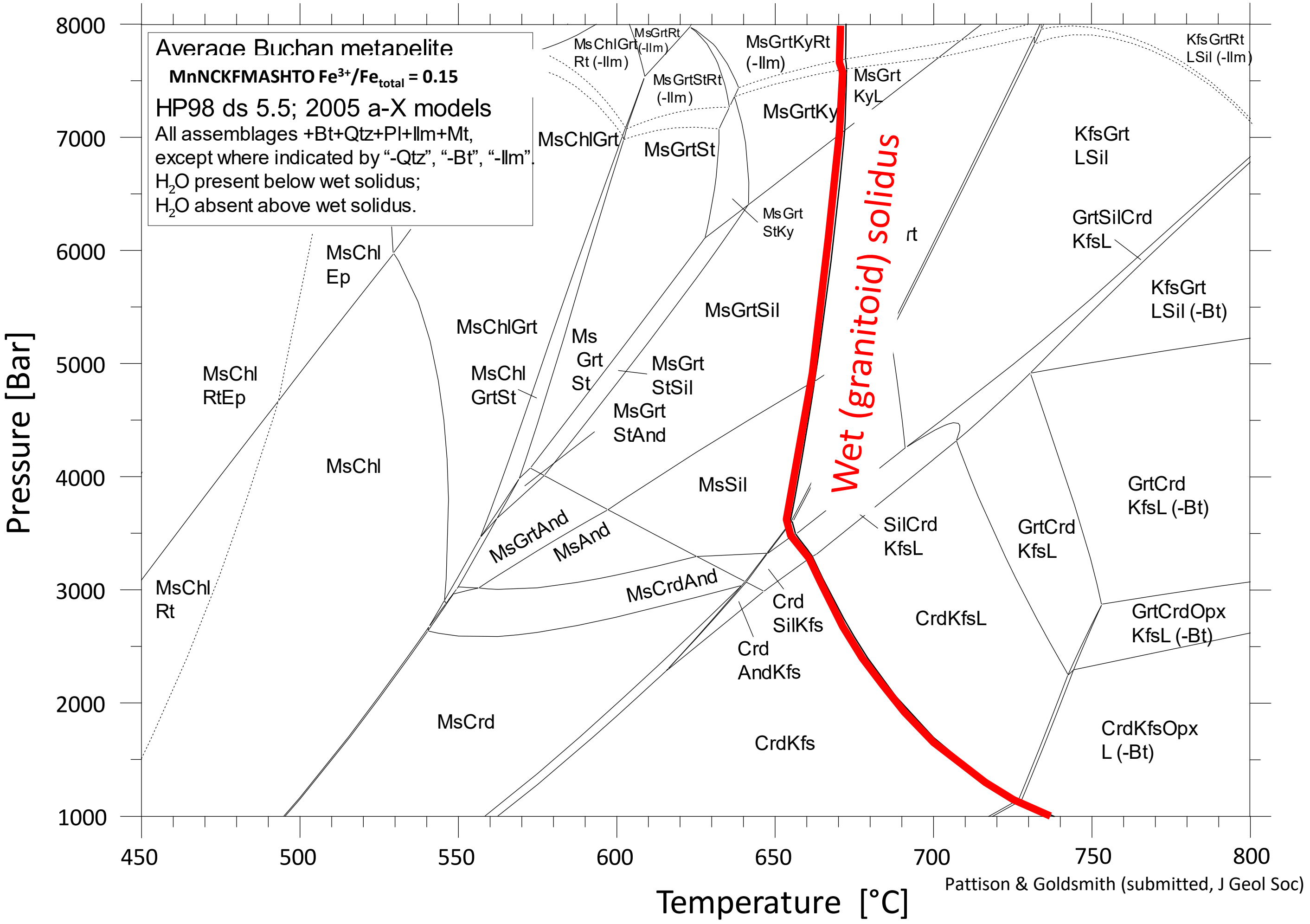
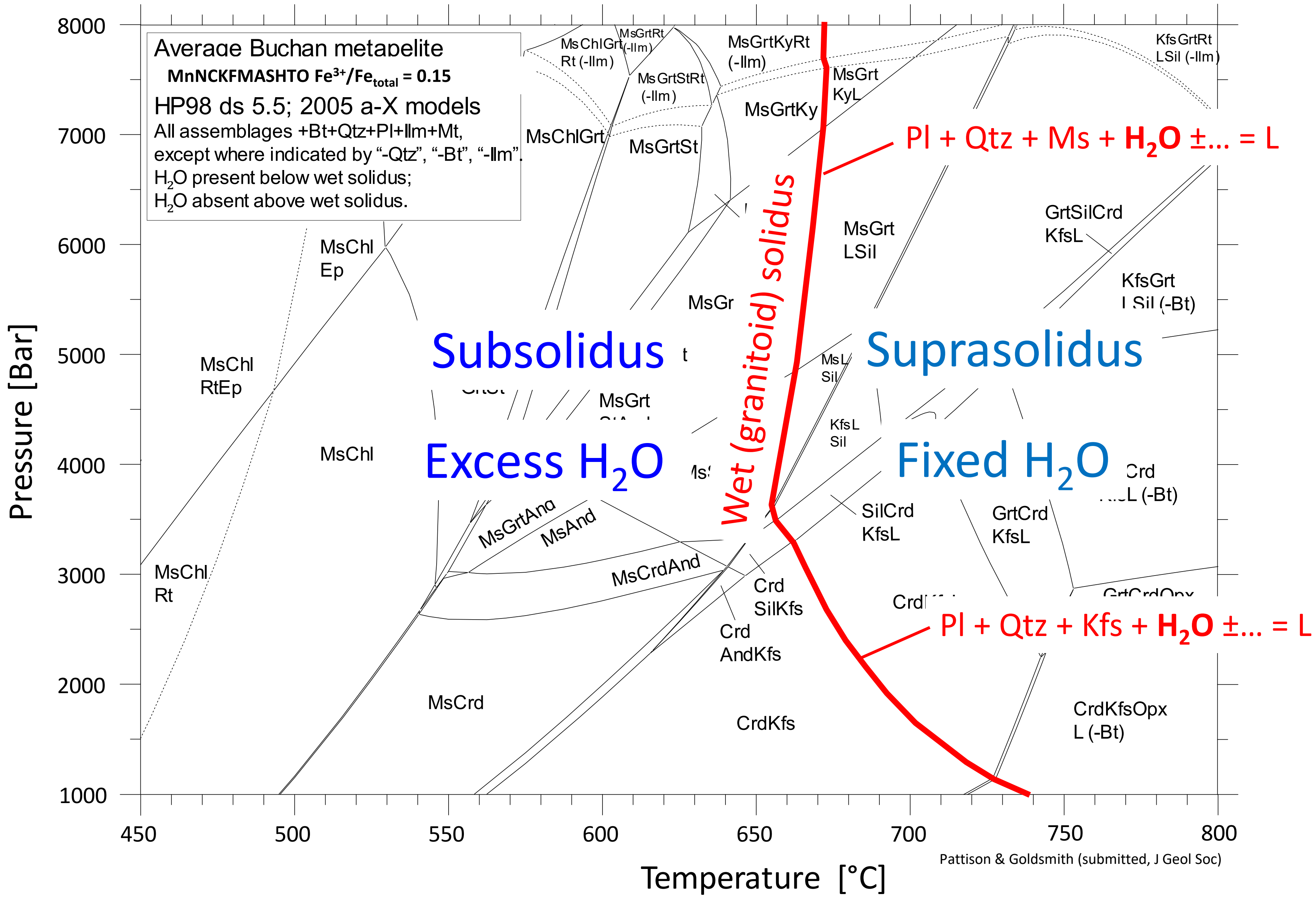
Building combined subsolidus-suprasolidus phase diagrams

(with implications for how you think about the behaviour of H2O in phase diagrams)



Dave Pattison, University of Calgary


Average Buchan metapelite
MnNCKFMASHTO Fe^{3+}/Fe_{total} = 0.15
HP98 ds 5.5; 2005 a-X models
All assemblages +Bt+Qtz+Pl+Ilm+Mt,
except where indicated by “-Qtz”, “-Bt”, “-Ilm”.
H_2O present below wet solidus;
H_2O absent above wet solidus.
Subsolidus
Excess H_2O
Suprasolidus
Fixed H_2O
Wet (granitoid) solidus
Pl + Qtz + Ms + H_2O ±… = L
Pl + Qtz + Kfs + H_2O ±… = L
MsChl Ep
MsChl RtEp
MsChl
MsChl Rt
MsChlGrt
MsChlGrt Rt (-Ilm)
MsGrtRt (-Ilm)
MsGrtStRt (-Ilm)
MsGrtSt
MsGrtKyRt (-Ilm)
MsGrtKy
MsGrt KyL
MsGrt LSil
MsGr
MsGrt
MsGrtAnd
MsAnd
MsCrdAnd
MsCrd
Ms L Sil
Kfs L Sil
SilCrd KfsL
GrtCrd KfsL
Crd SilKfs
Crd AndKfs
CrdKfs
GrtSilCrd KfsL
KfsGrt
KfsGrtRt LSil (-Ilm)
L (-Bt)
CrdKfsOpx L (-Bt)
Pressure [Bar]
8000
7000
6000
5000
4000
3000
2000
1000
Temperature [°C]
450
500
550
600
650
700
750
800
Pattison & Goldsmith (submitted, J Geol Soc)

Subsolidus phase diagram – excess H_2O

Rationale: low grade mineral assemblages have a lot of hydrous minerals like clays, chlorite, muscovite. These get consumed in prograde dehydration reactions to produce 1) less hydrous minerals like garnet, cordierite, etc., and 2) free H2O fluid that escapes the rock. Exceptions (i.e., prograde H2O-consuming reactions) occur but are relatively rare.

Excess H2O = enough H2O to ensure the lowest grade, most hydrous mineral assemblages on the phase diagram are stable (usually those in the low-T, high-P corner of the phase diagram). In practice, this means adding enough H2O to saturate the entire phase diagram (have free H2O present as a phase everywhere on the phase diagram). **Adding more H2O than needed to saturate the entire phase diagram makes no difference to the calculated phase equilibria, but having too little may result in incorrect phase equilibria – even if they don't look obviously incorrect!** You must check the phase diagram to be sure that H2O is present as a phase in every predicted subsolidus mineral assemblage.

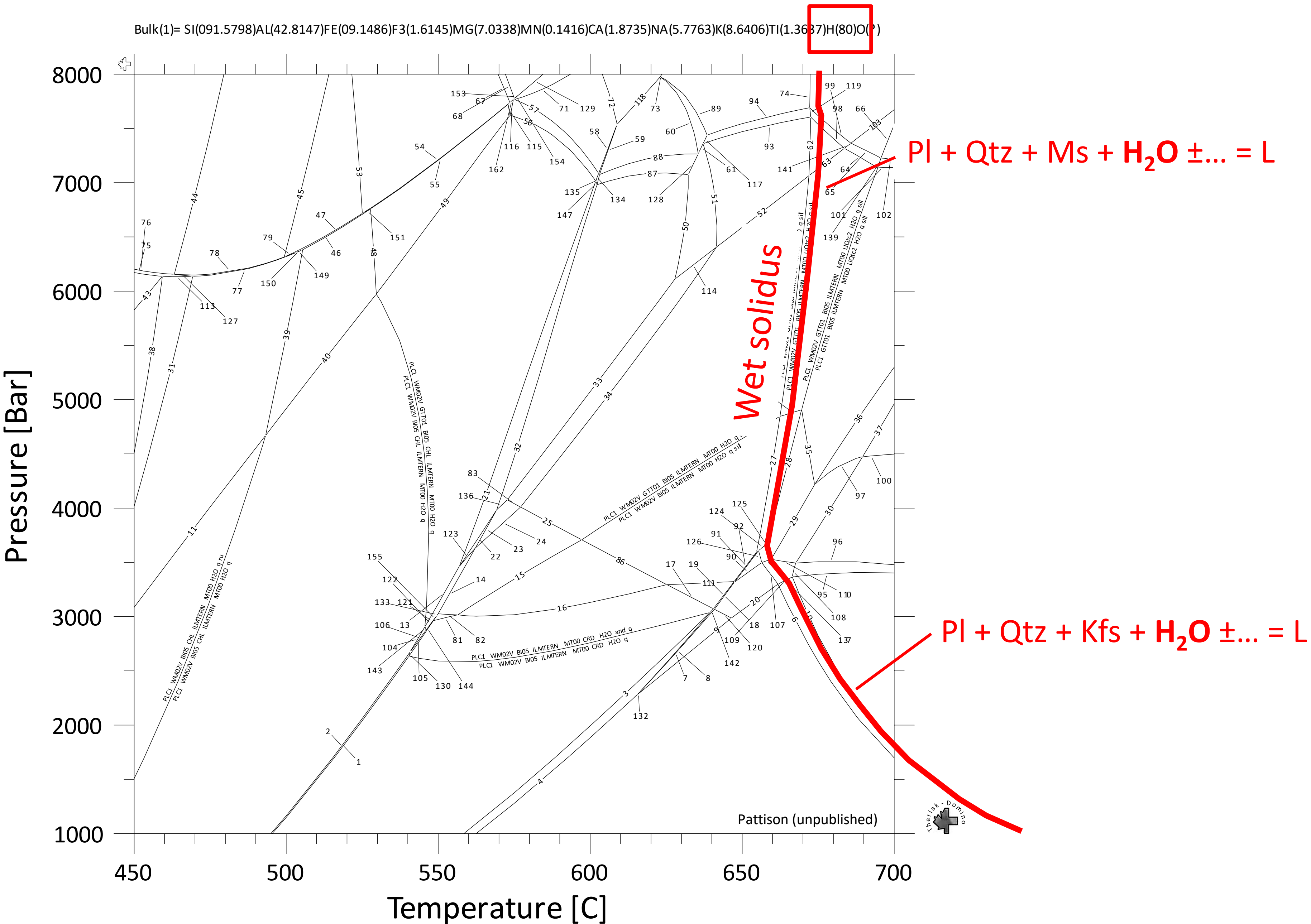
Upshot: you do not use the measured H2O content or LOI (loss on ignition) of a subsolidus rock (e.g., a garnet-kyanite schist) to calculate a subsolidus phase diagram **that extends to P-T conditions below those of the rock**: the lower grade phase equilibria will be wrong once H2O is no longer present as a free fluid phase.

Example input file in Theriak-Domino (using HP ds5.5) for the illustrated subsolidus phase diagram:

Excess H

SI(091.5798)TI(1.3637)AL(42.8147)FE(09.1486)F3(1.6145)MG(7.0338)MN(0.1416)CA(1.8735)NA(5.7763)K(8.6406)**H(80)**O(?)

(Mainly) subsolidus phase diagram calculated with **excess H2O** (H2O = 40, same as H = 80)



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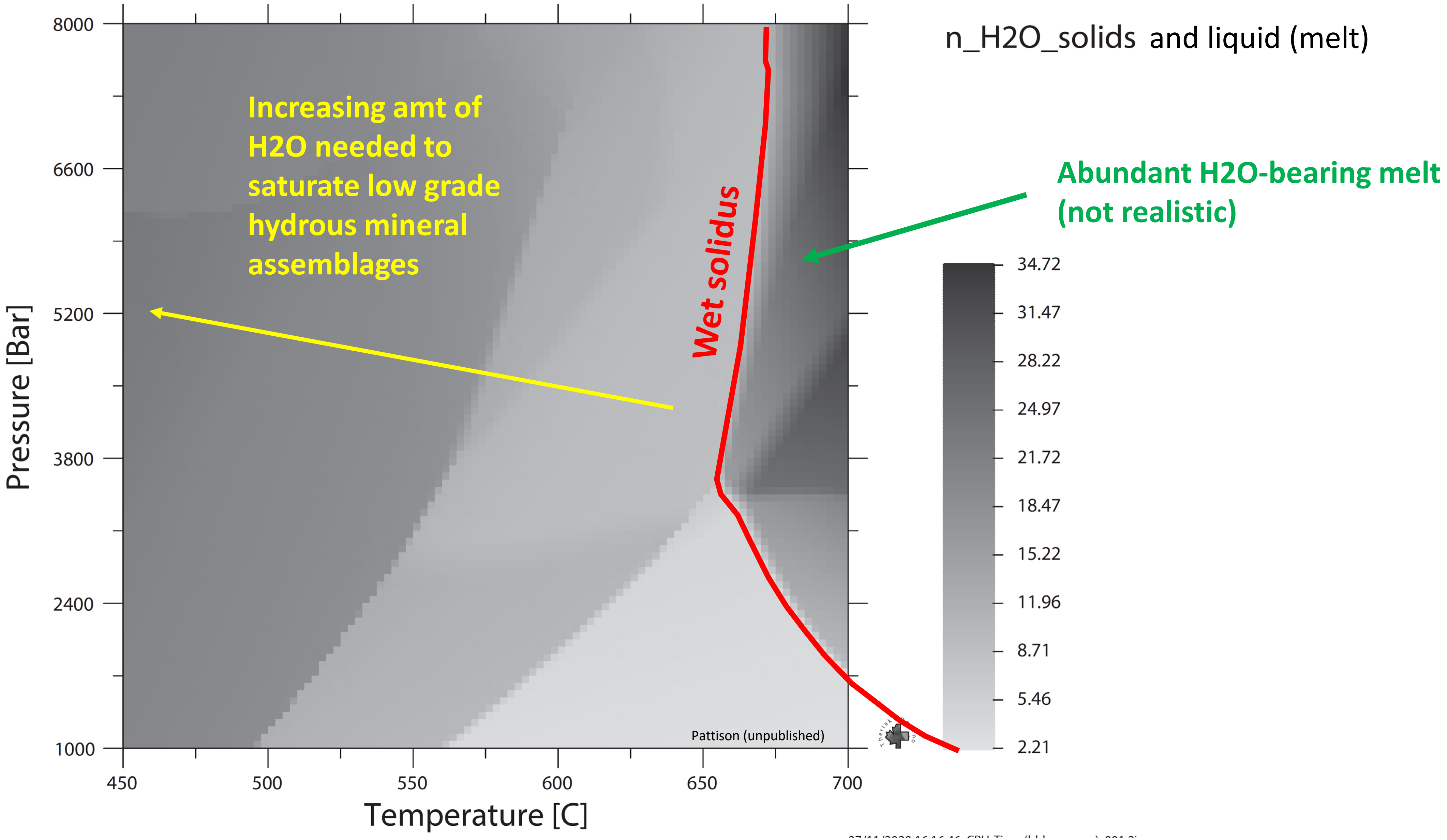
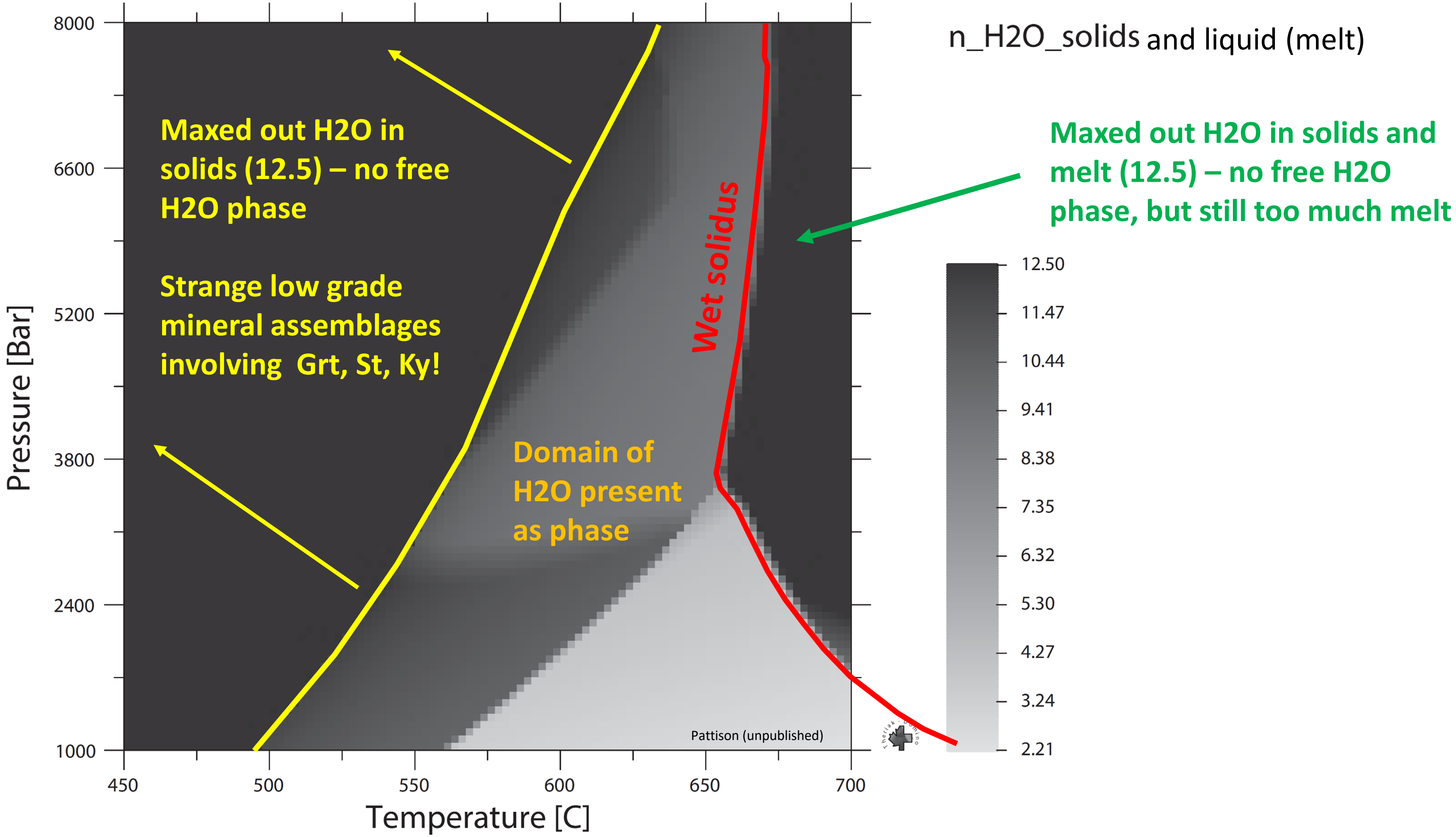
Moles of H2O contained in solid or melt phases - **excess H2O** (H2O = 40, same as H = 80)

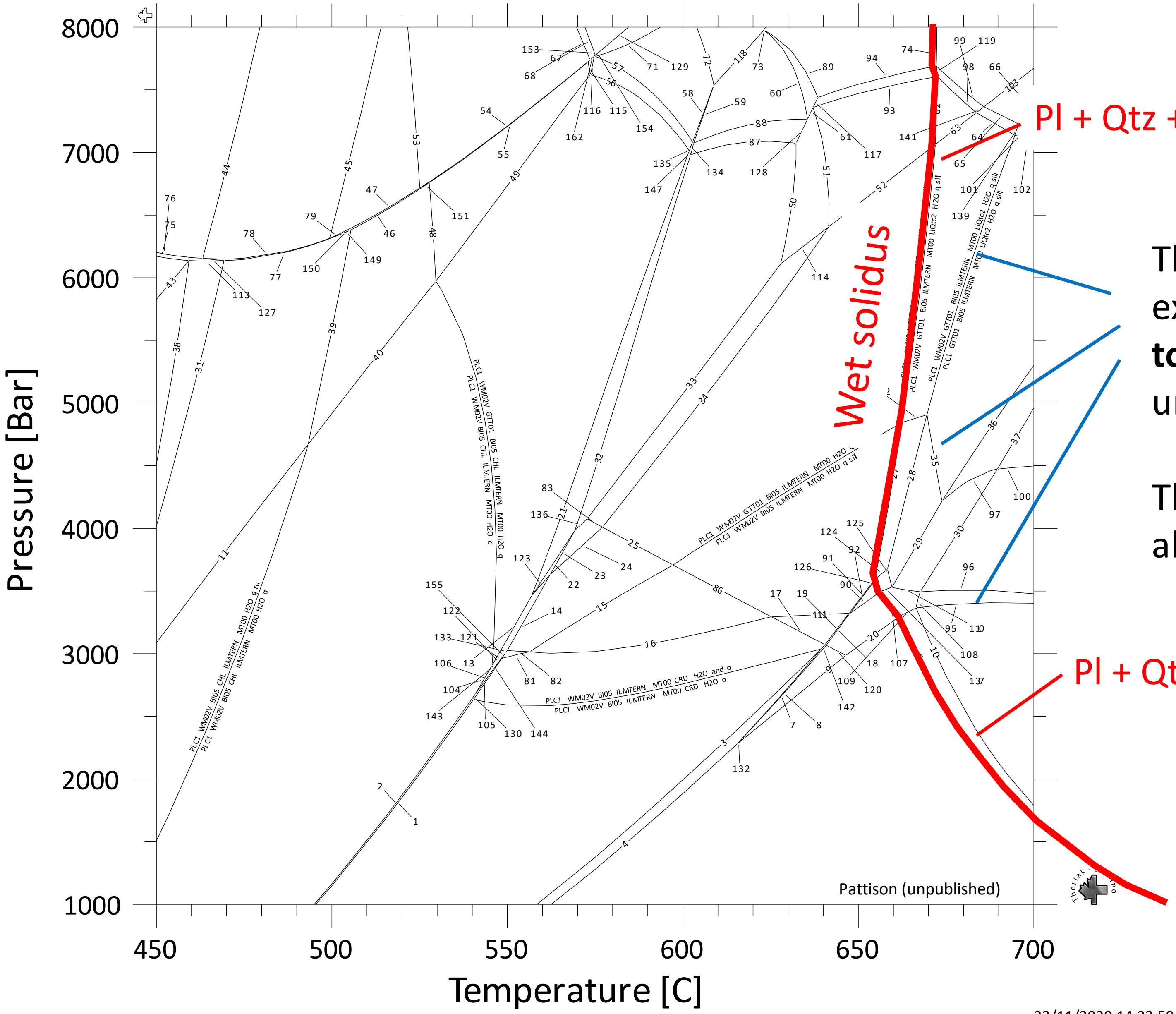


Moles of H2O contained in solid or melt phases - **not enough H2O to saturate** (H2O = 12.5, same as H = 25)



(Mainly) subsolidus phase diagram calculated with **excess H2O** (H2O = 40, same as H = 80)

Bulk(1)= SI(091.5798)AL(42.8147)FE(09.1486)F3(1.6145)MG(7.0338)MN(0.1416)CA(1.8735)NA(5.7763)K(8.6406)TI(1.3637)H(80)O(?)



These suprasolidus reactions assume excess H2O! **They do not correspond to natural reactions** (except in unusual situations).

Therefore, delete all reactions above the wet solidus.

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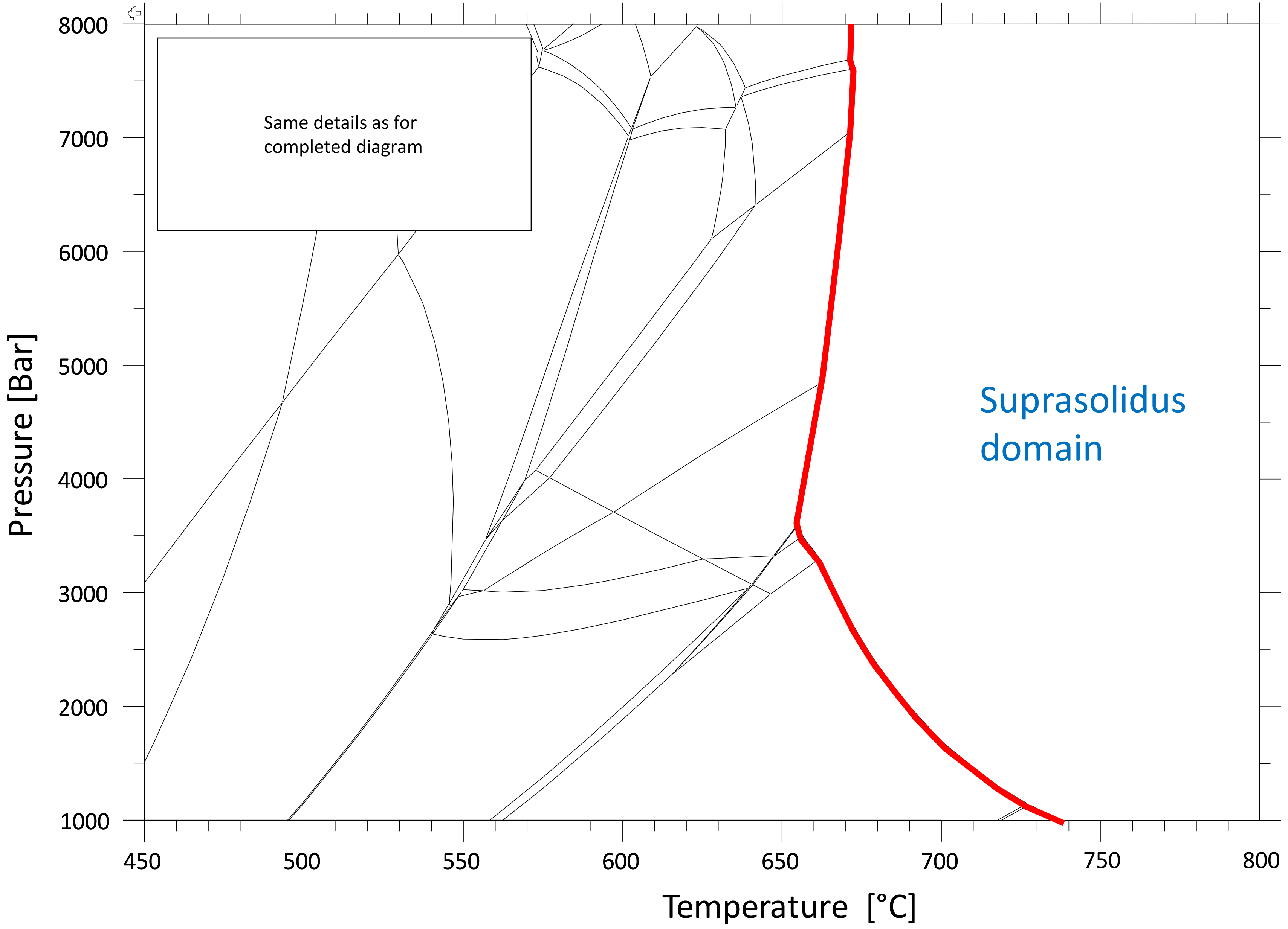
Subsolidus phase diagram calculated with **excess H2O**
(cleaned up but unlabelled, with some less relevant reactions removed)



Suprasolidus phase diagram – fixed H_2O

Rationale: in suprasolidus rocks above the wet solidus, **all hydrous fluid is consumed by H2O-consuming melting reactions.**

$$\text{Pl} + \text{Qtz} + \text{Ms-or-Kfs} + \mathbf{H_2O} \pm \ldots = \text{L}$$

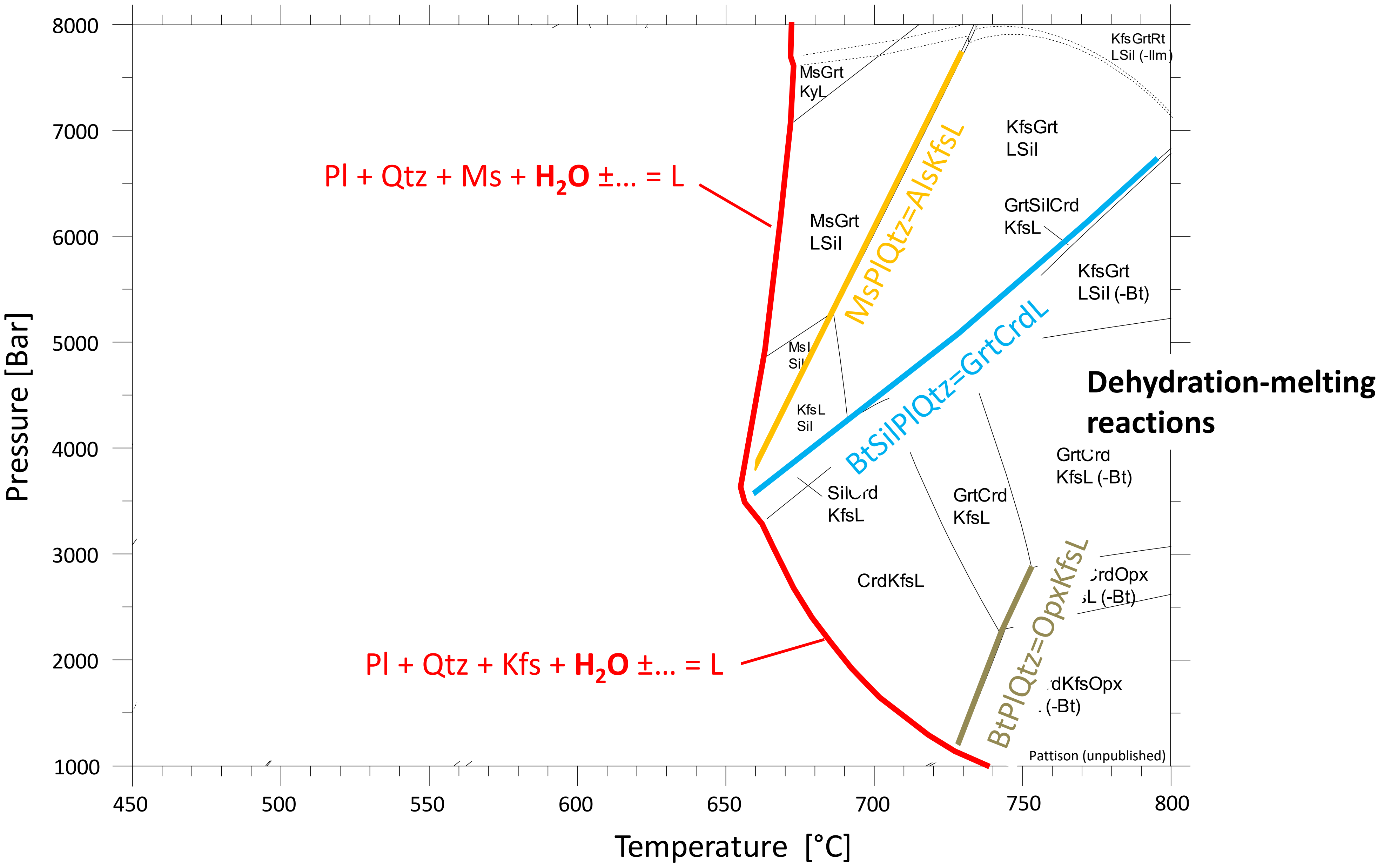
Because the porosity of high grade rocks is likely to be near-zero, so is the volume of free H2O fluid contained in the pores, meaning that imperceptible volumes of melt are produced at the wet solidus. That is why **"excess H2O" above the wet solidus is not realistic**, unless externally-derived fluid infiltration occurs when the rocks are at P-T conditions above the wet solidus.

In dehydration reactions above the wet solidus (e.g., Ms- or Bt-consuming suprasolidus reactions), the H2O released is dissolved into the melt phase, hence the term **dehydration-melting reactions**. Thus, in contrast to subsolidus reactions in which the H2O released in dehydration reactions escapes the rock, the H2O content of suprasolidus rocks is **retained in the rock (in the melt phase)** – that is, unless some of the melt escapes (next talk!).

Upshot: use a fixed H2O content for suprasolidus phase equilibria.

Complication: melt has a variable H2O content (higher H2O content at higher P, lower H2O content at lower P). Therefore, more than one fixed-H2O suprasolidus phase diagrams may need to be calculated, as explained below.

Suprasolidus domain



Fixed H2O suprasolidus phase diagram - Step 1.

Obtain the H2O content of the rock (contained in hydrous phases like muscovite and biotite) just below the wet solidus, i.e., modes x H-content (easy in T-D and Perplex, less so in Thermocalc?). Use this as a fixed value for the H2O content (or, in T-D, the H-content) of the rock. Typically one chooses a point on the solidus ~ in the middle of the pressure range of the diagram (in the example shown here, 3.6 kbar).

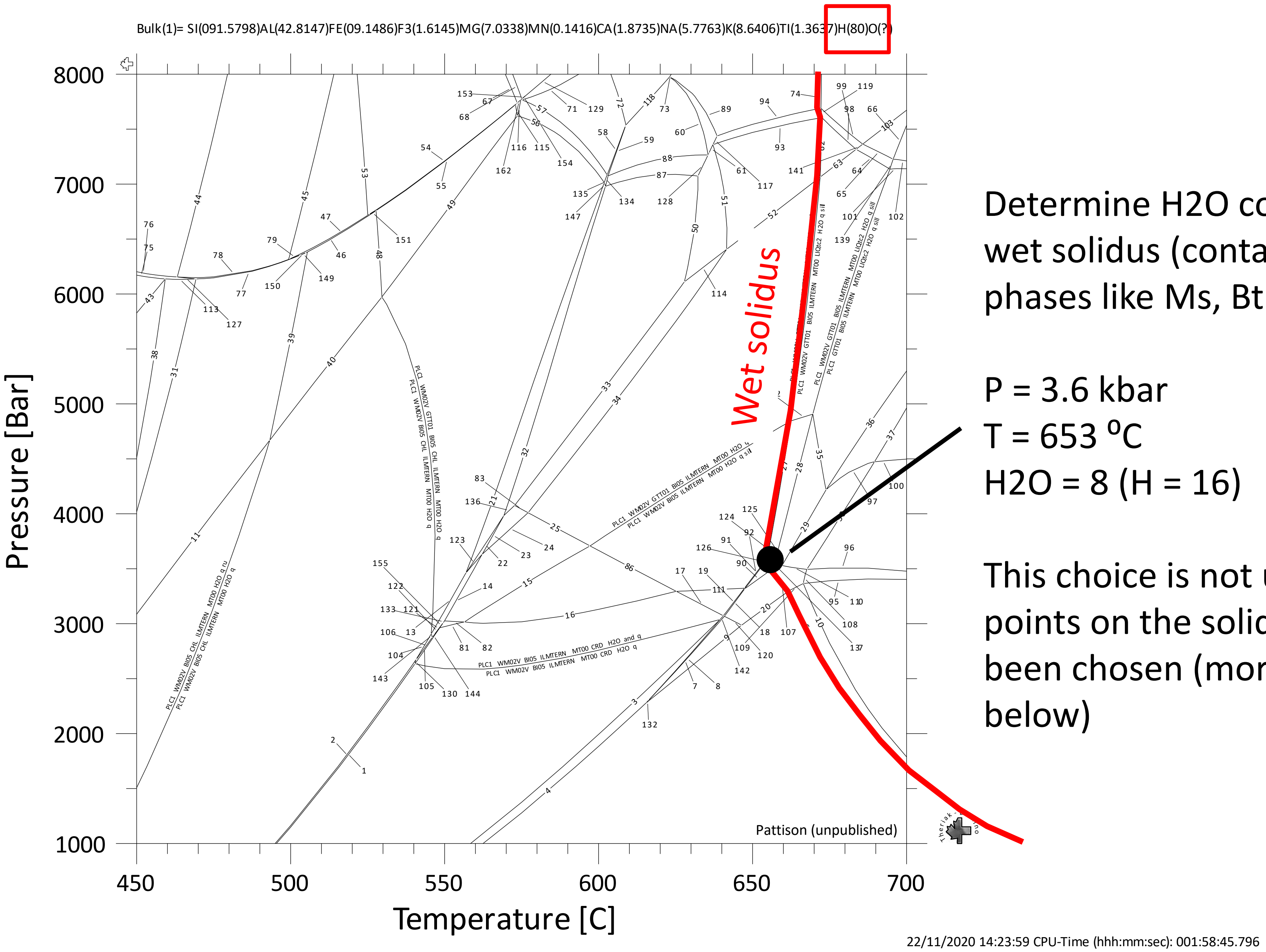
Example input file in Theriak-Domino (using HP ds5.5) for the illustrated phase diagram:

Fixed (non-excess) H

SI(091.5798)TI(1.3637)AL(42.8147)FE(09.1486)F3(1.6145)MG(7.0338)MN(0.1416)CA(1.8735)NA(5.7763)K(8.6406)**H(16)**O(?)

Note that the bulk composition is identical to the bulk composition for the subsolidus phase diagram except for the reduced H2O (H) content.

(Mainly) subsolidus phase diagram calculated with **excess H2O** (H2O = 40, same as H = 80)



Determine H2O content of rock on wet solidus (contained in hydrous phases like Ms, Bt):

P = 3.6 kbar

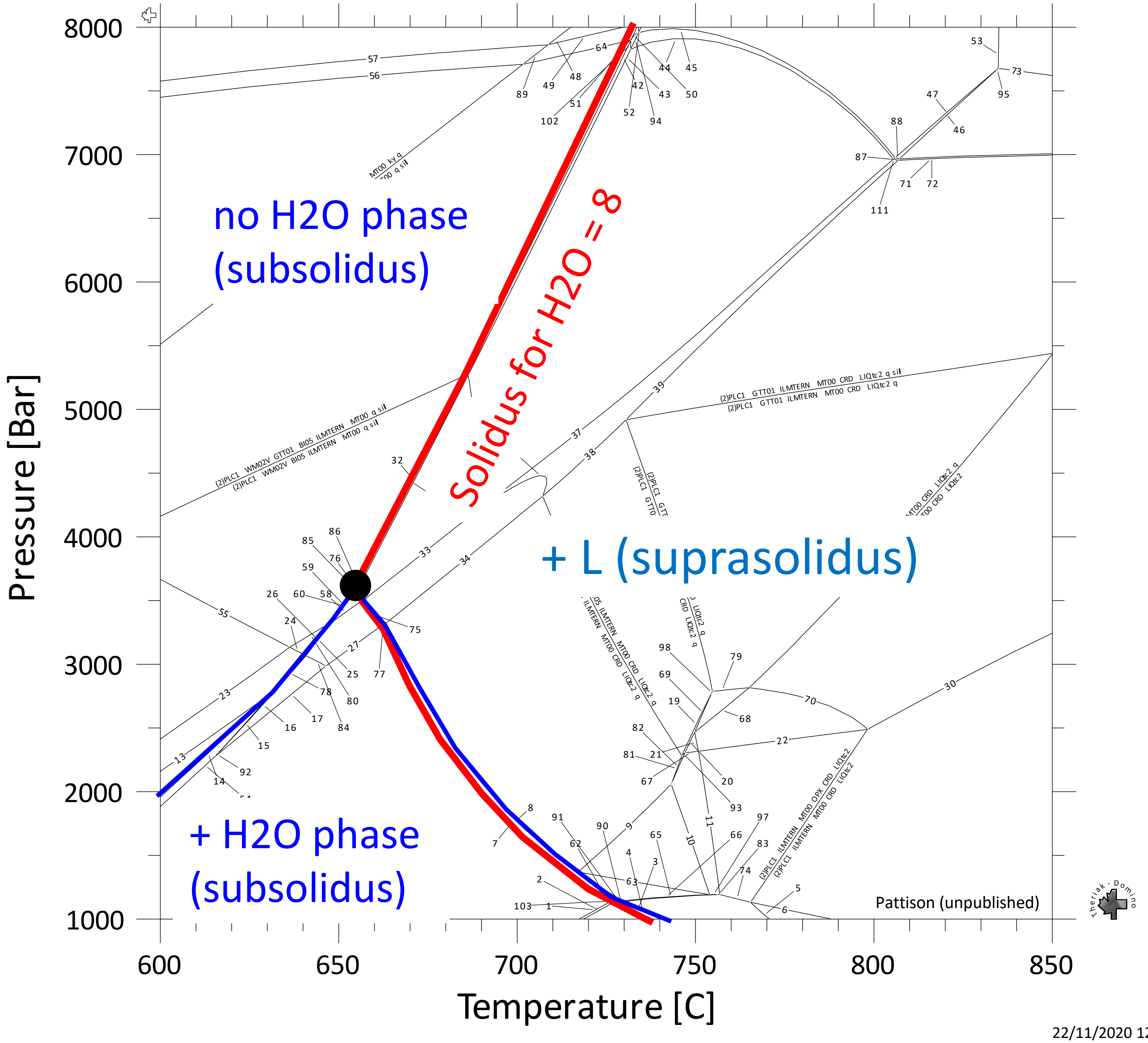
T = 653 ^oC

H2O = 8 (H = 16)

This choice is not unique; other points on the solidus could have been chosen (more discussion below)

Suprasolidus phase diagram calculated with **fixed (non-excess) H2O** (H2O = 8, same as H = 16)

Bulk(1)= SI(091.5798)AL(42.8147)FE(09.1486)F3(1.6145)MG(7.0338)MN(0.1416)CA(1.8735)NA(5.7763)K(8.6406)TI(1.3637)H(16)O(?)



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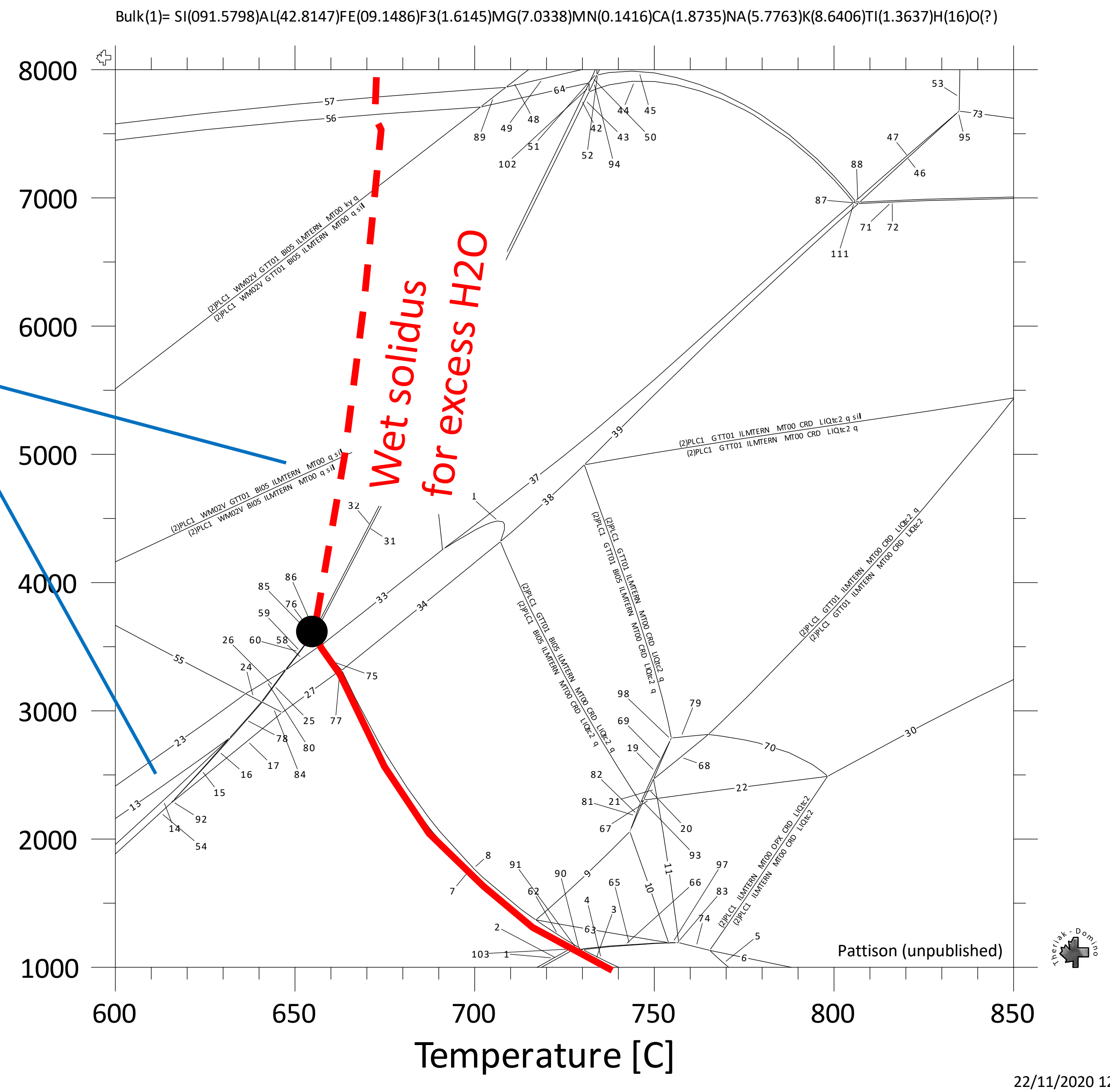
Suprasolidus phase diagram calculated with **fixed (non-excess) H2O** (H2O = 8, same as H = 16)

For this reduced-H2O bulk composition, these subsolidus reactions do not involve a free H2O phase, and so they do not correspond to natural reactions (in a prograde sense at least).

Therefore, delete all reactions below the wet solidus.



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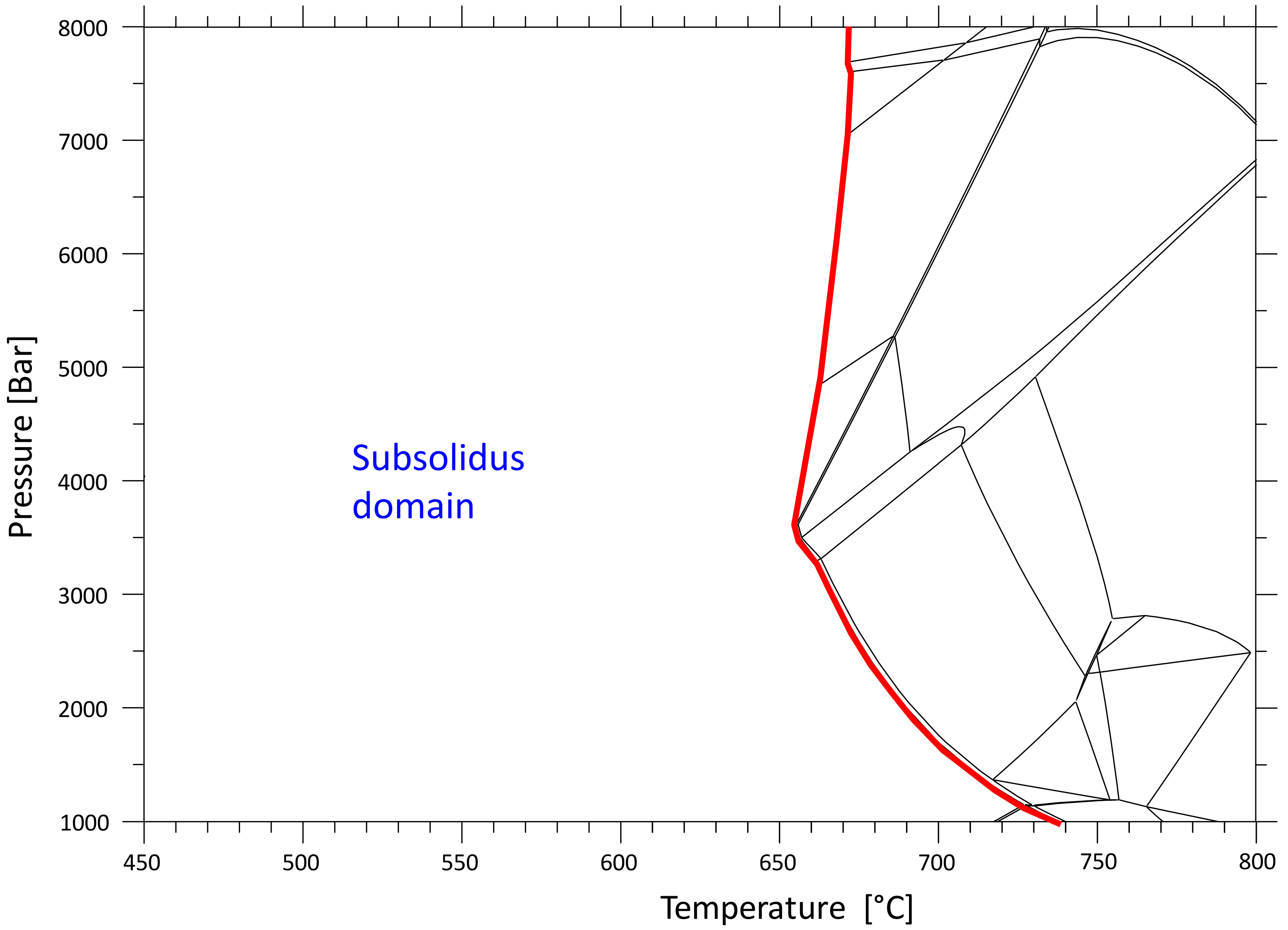
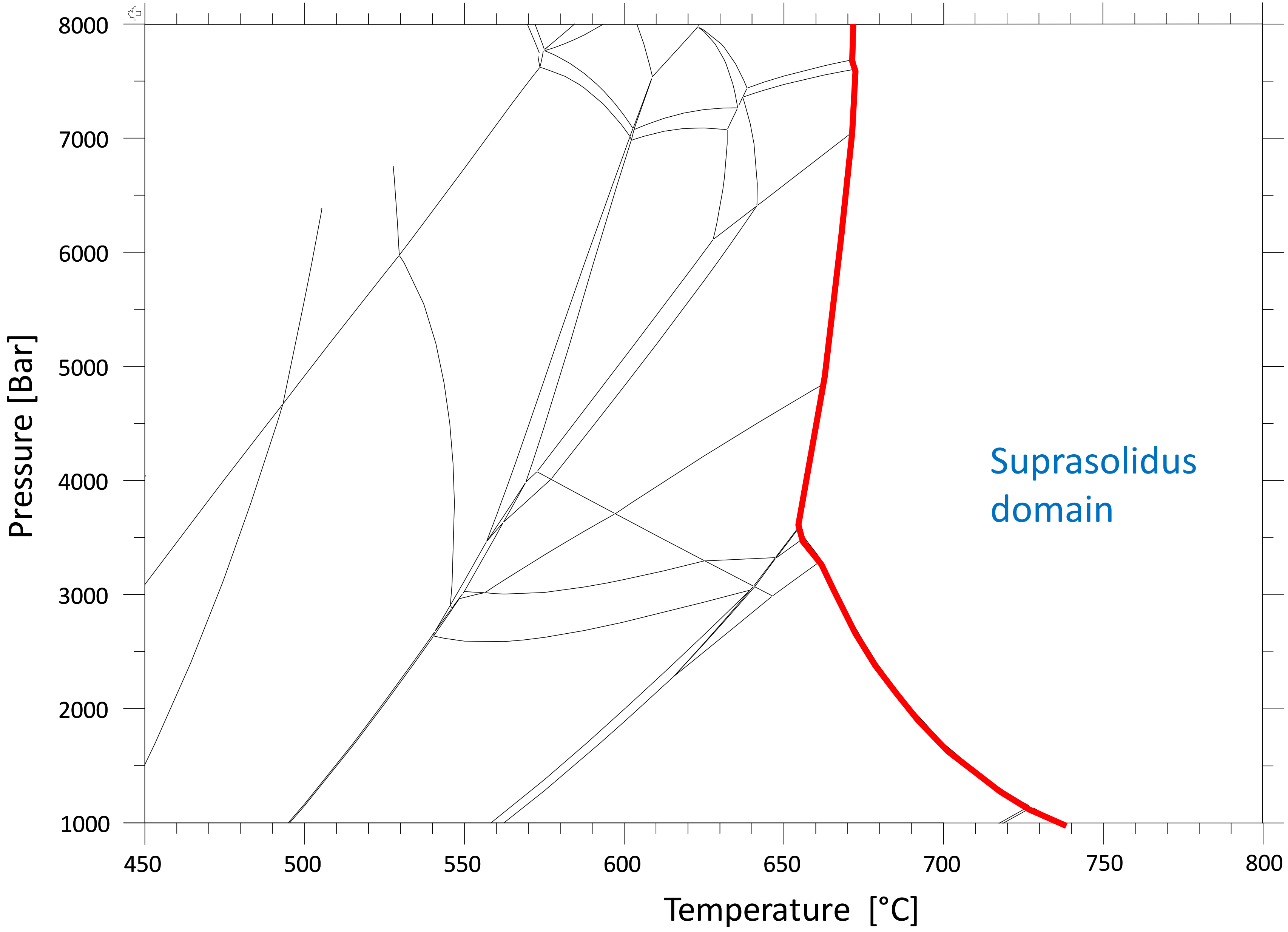
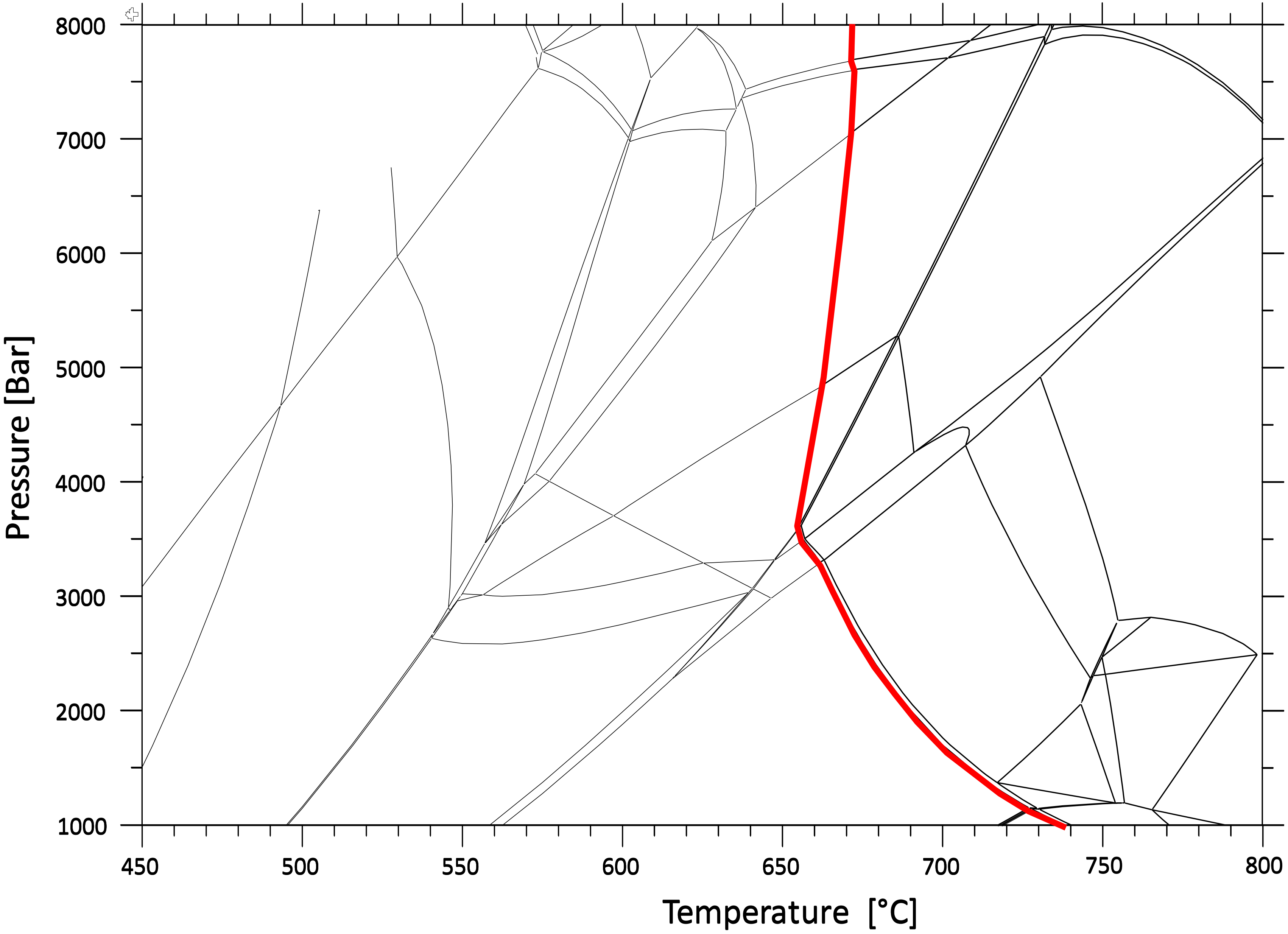
Suprasolidus phase diagram (cleaned up but unlabelled)



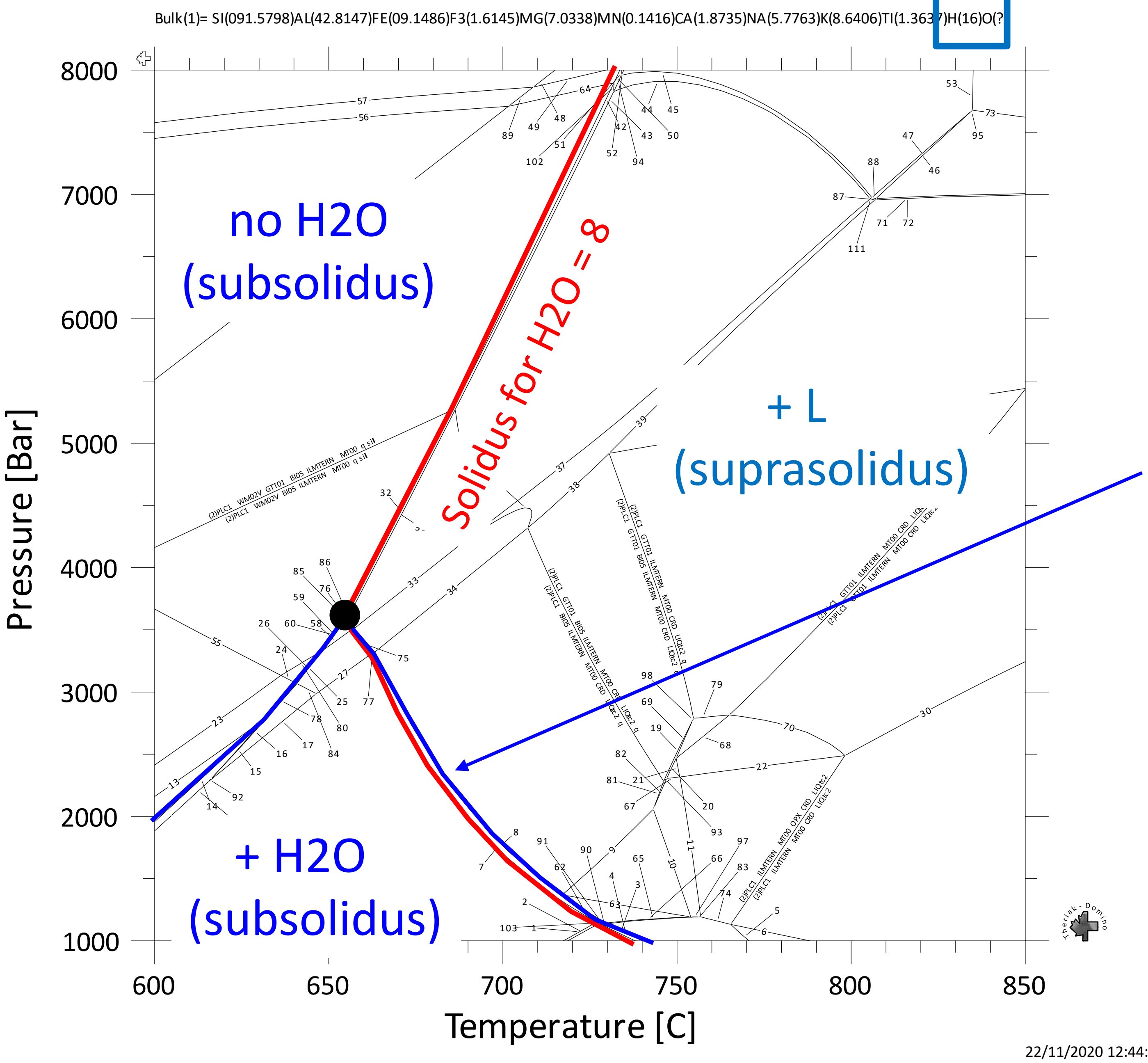
Subsolidus phase diagram (cleaned up but unlabelled)



Combined subsolidus-suprasolidus phase diagram (unlabelled)



Suprasolidus phase diagram calculated with **fixed (non-excess) H2O** (H2O = 8, same as H = 16)



Complication

Notice the blue line in the suprasolidus field – it is an H2O-consuming reaction above the wet solidus (i.e., it is an artifact of the modelling, due to the progressively lower H2O content of the melt)

This results in too much melt being generated at low P, which has a knock-on effect on the lower-P phase equilibria!

Fixed H2O suprasolidus phase diagram - Step 2.

Calculate another suprasolidus phase diagram, but with a fixed H2O content for a low pressure (e.g., 1.8 kbar).

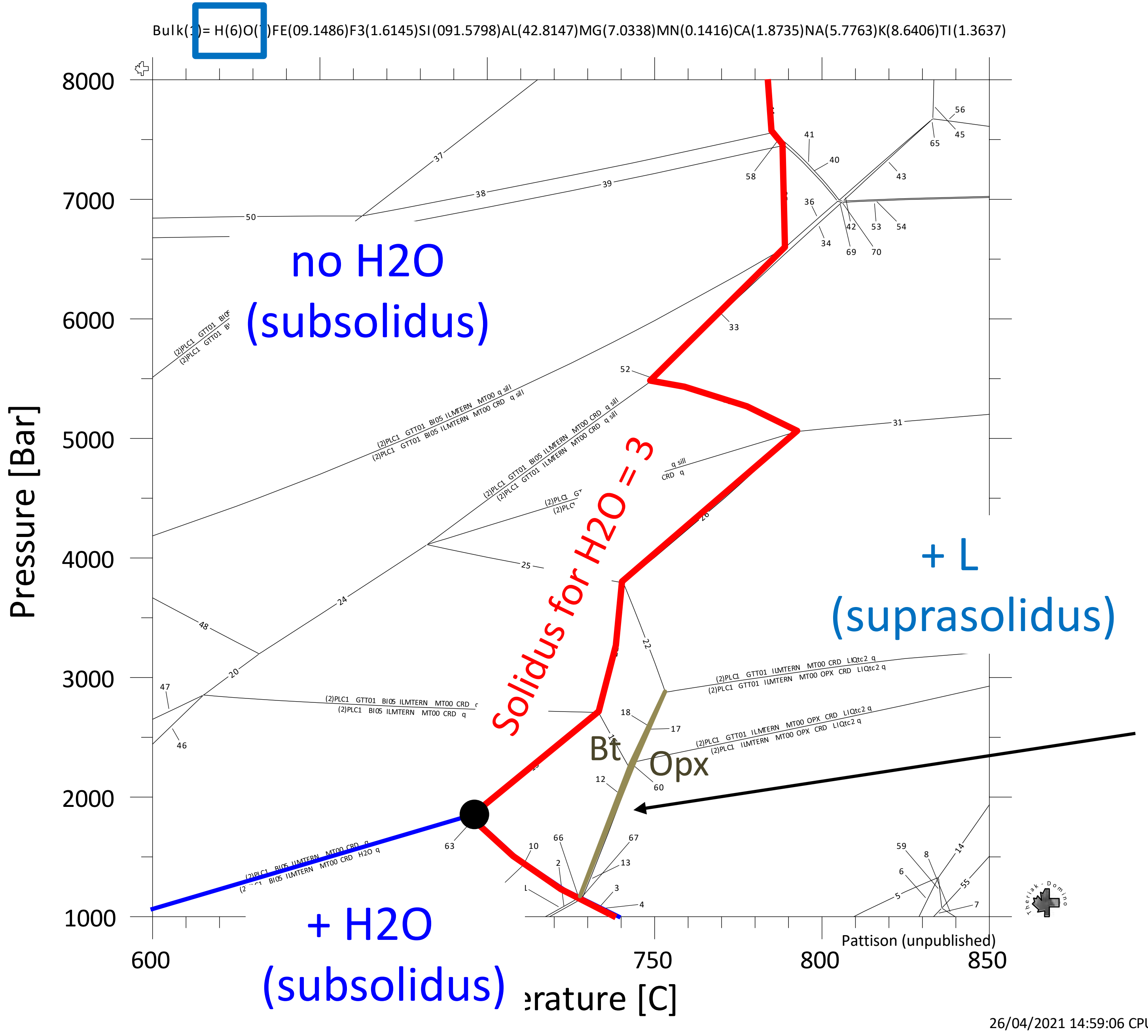
Example input file in Theriak-Domino (using HP ds5.5) for the illustrated phase diagram:

Fixed (non-excess) H

SI(091.5798)TI(1.3637)AL(42.8147)FE(09.1486)F3(1.6145)MG(7.0338)MN(0.1416)CA(1.8735)NA(5.7763)K(8.6406)**H(6)**O(?)

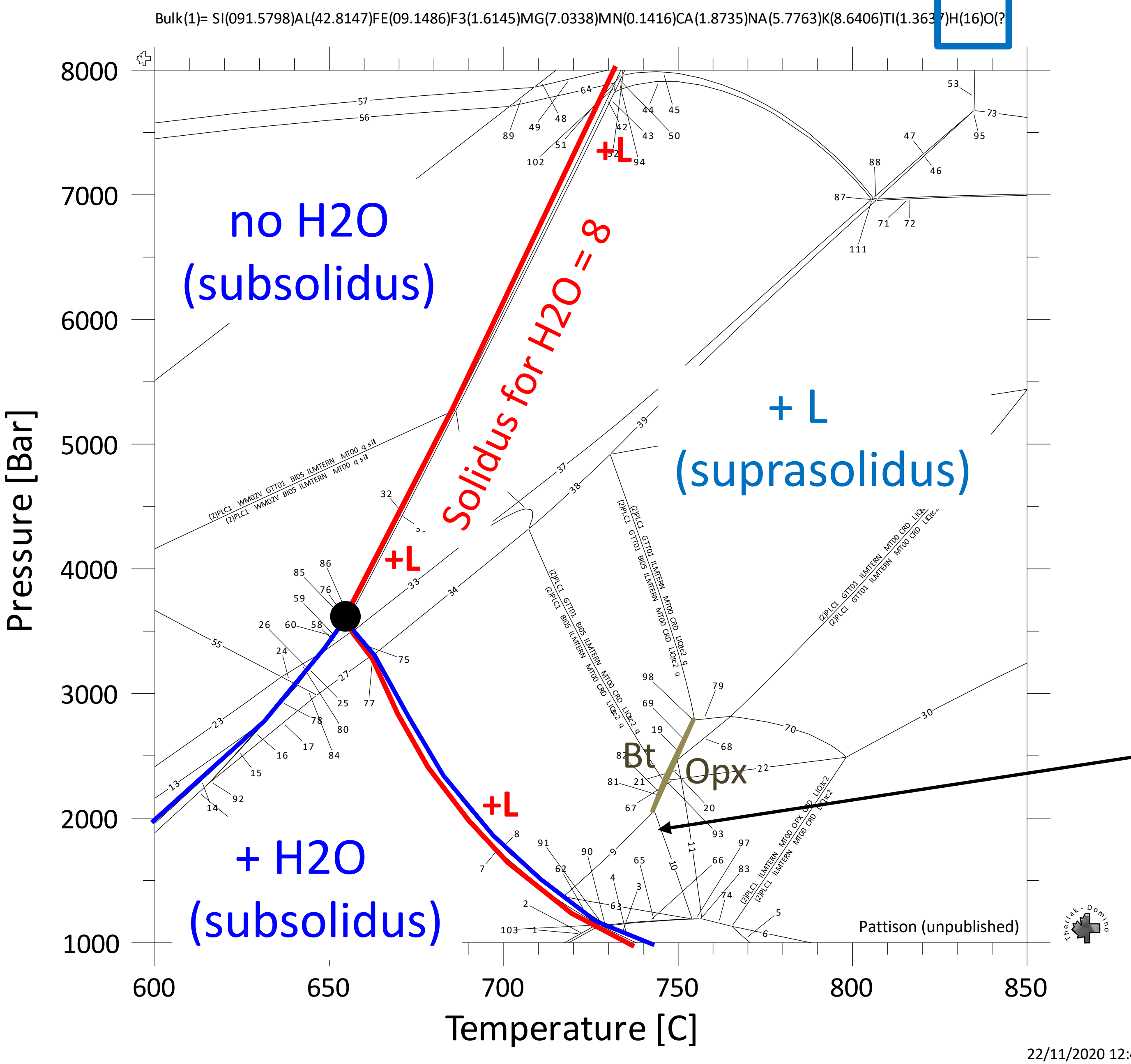
Notice again that the bulk composition is identical to the bulk composition for the other phase diagrams except for the further-reduced H2O (H) content.

Suprasolidus phase diagram calculated with **fixed (non-excess) H2O** (H2O = 3, same as H = 6)



Notice the different phase equilibria involving Bt going to Opx between phase diagrams calculated for H2O=8 vs. H2O=3

Suprasolidus phase diagram calculated with **fixed (non-excess) H2O** (H2O = 8, same as H = 16)



Notice the different phase equilibria involving Bt going to Opx between phase diagrams calculated for H2O=8 vs. H2O=3

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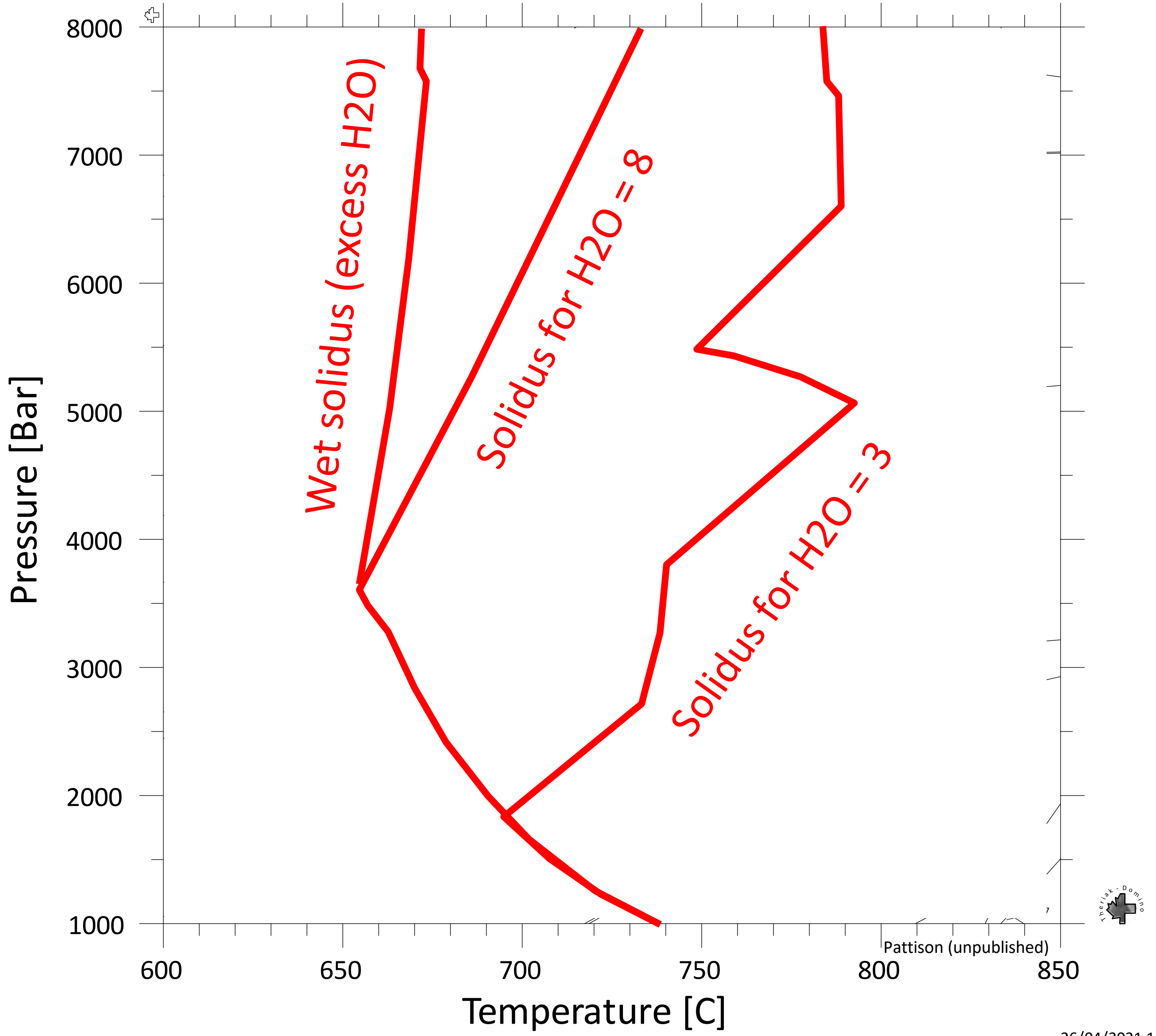
Position of solidus for three different assumed values of molar H2O (excess, 8 and 3)



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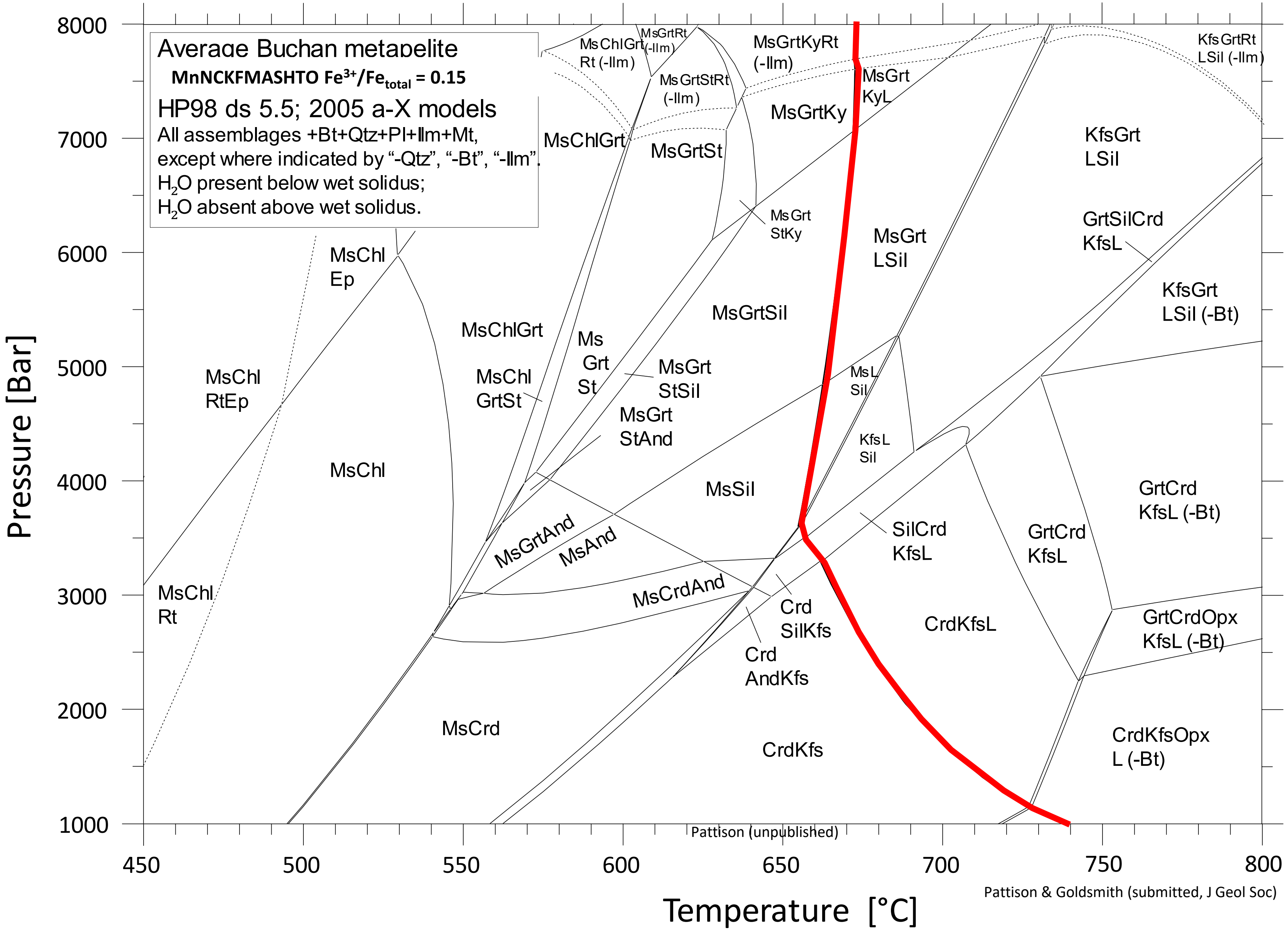
Can I use the measured H_2O content of a suprasolidus rock as the value of the fixed H_2O content for the phase diagram? (Or, use LOI - loss on ignition - if the rock isn't too altered?)

Yes, if focusing just (mainly) on the P-T conditions of that rock. But you need to be very careful if using the resultant phase diagram to make petrological inferences at higher and especially lower P-T conditions because of the H_2O matter! Plus, good to compare thermodynamically-computed H-content of rock, based on the predicted hydrous phases, with the measured H_2O/LOI content.

The final result: a combined subsolidus-suprasolidus phase diagram



Pattison & Goldsmith (submitted, J Geol Soc)