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Why discuss kinetics when this is a workshop on phase equilibrium modelling?

Answer: our ultimate goal is to understand the P-T evolution of metamorphic rocks.

Phase equilibrium modelling underpins this endeavour, but kinetics also has an influence whose importance may be greater than widely assumed

Metamorphic facies: evidence that an equilibrium model for metamorphism largely pertains...



Table 2-2. Correlation among Barrows zones (for pelitic rocks), metamorphic facies (for mafic rocks) and calc-silicate mineral assemblages for Barrovian metamorphism (after Thompson and Norton, 1968).

Pelitic Rocks	Mafic Rocks	Calc-silicate Rocks	
Biotite zone	Greenschist facies	Talc, Phlogopite	
Garnet zone	Epidote-amphibolite	Tremolite, Actinolite Epidote, Zoisite	
Staurolite zone	facies		
Staurolite-kyanite zone	Amphibolite facies	Diopside	
Sillimanite zone		Grossularite, scapolite	
Sillimanite- K-Feldspar zone	Hornblende-Pyroxene Granulite facies	Forsterite	

Spear, 1993

... to the peak P-T conditions of metamorphic rocks

Expanded concept: equilibrium is maintained throughout a rock's prograde evolution (the concept of "progressive metamorphism")



Implies that the only reactions rocks see are equilibrium reactions

Implies that rate of reaction and compositional equilibration is always faster than rate at which P-T conditions change

more contentious

in detail can't be true (thankfully)...



Stranded reaction textures

Coronitic metagabbro (Opx-Hbl/Spl-Grt shells between original igneous Ol and Pl)

Decompression texture of Crd replacing St in Crd-Anth rock

Zoned minerals



Different scales of equilibration for different elements = "partial chemical equilibrium"



Yang & Rivers, 2001

Carlson et al., 2015

Prograde unreactivity (or sluggish reactivity) of porphyroblasts

Predicted rxn according to equilibrium:

Ms <u>**Grt**</u> Chl Qtz = St Bt H_2O

Actual rxn:

Ms Chl Qtz = **St** Bt H_2O

(Grt ~ inert)





Predicted rxn according to equilibrium :

Ms <u>St</u> Qtz \pm Chl = And Bt H₂O

Actual rxns: Ms Chl Qtz = **St** Bt H₂O

Ms Chl Qtz = And Bt H_2O Many of these exceptions can be handled using the concept of "local equilibrium" ("reactive bulk composition"), or with the application of chemical potential gradients

Others can't: the focus of this presentation.

What an equilibrium phase diagram doesn't tell us



The magnitude of free energy differences amongst competing configurations

Anything about:

how long something took to happen (rates)
how (by what mechanisms) a rock changes
from one mineral assemblage to another

Kinetics (in context of metamorphic petrology): rates and mechanisms of changing one mineral assemblage into another (ie, how a rock recrystallizes)



- Dissolution of reactant minerals
- Nucleation of product minerals
- Transport of material from reactants to products
- Growth of product minerals



Yardley, 1989



Chlorite phyllite

Garnet schist

General kinetic rate equation (according to transition state theory):

Rate = a * [1 – exp($-\Delta_r G_{P,T} / RT$)] * exp($-G_{act} / RT$)

Free energy driving force for reaction

Activation energy barrier of rate-limiting process (nucleation, transport, dissolution, growth) Rates of different steps in recrystallization process Rate = a * $[1 - \exp(-\Delta_r G_{P,T} / RT)]$ * $\exp(-G_{act} / RT)$

Dissolution, growth, transport:

approximately "linear" rate laws as function of T overstep (if overstep is not too large, ie $\Delta_r G_{PT} \ll RT$)

i.e., Rate $\propto \Delta T$ - assumes small change in Arrhenius (activation energy) term over range of T-overstep

Absolute values vary amongst the different processes

Nucleation:

Activation energy for nucleation is function of **T overstep – squared!**

i.e., Rate $\propto \Delta T^* \exp(\Delta T^2)$ - turbo-charged exponential rate law

Result: interval of no nucleation (= overstepping), followed by rapid nucleation, giving rise to notion of critical overstep



Equilibrium





(Uncomfortable?) fact:

Every reaction has to be overstepped to proceed

Main questions as petrologists:

How much? Is it petrologically significant?

Does it affect how we interpret P-T conditions of metamorphism, or P-T paths?



How much overstepping is needed?

Is every reaction overstepped by the same amount?

Related to:

activation energy barrier of rate-limiting process (especially nucleation)

macroscopic (free energy) driving force for reaction: "reaction affinity"



Macroscopic driving force for reaction

Reaction affinity, A

Defined in context of overstepping as Gibbs free energy difference between stable (but not yet crystallized) products, and metastable reactants

Built-up energy needed to overcome kinetic barriers to nucleation and growth

For isobaric heating:

$$\mathbf{A} = - \mathbf{\Delta}_{\mathbf{r}} \mathbf{G}_{\mathbf{P},\mathsf{T}} = \mathbf{\Delta} \mathbf{T} (\mathsf{T} \text{ overstep}) * \mathbf{\Delta}_{\mathbf{r}} \mathbf{S}_{\mathbf{P},\mathsf{T}}$$

Rate of build-up of reaction affinity with ΔT (= temperature overstep) = $\Delta T * \Delta_r S_{PT}$



Sensitivity of assemblage field boundaries



PHASE EQUILIBRIUM MODELLING: APPROACHES AND PITFALLS

Uncertainty: sources – **in phase diagrams** – in assemblages – in P-T calculations | Best practices



How much variation is there amongst reactions in this phase diagram?



Reaction affinity maps



Chlorite-free and alusite-cordierite reaction



Some questions

Is there petrological evidence for kinetically-controlled overstepping?

How important is it?

What are some of the petrological consequences?

Does it occur in regional and contact metamorphism?

Assessing the extent of disequilibrium and overstepping of prograde metamorphic reactions in metapelites from the Bushveld Complex aureole, South Africa

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Bt overgrown (partially pseudomorphed) by St

A. Qualitative mineral growth/consumption sequence from textures



B. Predicted mineral growth/consumption sequence (equilibrium)



Waters & Lovegrove, 2002



B. Predicted mineral growth/consumption sequence (equilibrium)











Nelson batholith and aureole, SE British Columbia

middle Jurassic

2.5 - 4 kbar (tilted after emplacement)

abundant graphitic metapelitic host rocks of uniform composition





Equilibrium

Zones of overstepped reaction

Violation of the metamorphic facies principle?

Strictly speaking, yes (in zones where stable mineral assemblages do not form).

In practice, maybe not so much (at Nelson, spacing of isograds has been affected, but order of metamorphic index minerals is the same as in other Grt-St-And sequences)



Pattison (unpublished) based on Pattison & Tinkham (2009)

Some questions

Is there petrological evidence for kinetically-controlled overstepping? Yes: Bushveld and Nelson (and others not described here)

How important is it? Small to 80 °C overstepping, varying as function of ΔS of rxn

What are some of the petrological consequences?

- 1. Onset of reaction can be delayed by petrologically significant degrees Implication: estimation of P-T conditions of metamorphic mineral assemblages
- 2. Reactions other than those in equilibrium phase diagrams are possible Implication: interpretation of P-T paths from textures, mineral inclusions
- 3. Discrete intervals of reaction (and fluid release) may be episodic rather than continuous, and may not bear obvious relationships to equilibrium phase boundaries Implication: interpretation of fluid release and movement in metamorphism

4. Much (most?) reaction may occur at facies boundaries (marked by high- Δ S dehydration reactions involving consumption of hydrous phases like Chl, Ms, Bt), with less or overstepped - reaction within facies (lower- Δ S rxns)



Greenschistamphibolite facies boundary marked by Chl-consuming reactions (= high ΔS reactions)

Compilation of estimates of overstepping:

Does overstepping occur in regional as well as contact metamorphism?

Differences between contact and regional metamorphism:

1. Generally slower heating rates may favour closer approach to continuous equilibrium during prograde metamorphism. *BUT.... for nucleation, heating rate is not as critical a factor as degree of T-overstep (e.g.: aureole of huge Bushveld complex, whose timescale of metamorphism approaches regional timescales)*

2. Enhanced deformation in regional metamorphism (defects, strain energy, damaged crystal surfaces, migrating grain boundaries) may lower kinetic barriers to nucleation and growth, leading to smaller degrees of overstepping



Pattison, unpublished images

Regional example: staurolite-Al₂SiO₅ relations

first appearance of Al₂SiO₅ (Ky, Sil, And) in most metapelites predicted by equilibrium to be due to St-breakdown







Commonly no evidence for growth of And, or especially Ky, from St

Independent growth from matrix minerals (Ms, Chl)?

Pattison & Spear, 2018; Pattison & Tinkham, 2009

Maximum gap between stable Chl \rightarrow St and metastable Chl \rightarrow Als curves = 10 °C



Staurolite has kyanite unit cells in its structure:

Kinetically easier to just form kyanite?



Fig. 1. z-axis projection of the structure of staurolite; shown in the lower right corner is an epitaxial intergrowth with kyanite.



Glen Clova, Scotland Pesch, 2014



Glacier Creek aureole, BC (Pattison & Spear, 2018)





Some questions

Is there evidence for kinetically-controlled overstepping? Yes.

How important is it? Small to ~80 °C, depending on locality, grade and type of reaction

What are some of the petrological consequences? 1. Onset of reaction can be delayed by petrologically significant degrees 2. Reactions other than those in equilibrium phase diagrams are possible 3. Discrete intervals of reaction (and fluid release) may be episodic, and may not bear obvious relationships to equilibrium phase boundaries 4. Much (most?) reaction may occur at facies boundaries (marked by high- Δ S rxns), with less - or overstepped - reaction within facies (lower- Δ S rxns)

Does kinetically-controlled overstepping occur in regional metamorphism? Yes – but needs to be considered more

How much is the initial garnet-forming reaction overstepped?

Zeh and Holness (2003) Regional Buchan	Wilbur & Ague (2006) Barrovian	Pattison & Tinkham (2009) <mark>Aureole</mark>	Kelly et al. (2013) Various regional	Caddick, in Carlson et al. (2015) Blueschist	George & Gaidies (2017) Barrovian	Spear et al. (2014), Castro & Spear (2016), Wolfe & Spear (2018) Barrovian/Blueschist
80°C	Unspecified	30°C	5 - 67°C	80 °C, 4-6 kbar	Negligible	20-80°C 2-8 kbar
Phase equilibrium modelling of unusual bulk comps	Growth modelling of "branched" garnet	Isograd sequence and phase equil. modelling	Crystal size distributions (CSDs) and numerical modelling	Grt isopleth intersections and phase equil. modelling	CSDs, chemical zoning and numerical modelling	QuiG/TE-based thermobarometry and phase equil. modelling
Non-state State State		a) Mapped isograds upper lisograds upper lisograds upper lisograds upper lisograds upper lisograds upper lisograds upper lisograds Nelson Batholith lkm		2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		TM-675 OS

What do all these approaches have in common?

Comparison with the equilibrium position of the garnet-in line for the rock composition of interest

Predicted garnet-in line and garnet stability using different datasets/a-X models Same rock composition and chemical system (MnNCKFMASHTO)



Conclusions

Phase equilibrium modelling remains the foundational approach for P-T estimation and P-T path determination of metamorphic rocks

Metamorphic recrystallization is an interplay between equilibrium and kinetics, so accepting that kinetics has a role to play offers the potential for better interpretations (and possibly for avoiding misinterpretations)

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