Phase Equilibrium Modelling: Approaches and Pitfalls

Choosing the best chemical system and handling Fe^{3+}

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Is there a best chemical system? and handling Fe^{3+}?

The best system is dependent on what you're trying to model:

- What rock type are you considering?
- What P-T conditions are you interested in?
- What is the specific problem you're trying to solve?

This short talk will not give you the correct answer for your rock because there is no "one size fits all" solution. However, it will show:

1. What factors you should consider when making a choice about which chemical system to use.
2. Examples of diagrams produced in different chemical systems
3. The ways to consider Fe^{3+} as a component

Is more necessarily better?

Lanari & Duesterhoft (2019)

	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
HP85	Holland & Powell (1985)	none	REG	43	x	x	x	x	x	x															x	x	
B88	Berman (1988)	*JUN92; DEC06*	MAP	67	x	x	x	x	x	x	x	x	x												x	x	
HP90	Holland & Powell (1985)	none	REG	123	x	x	x	x	x	x	x	x	x	x											x	x	x
G97	Gottschalk (1997)	none	IREG	94	x	x	x	x	x	x	x	x	x												x	x	x
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
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
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

Should you include every component possible?

Are more complicated systems better than simpler ones?

1. What factors should you consider?

a) Elements present in your rock.

We've been able to explain the majority of phase relations in metapelites using a KFMASH system since Thompson (1957)

These represent the more major elements in metapelites (>2.5 wt% in the average analysis presented here)

wt%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Bulk	59.12	0.94	19.73	1.67	6.11	0.14	2.79	0.91	1.41	3.98
Qz	x									
Ms	x	o	x	o	o		o		o	x
Bt	x	o	x	o	x		x		o	x
Chl	x		x	o	x		x			
Grt	x		x	o	x	x	x	x		
St	x		x	o	x	o	x			
Crd	x		x		x	o	x			
Als	x		x							
Pl	x		x					x	x	
Kfs	x		x							x
Ilm		x		o	x					
Mag				x	x					
Rt		x								

1. What factors should you consider?

a) Elements present in your rock.

Plenty of examples where other components are important:

- TiO_2 – Bt/Ilm/Rt
- Fe_2O_3 – Ms/Bt/Hem (e.g., Chinner, 1960)
- MnO – Grt (e.g., Symmes & Ferry, 1992)
- CaO – Grt/Pl
- Na_2O – Ab/Pa/Ms

wt%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Bulk	59.12	0.94	19.73	1.67	6.11	0.14	2.79	0.91	1.41	3.98
Qz	x									
Ms	x	o	x	o	o		o		o	x
Bt	x	o	x	o	x		x		o	x
Chl	x		x	o	x		x			
Grt	x		x	o	x	x	x	x		
St	x		x	o	x	o	x			
Crd	x		x		x	o	x			
Als	x		x							
Pl	x		x					x	x	
Kfs	x		x							x
Ilm		x		o	x					
Mag				x	x					
Rt		x								

1. What factors should you consider?

b) Elements in datasets and solution models

HP1

HP2

ds62

wt%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Bulk	59.12	0.94	19.73	1.67	6.11	0.14	2.79	0.91	1.41	3.98
Qz	x									
Ms	x	o	x	o	o		o		o	x
Bt	x	o	x	o	x		x		o	x
Chl	x		x	o	x		x			
Grt	x		x	o	x	x	x	x		
St	x		x	o	x	o	x			
Crd	x		x		x	o	x			
Als	x		x							
Pl	x		x					x	x	
Kfs	x		x							x
Ilm		x		o	x					
Mag				x	x					
Rt		x								

2. Different systems

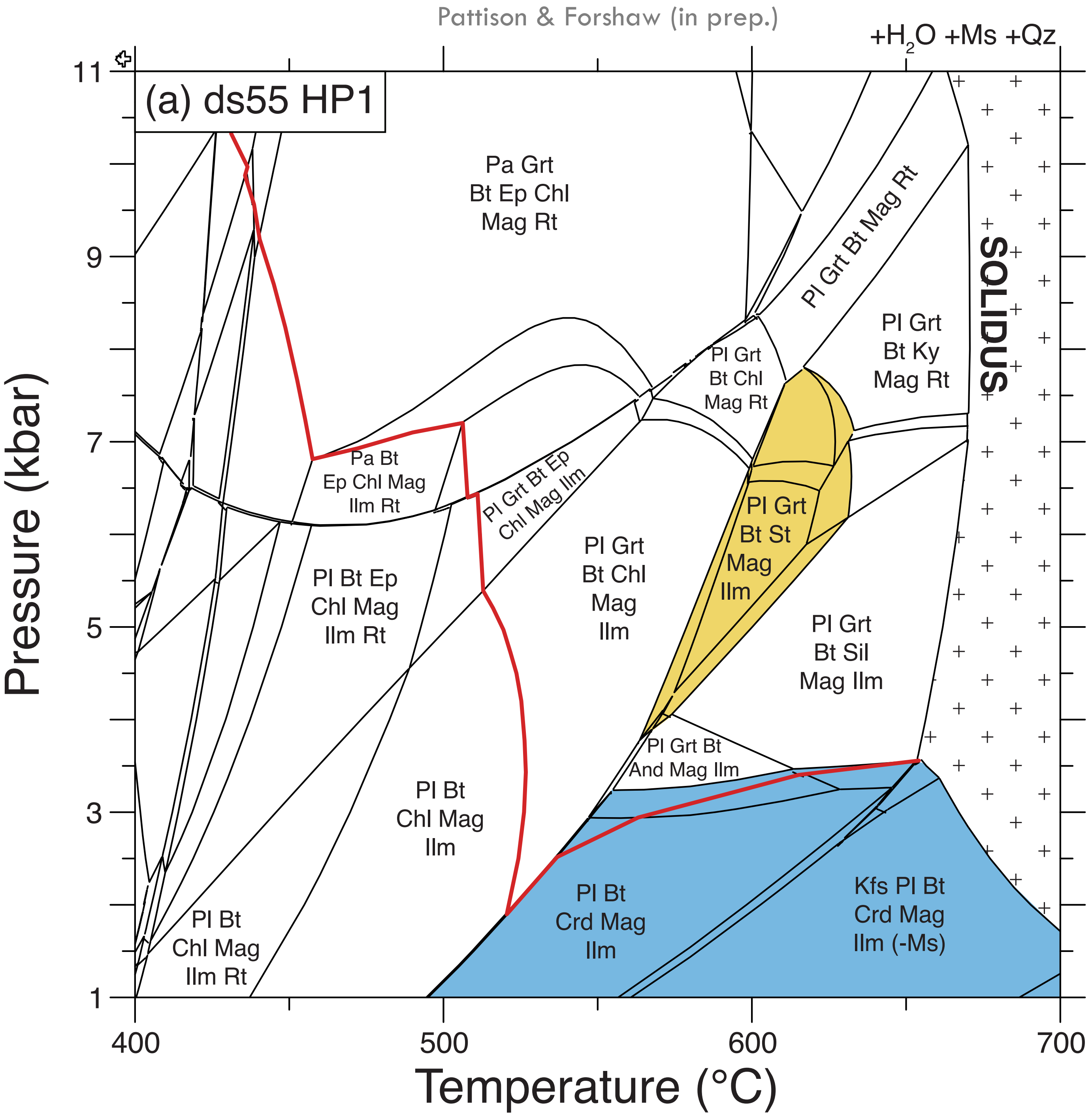
Avg. metapelite (n = 2469)

ds55 HP1 (previous talk)

MnNCKFMASHTO

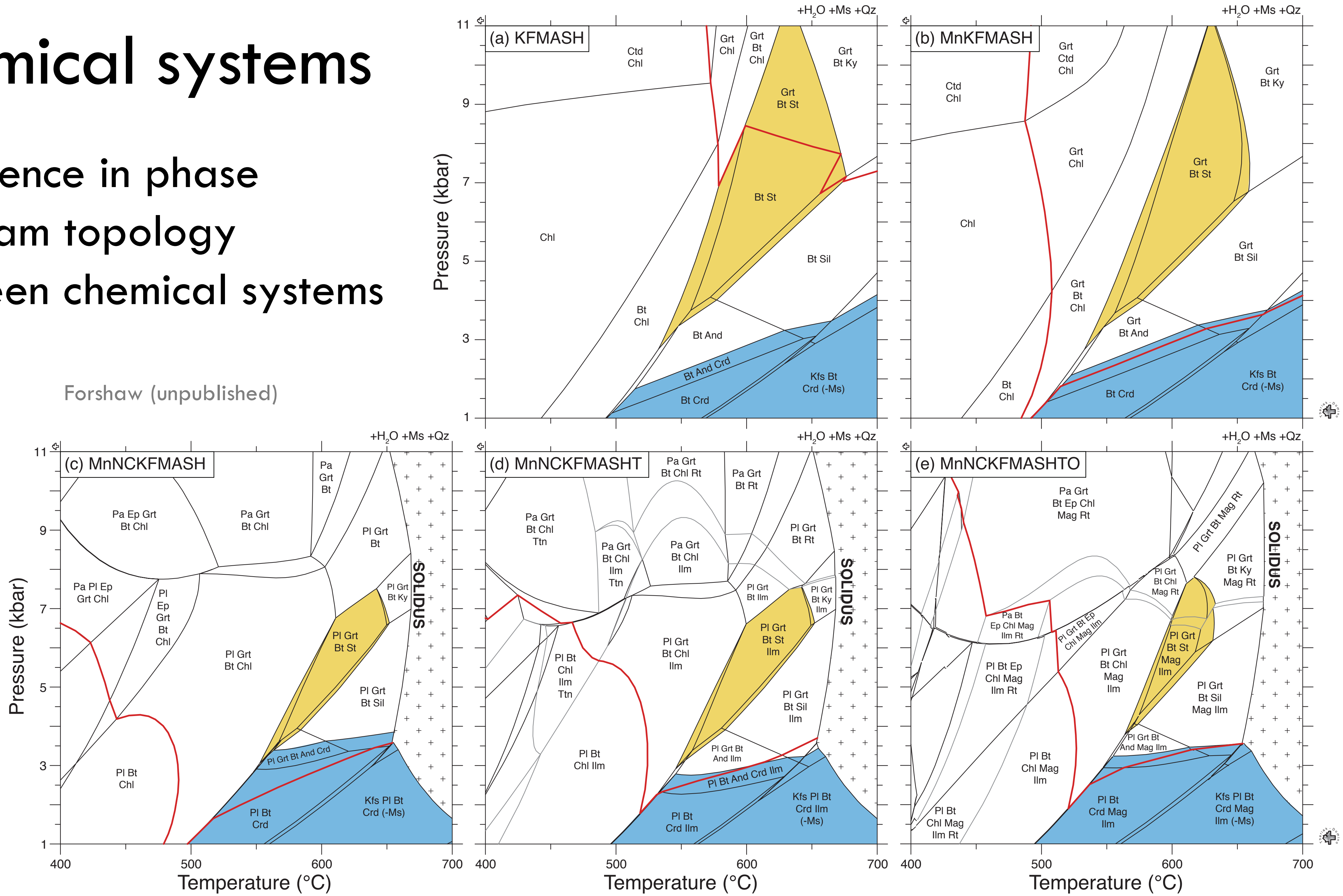
Solution models:

Bt – White et al. (2005)
Grt – Tinkham et al. (2001)
Ilm – Tinkham & Ghent (2005)
Ms – Coggon & Holland (2002)
Pl-Kfs – Holland & Powell (2003)
Mag – White et al. (2002)
Melt – White et al. (2007)
Chl, Crd, St, Ep, Opx – Holland & Powell (1998)



Chemical systems

Difference in phase diagram topology between chemical systems

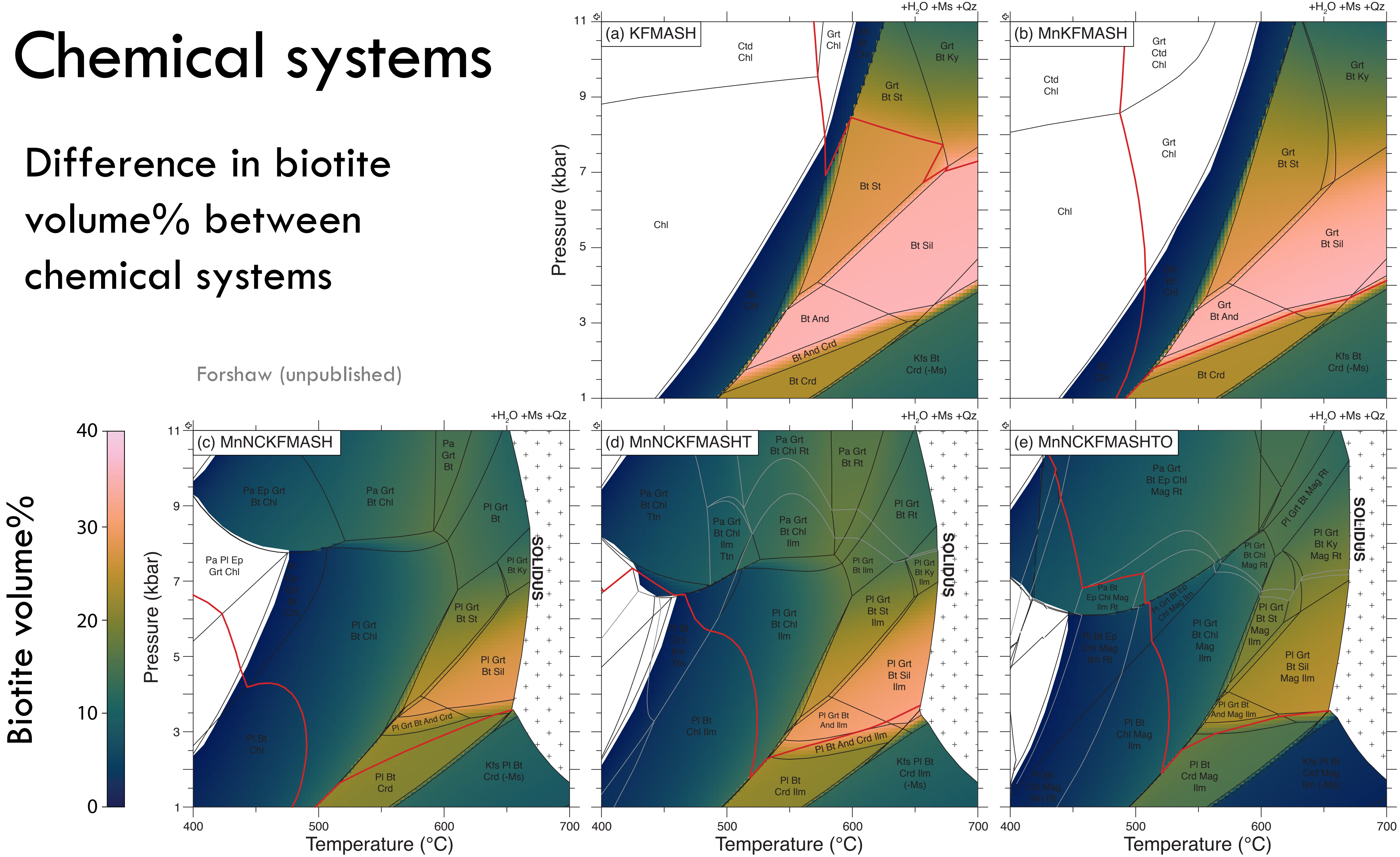


Forshaw (unpublished)

Chemical systems

Difference in biotite volume% between chemical systems

Forshaw (unpublished)



3. How do you handle Fe^{3+}?

Avg. metapelite

Oxide	wt%
SiO_2	59.12
TiO_2	0.94
Al_2O_3	19.73
FeO^T	7.61
MnO	0.14
MgO	2.79
CaO	0.91
Na_2O	1.41
K_2O	3.98
P_2O_5	0.16

= total iron as FeO

What proportion is Fe^{3+}?

FeO (Fe^{2+})

vs.

Fe_2O_3 (Fe^{3+})

There are two ways to deal with this:

a) Measure Fe^{3+}

- Bulk rock
- Minerals (combine with modes)

b) Estimate Fe^{3+}

- Bulk rock (based on comparison)
- Minerals (combine with modes)

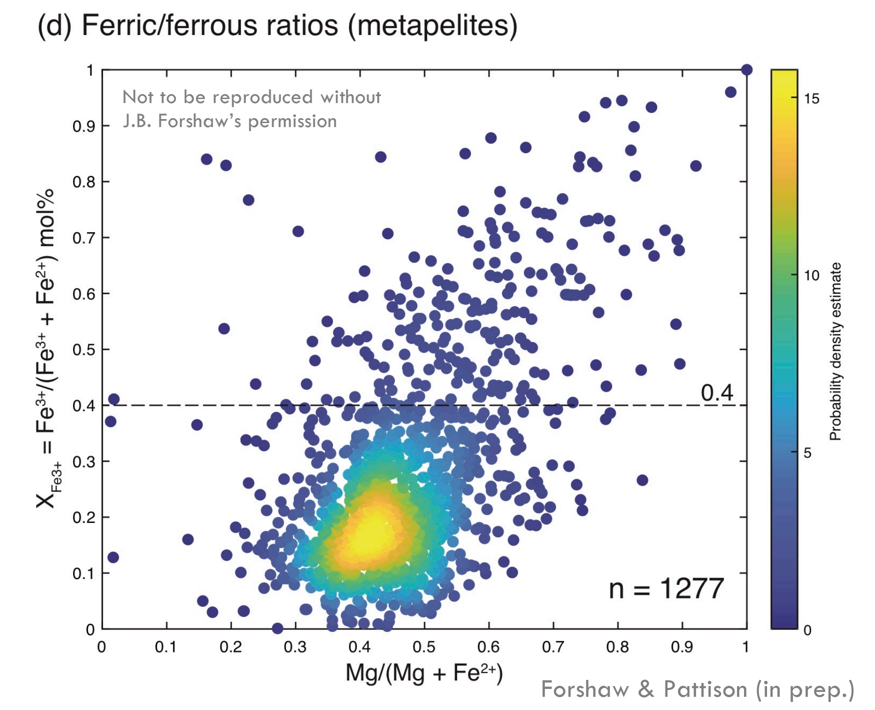
Phase equilibrium modelling of Fe^{3+}

a) Measure Fe^{3+}

Bulk rock	Mineral X_{Fe3+} combined with modes for whole rock
Two steps: Measure FeO^T using XRF or ICP-OES and then conduct a titration to get proportion of FeO **Pros:** • Quite commonplace in commercial labs that complete XRF or ICP-OES analyses. **Cons:** Bulk analysis • Can't use to consider your reactive bulk composition. • Includes any late alteration to the rock or retrograde minerals which may have formed under different oxidation conditions. • Is often considered a maximum value due to the possibilities of oxidation during sample preparation or incomplete dissolution.	Measure X_{Fe3+} in your minerals using wet chemical methods, Mössbauer, or XANES spectroscopy. **Pros:** • Values for individual minerals with which you can adjust your reactive bulk composition **Cons:** Not routine • Time-consuming – Separation of minerals • Relatively few Mössbauer instruments and hard to get time at at Synchrotron for XANES work. • Uncertainty 1. Wet chemical/Mössbauer spectroscopy are bulk techniques and so average any X_{Fe3+} variation 2. XANES – in-situ so measures any X_{Fe3+} variation but often large uncertainty on each measurement

b) Estimate Fe^{3+}

Bulk rock	Mineral X_{Fe3+} combined with modes for whole rock
Compare with other analyses in the literature for rocks of a similar composition and mineralogy.	Estimations based on charge-balancing and stoichiometric constraints:



Need to understand the minerals in your rock

- What's the Fe-oxide phase?
- Are there significant sinks of Fe^{3+}?

Estimations based on charge-balancing and stoichiometric constraints:

Category 1 – Fixed amounts of cations/anions

e.g., Garnets, pyroxenes, etc.

Category 2 – One partially filled site

e.g., Amphiboles

Estimations based on comparison with analyses of Fe^{3+} in the literature

Category 3 – More than one partially filled site

e.g., Biotite, muscovite, chlorite, and staurolite

Pros:

- Easy to apply to EPMA analyses

Cons:

- Accuracy depends on the mineral analysis

Categories after Schumacher (1991)

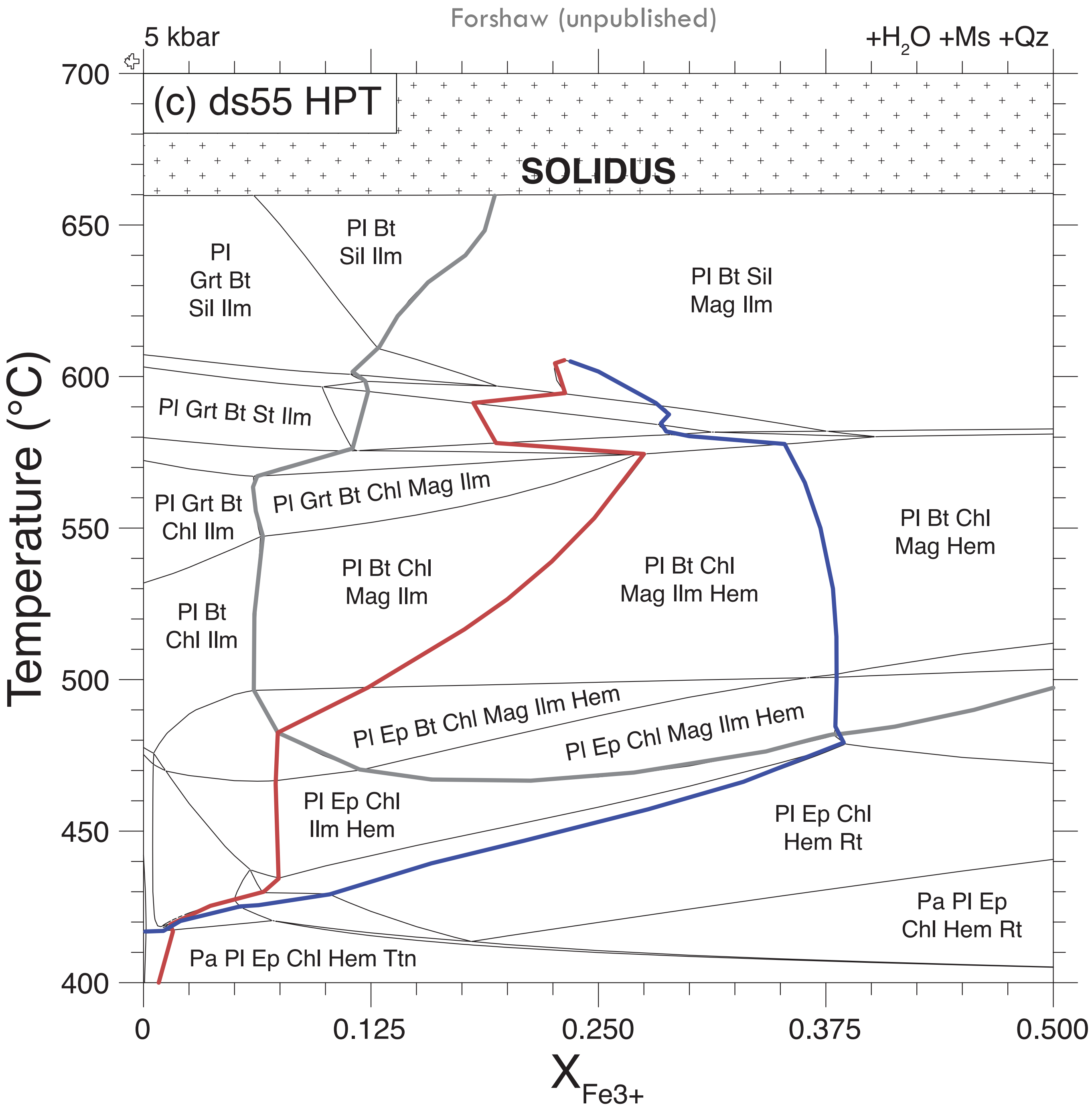
T-X_{Fe3+} diagram

Not trying to get X_{Fe3+} of your rock, but instead ensure your estimate is consistent with the models

Mag-in

Hem-in

Ilm-out



T-X_{Fe3+} diagram

Different solution models can incorporate varying amounts of Fe^{3+}

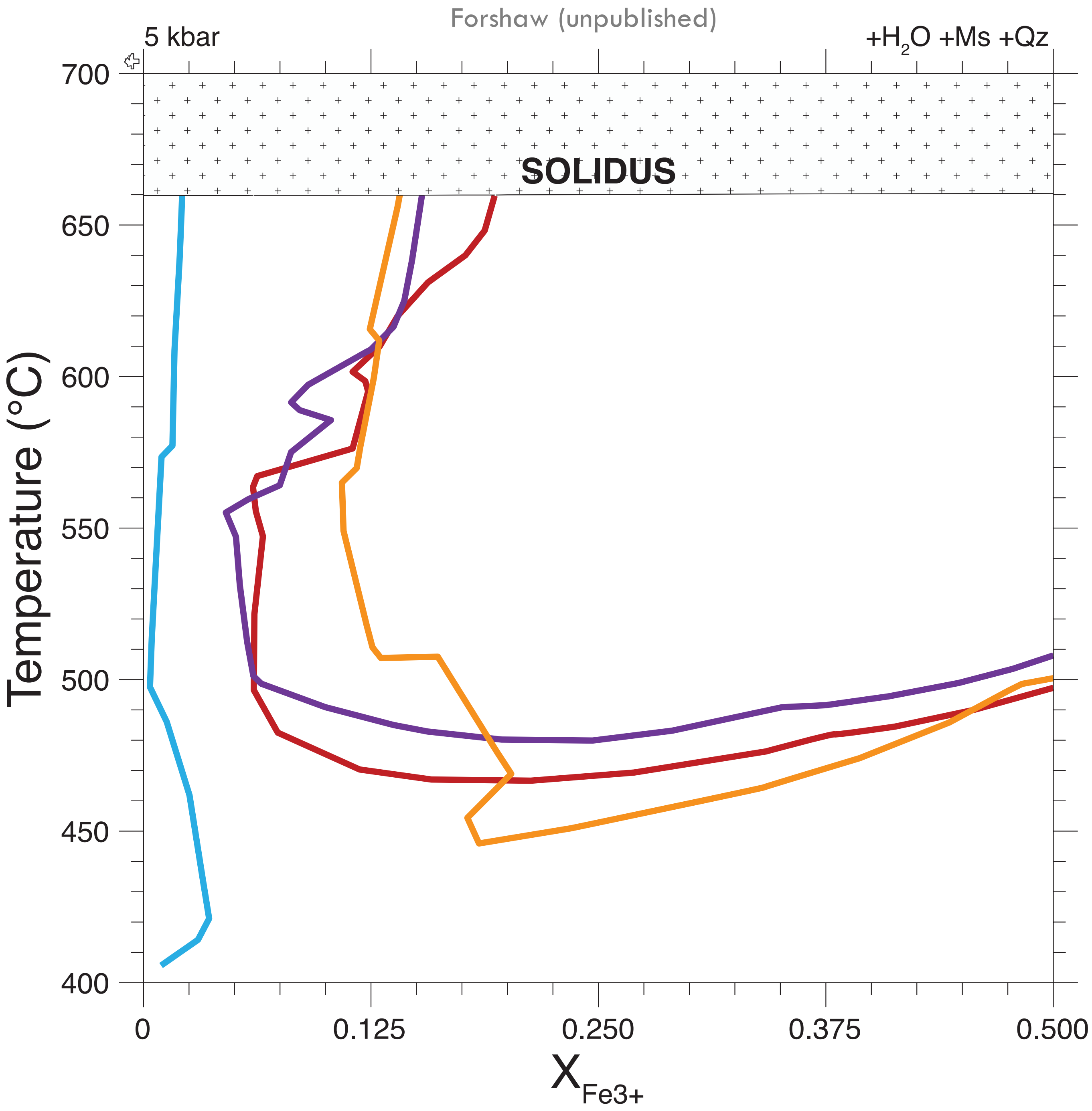
Mag-in lines plotted

HP1

HP2

HPT

ds62

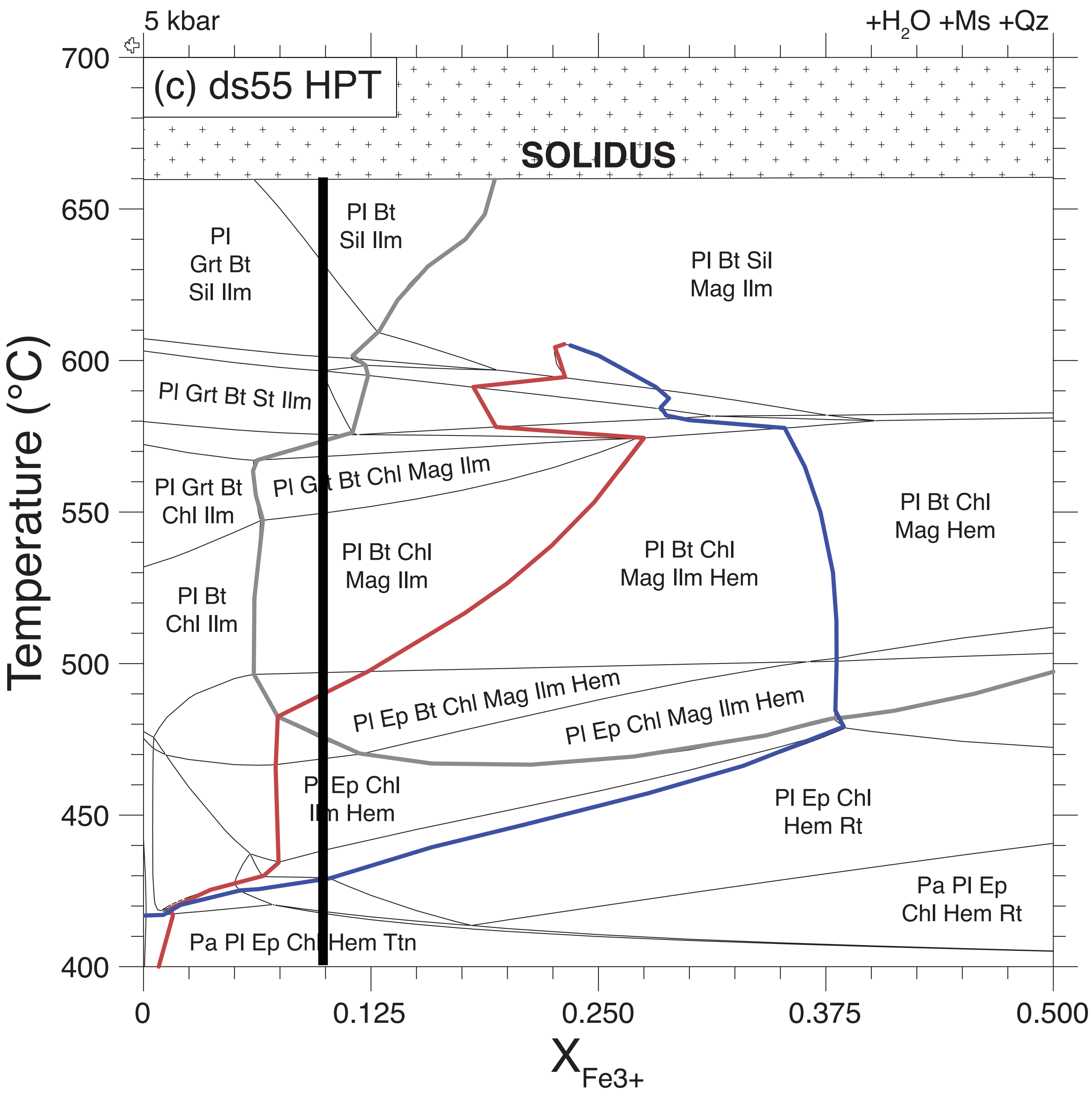


Extra Slides

Conclusions

Fe^{3+} is important and presents a problem

There are several ways in which we can measure it or estimate it. I recommend a combination of at least two or three of these

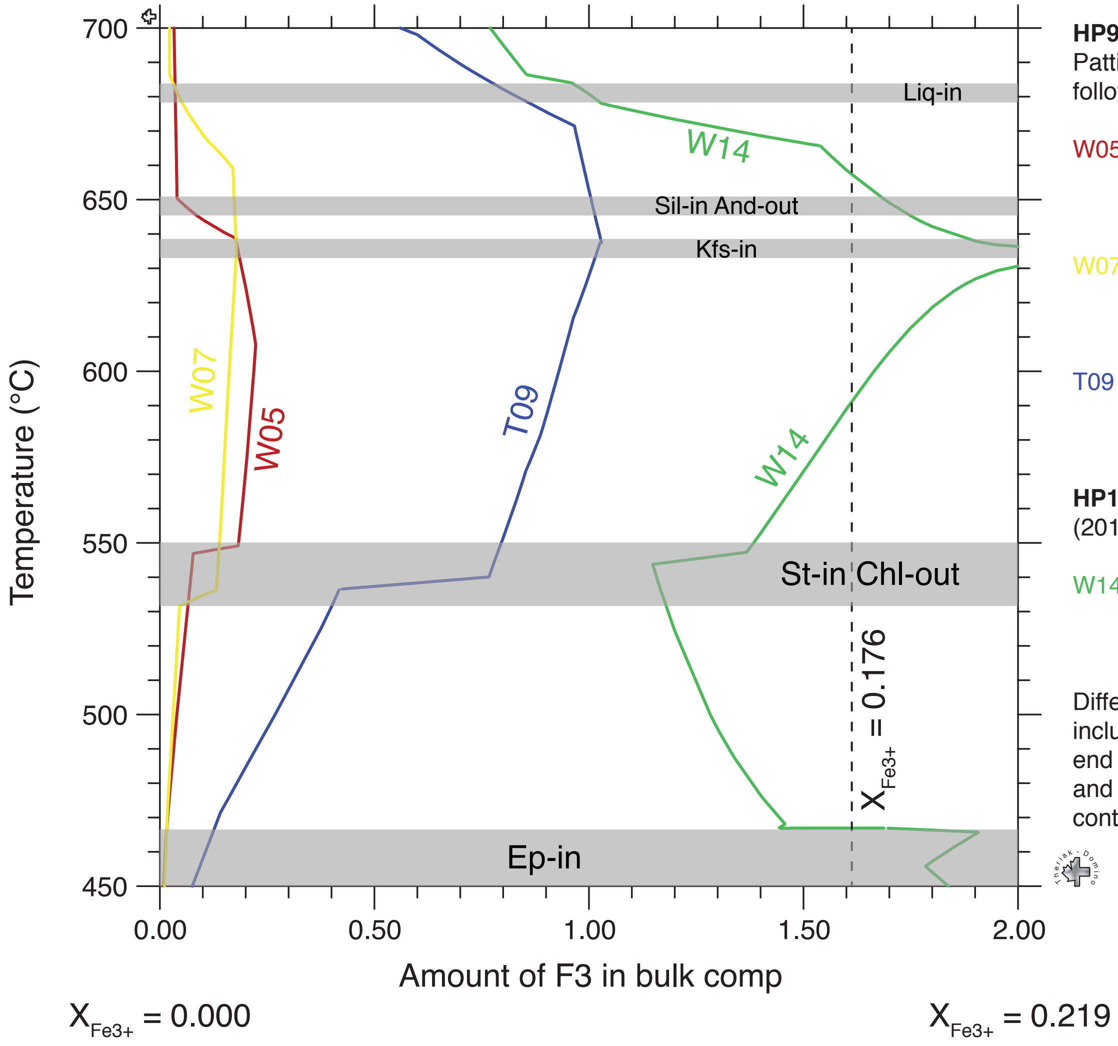


T-X_{Fe3+} diagram

Avg. metapelite (n = 2469)

Different solution models can incorporate varying amounts of Fe^{3+}

Mag-in lines from different datasets and a-x relations at 3 kbar for varying X_{Fe3+} ratios



HP98 dataset - all models same as HP1 in Pattison and Debuhr (2015) apart from the following (Fe^{3+} end member when stated):

W05	Bt	White et al. (2005) - Fe^{3+}
	Grt	Tinkham et al. (2001)
	Ilm	Tinkham + Ghent (2005)
W07	Bt	White et al. (2007) - Fe^{3+}
	Grt	White et al. (2007) - Fe^{3+}
	Ilm	Tinkham + Ghent (2005)
T09	Bt	Tajcmanova et al. (2009) - Fe^{3+}
	Grt	Tinkham et al. (2001)
	Ilm	Tinkham + Ghent (2005)

HP11 dataset - same setup as White et al. (2014) paper

W14	Bt	White et al. (2014) - Fe^{3+}
	Grt	White et al. (2014) - Fe^{3+}
	Ilm	White et al. (2014) - Fe^{3+}

Difference is that Fe^{3+} end members now included for Ms, Chl and St. Note that Fe^{3+} end member were previously available for Grt and Ilm. But these typically overpredict Fe^{3+} contents in both compared to nature.

T-X_{Fe3+} diagram

Different solution models can incorporate varying amounts of Fe^{3+}

Mag-in

Hem-in

Ilm-out