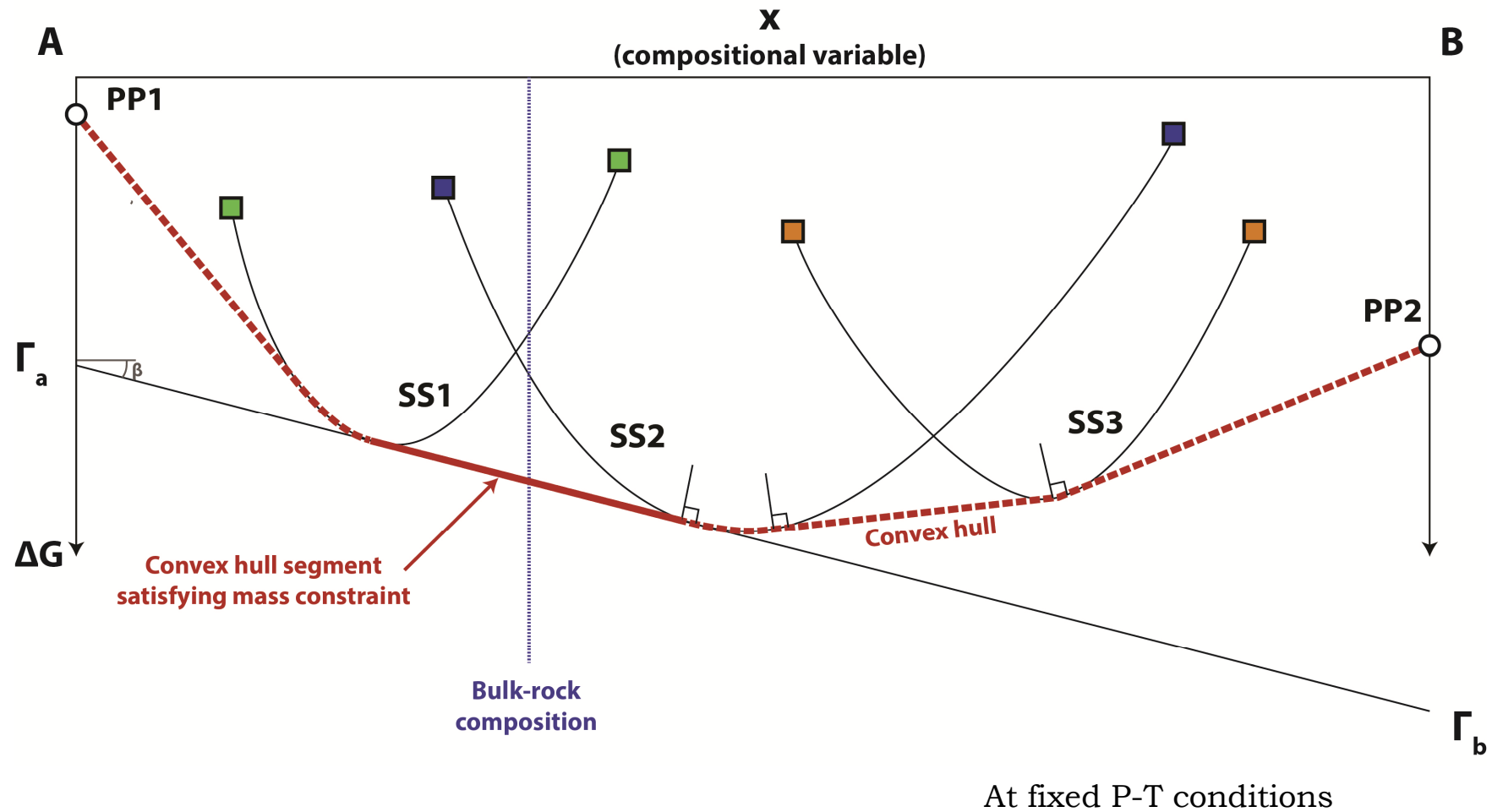
At fixed P-T conditions

Thermodynamic equilibrium: an optimization problem



At fixed P-T conditions

Thermodynamic equilibrium: an optimization problem



Linking Site-Fraction phase in PGE

Link mass balance with chemical potential of oxides

$$b_j = \sum_{l=1}^L n_l \sum_{i=1}^{N_l} \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^{\circ} - g_{i(l)}^{ex} \right) a_{ij} + \sum_{k=1}^K n_k a_{kj}$$



Method developped for « simple » solid solutions without site-mixing

Non-ideal solution phase

$$\mu_i = \frac{\tilde{\mu}_i}{RT} = g_{i(l)}^{\circ} + \ln(x_{i(l)}) + g_{i(l)}^{ex},$$

$$x_{i(l)} = \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^{\circ} - g_{i(l)}^{ex} \right)$$

Site-Mixing Non-ideal solution phase (Thermocalc)

$$\mu_i = G_i^0 + RT \ln(idm_i) + G_i^{Ex}$$

$$\mu_i = G_i^0 + RT \ln(x_i) + RT \ln\left(\frac{idm}{x_i}\right) + G_i^{Ex}$$

$$x_i = \exp \left(\frac{\sum_{j=1}^C a_{ij} \Gamma_j - G_i^0}{RT} \right) \left(\frac{\frac{p_i}{idm_i}}{\exp\left(\frac{G_i^{Ex}}{RT}\right)} \right) \quad G_i^{EX}$$

Partitioning Gibbs Energy

○ Solve for PGE system of non-linear equations

$$\left\{ \begin{array}{l} f_v = \sum_{l=1}^L n_l^s \sum_{i=1}^{N_l} \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^\circ - g_{i(l)}^{\text{ex}} \right) a_{iv} \\ \quad + \sum_{k=1}^K n_k^p a_{kj} - b_j = 0, \\ h_l = \sum_{i=1}^{N_l} \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^\circ - g_{i(l)}^{\text{ex}} \right) - 1 = 0, \\ q_k = \sum_{j=1}^C a_{kj} \Gamma_j - \mu_k = \sum_{j=1}^C a_{kj} \Gamma_j - g_k^0 = 0, \end{array} \right.$$

- Update Γ and Solution/Pure phase fractions

$$dx_j = (d\Gamma_1, \dots, d\Gamma_C, dn_1^s, \dots, dn_L^s, dn_1^p, \dots, dn_K^p)$$

- Calculate mass balance residual
- Calculate Γ penalty based on mass balance residual

- Remove or add solution/pure phases (1 at a time)

- Remove Solution/Pure phases if fraction < 0.0

- Add phases:

- Pure phases

(driving force < 0.0)

- Solution phases

(Sum of EM fractions > 1.0)

$$D = g_i^\circ - \sum_{j=1}^C a_{ij} \Gamma_j$$

$$x_L = \sum_{i=1}^{N_l} x_{i(l)} = \sum_{i=1}^{N_l} \exp \left(\sum_{j=1}^C a_{ij} \Gamma_j - g_{i(l)}^\circ - g_{i(l)}^{\text{ex}} \right)$$