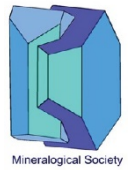
Part 9d
Mixed volatile calculations

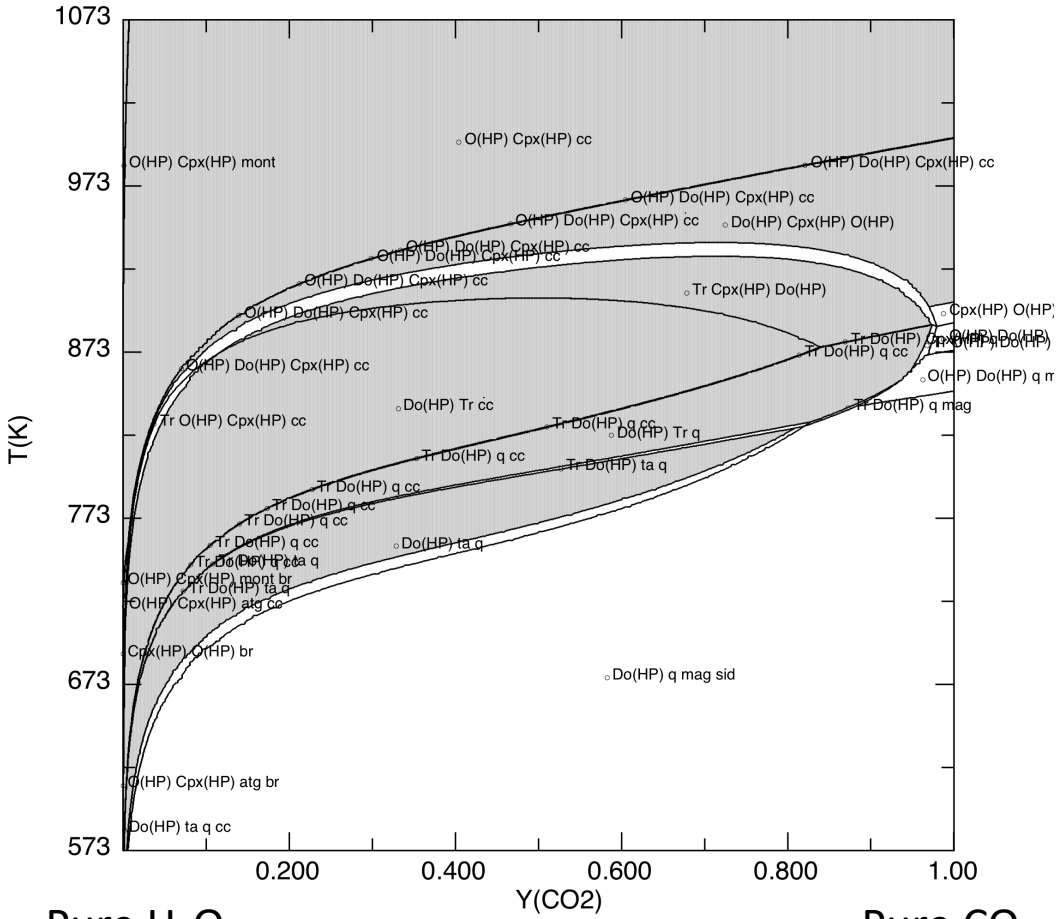
Mark Caddick & Doug Tinkham

PHASE EQUILIBRIUM MODELLING: APPROACHES AND PITFALLS



In the context of the metamorphic phase equilibria modeling we have discussed this week, one of two end-member scenarios is generally employed for dealing with fluids (generally because these are easily implemented)

1. Fix the amount of each component (e.g., Na_2O, K_2O, SiO_2) in the rock, but not the amount of fluid-forming components. Instead, constrain the composition of the fluid (e.g. H_2O, CO_2). Force the rock to equilibrate with this.



Pure H_2O Pure CO_2

Calculated with a 2002 update to the Holland & Powell dataset with the composition 20 wt% MgO, 20% CaO, 10% FeO, 50% SiO2 + fluid of constrained CO_2:H_2O. 5 kbars

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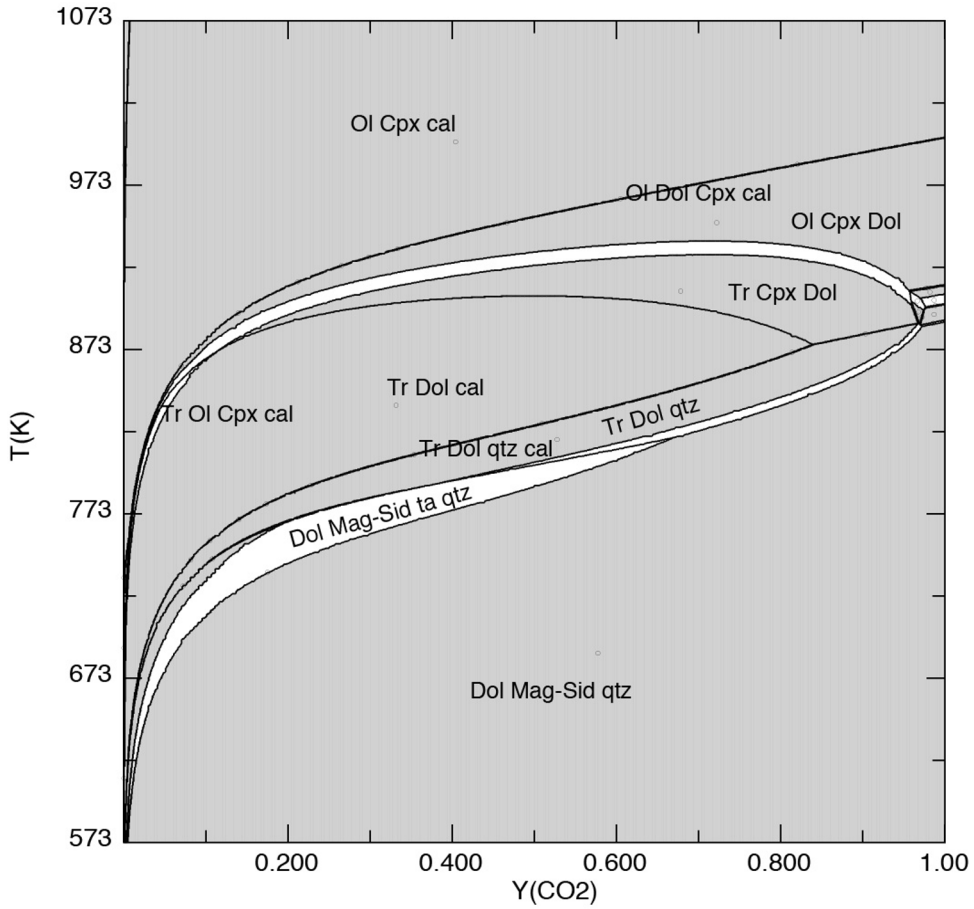

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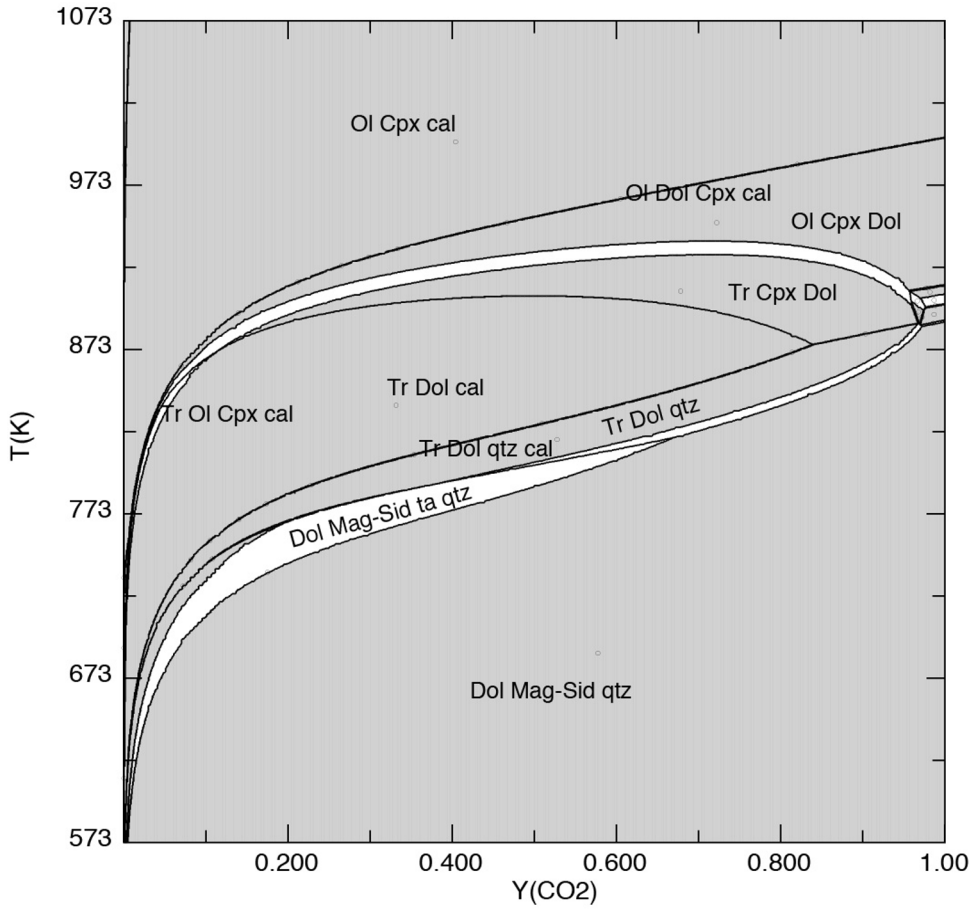

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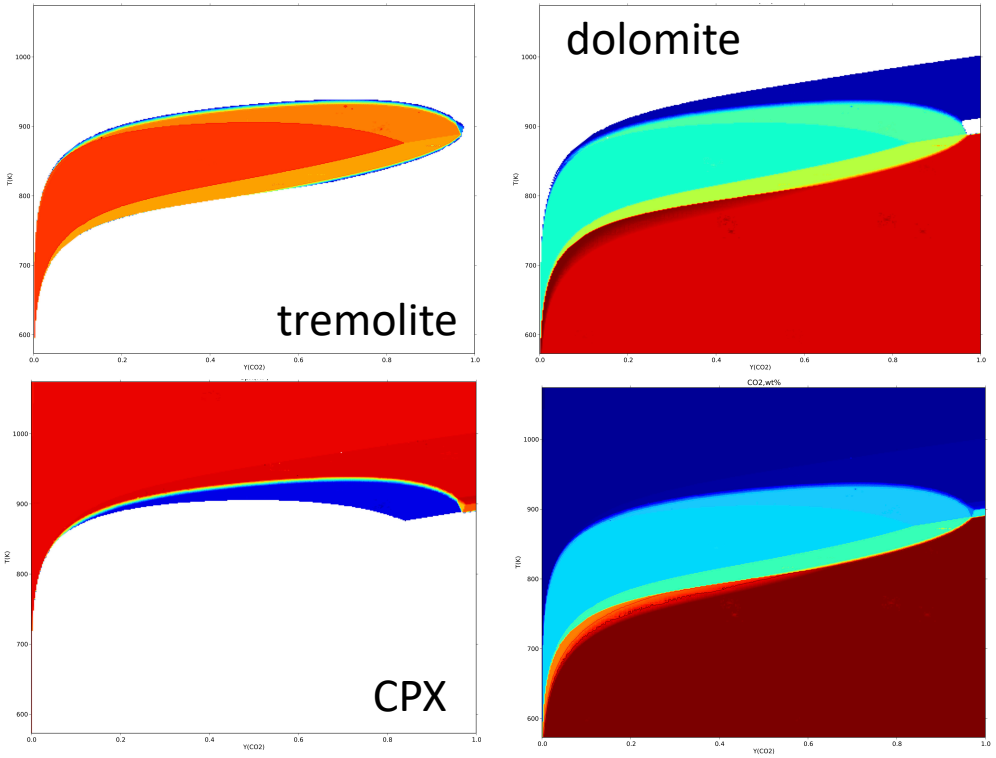

CO_2 content of the mineral assemblage

Calculated with a 2002 update to the Holland & Powell dataset with the composition 20 wt% MgO, 20% CaO, 10% FeO, 50% SiO2 + fluid of constrained CO_2:H_2O. 5 kbars

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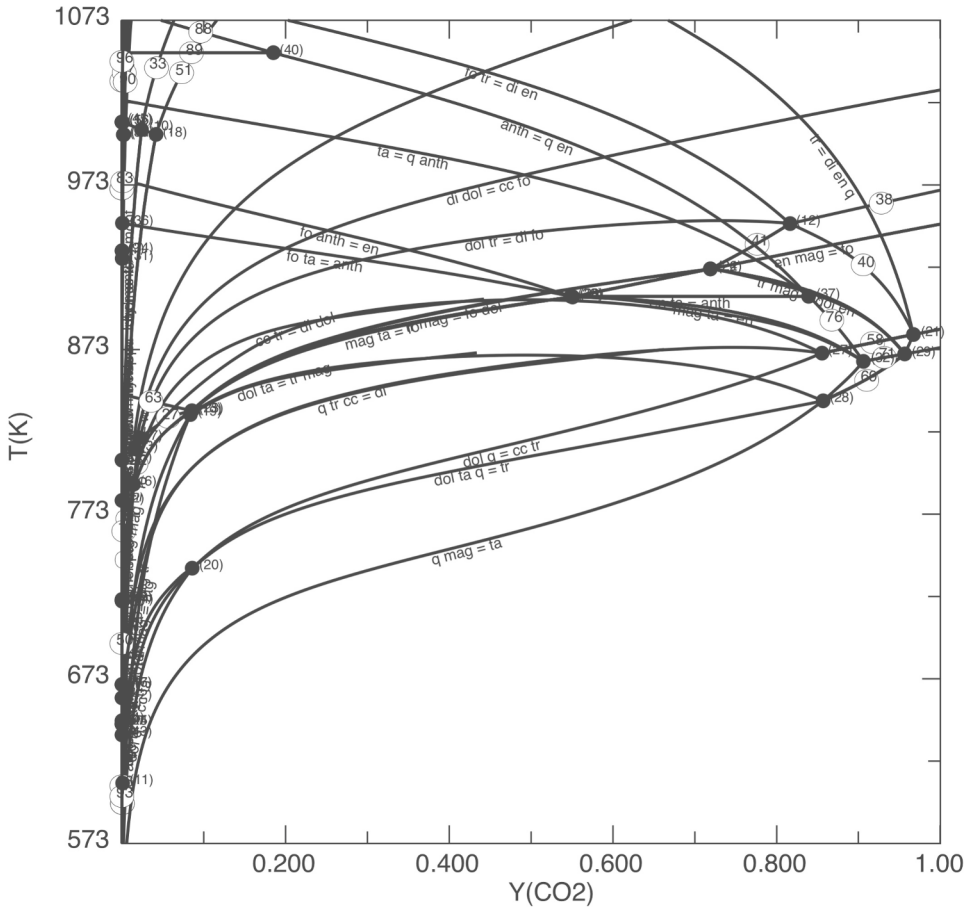

Pure H_2O

Pure CO_2

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This is broadly comparable to Figure 12-3 of Frank Spear's book

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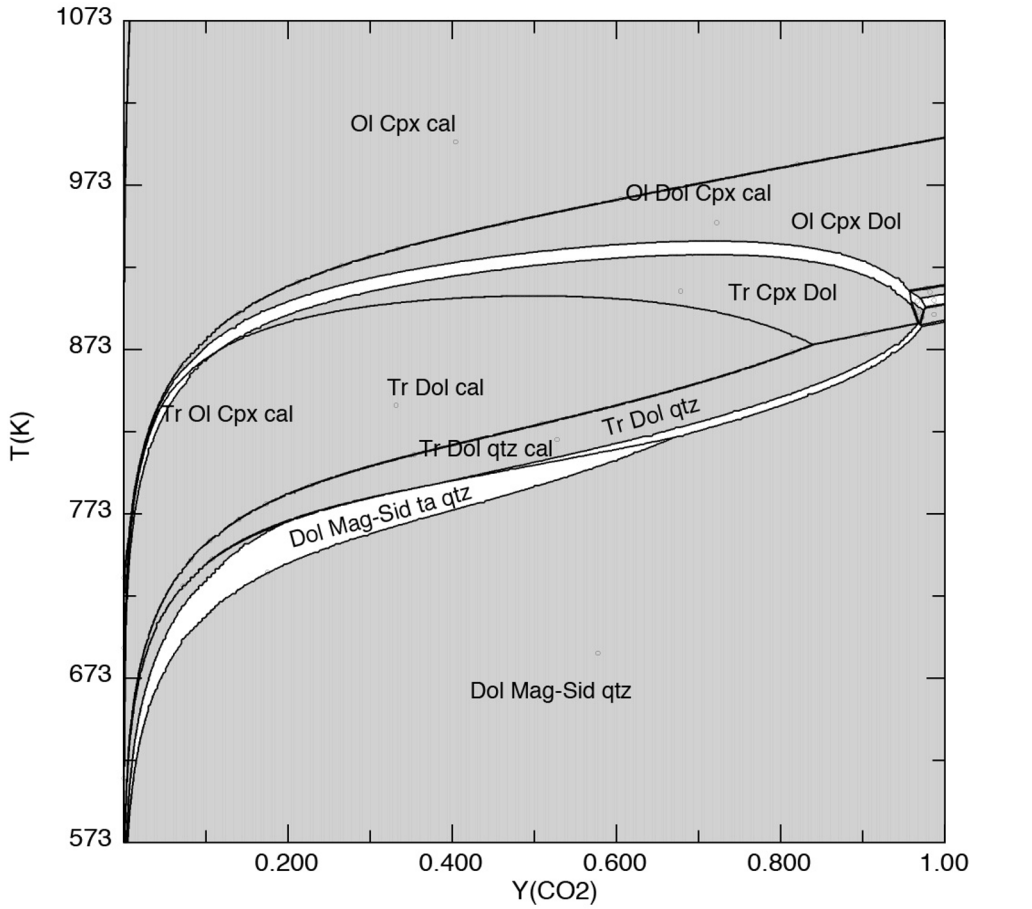

Different pathways through the diagram can simulate different processes.

DOUG WILL DISCUSS THIS IN A FEW MINUTES

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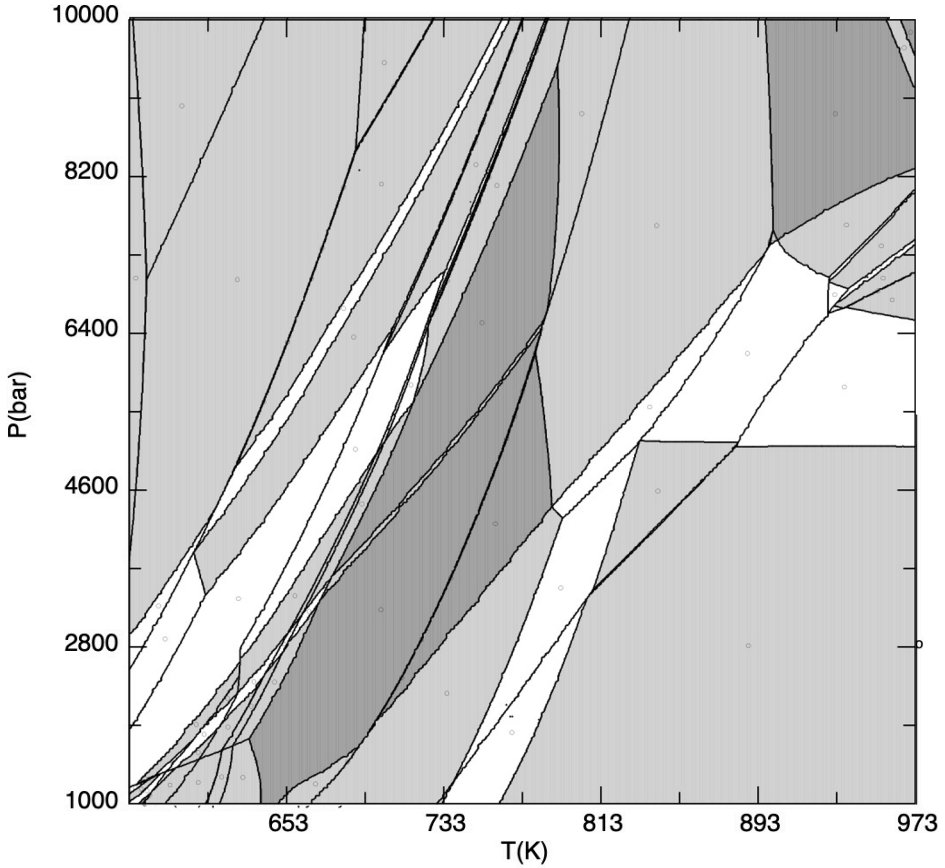

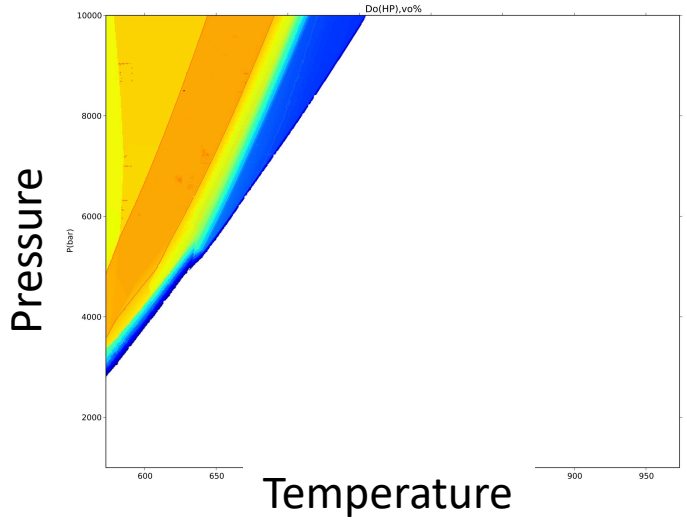

Dolomite stability abundance in the presence of a fluid with 1 mol % CO_2

52% SiO_2, 14.5% Al_2O_3, 8.5% CaO 4.3% MgO, 15.1 FeO
Fluid with X_{CO2} = 0.01 in excess.

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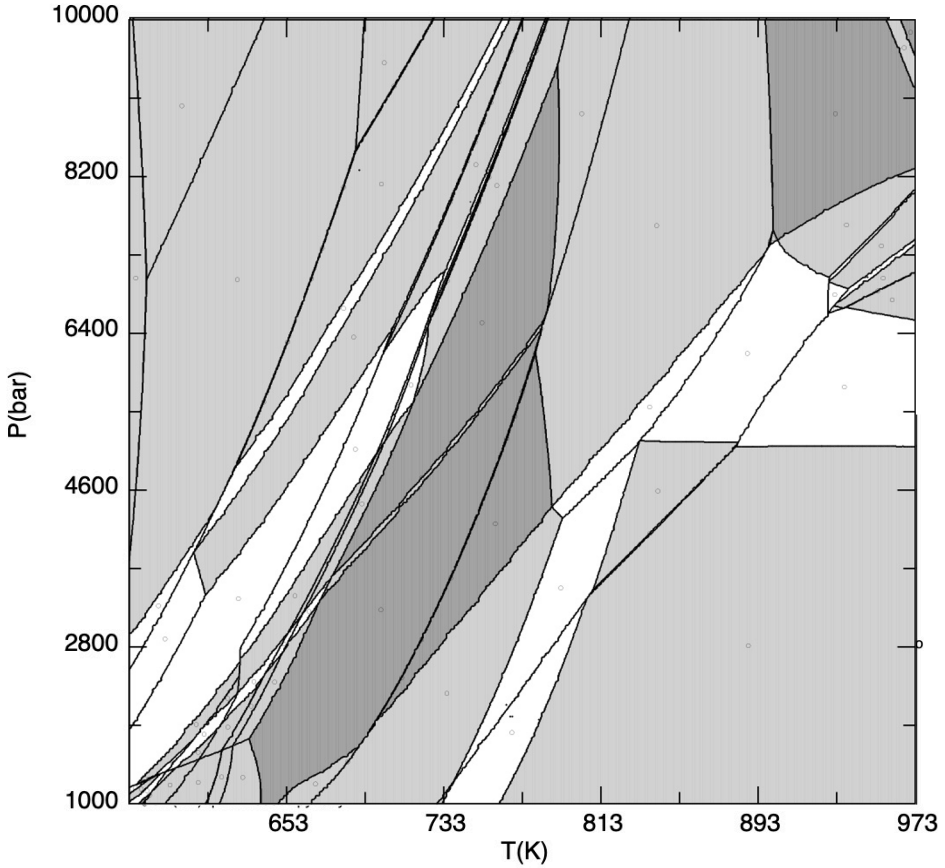

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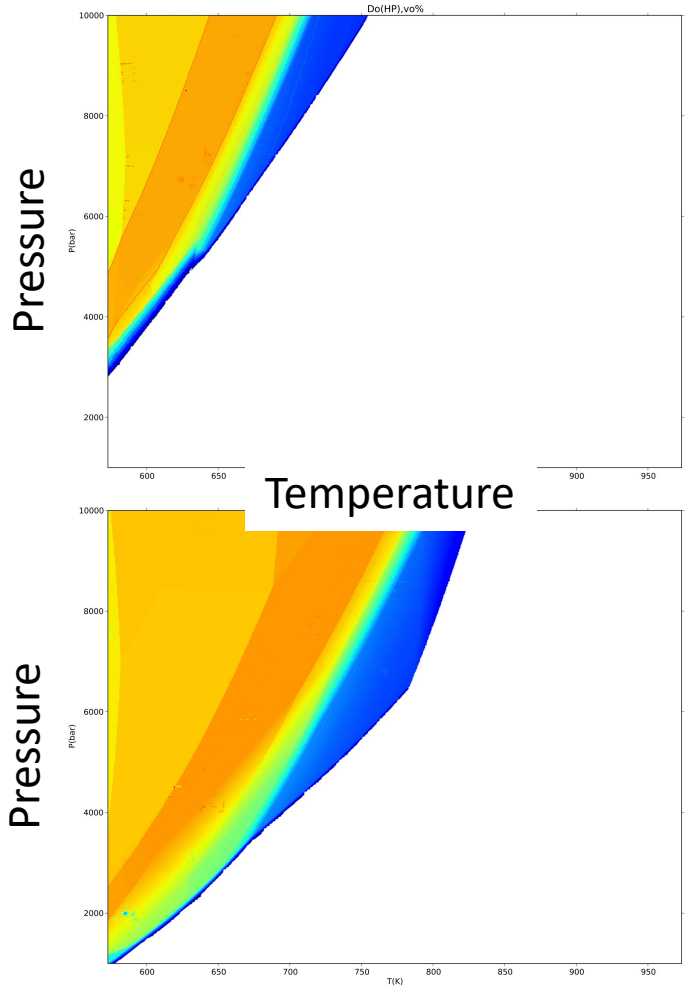


Dolomite stability abundance in the presence of a fluid with 1 mol % CO_2

Dolomite stability abundance in the presence of a fluid with 5 mol % CO_2

2. Fix the amount of each component in the rock including the amount of volatile components. Allow the calculation to decide whether a fluid will be stable and what its composition would be.
   - Less elegant than method 1.
   - To generate a traditional T-$X_{CO2,fluid}$ diagram, where the program/user controls the fluid composition with the system composition, we need to specify an unreasonable amount of fluid in the system (crystals floating in a deep ocean!)
3. Buffer fluid composition against specific mineral phases.
   - Let the volatile-producing or consuming reactions control the fluid composition
   - relevant to closed systems (but, are closed systems really relevant ☺)

Let's look at a textbook case in a simple system (CMS+H_2O+CO_2)

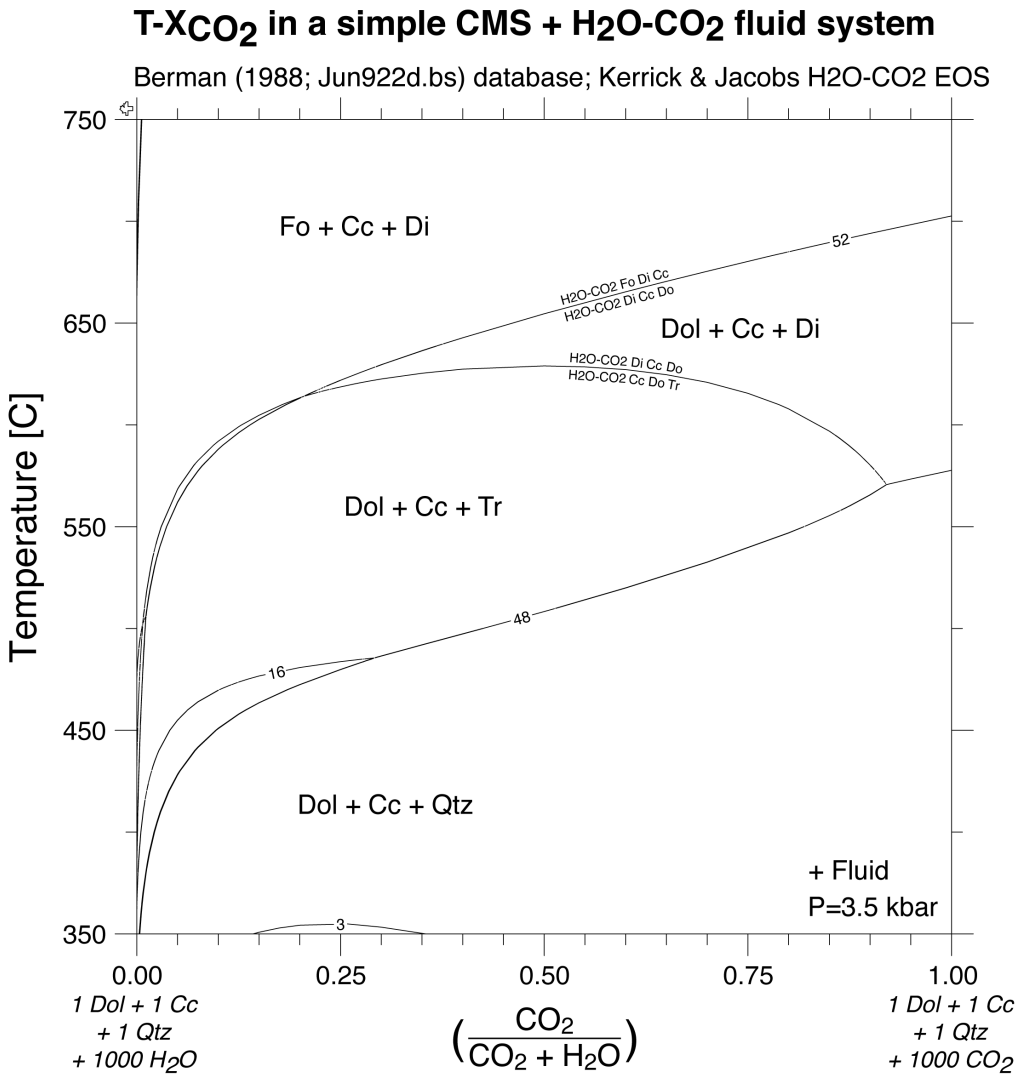
2. Fix the amount of each component in the rock including the amount of volatile components.

Composition:

- 1 Dol + 1 Qtz + 1 Cc
- Add such a large amount of system H2O and CO2 across the binary that the fluid H2O:CO2 approaches the H2O:CO2 of the system
- This is really just a trick so the X axis reflects the $CO_2/(CO_2+H_2O)$ of the fluid

Visualizing internal and external buffering of fluid composition:

- Devolatilization reactions control the resulting fluid composition in a closed system



example modified after de Capitani (2010), U. Calgary short course on Theriak-Domino

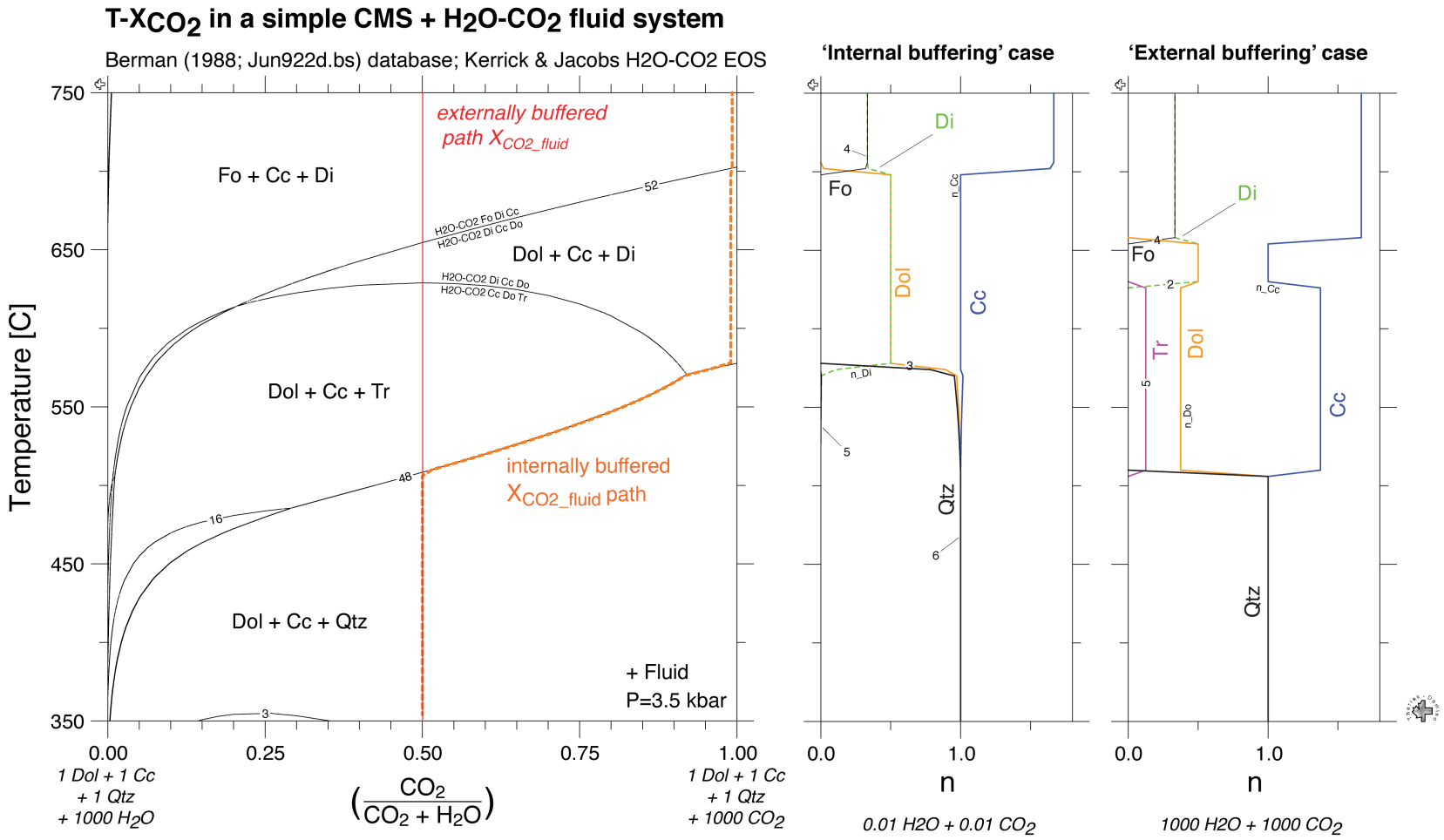
Internal vs external buffering in a simple system

Visualizing external buffering of fluid composition:

- Specify large amounts of H_2O and CO_2 to fix the composition. Not easily applied to more complicated systems and fluids (COHS)
- Example at the right is fixed at 50% H_2O and 50% CO_2

Internal buffering of fluid composition:

- Add only a very small amount of fluid and let the devolatilization reactions control fluid composition
- This does not work as intended/hoped in some cases; adding just a small amount of fluid to initial composition results in different assemblage or immediate reaction of fluid with phases to produce a drastically different fluid composition before intersecting the devolatilization reaction of interest to investigator (tough to control initial fluid composition at low-T)

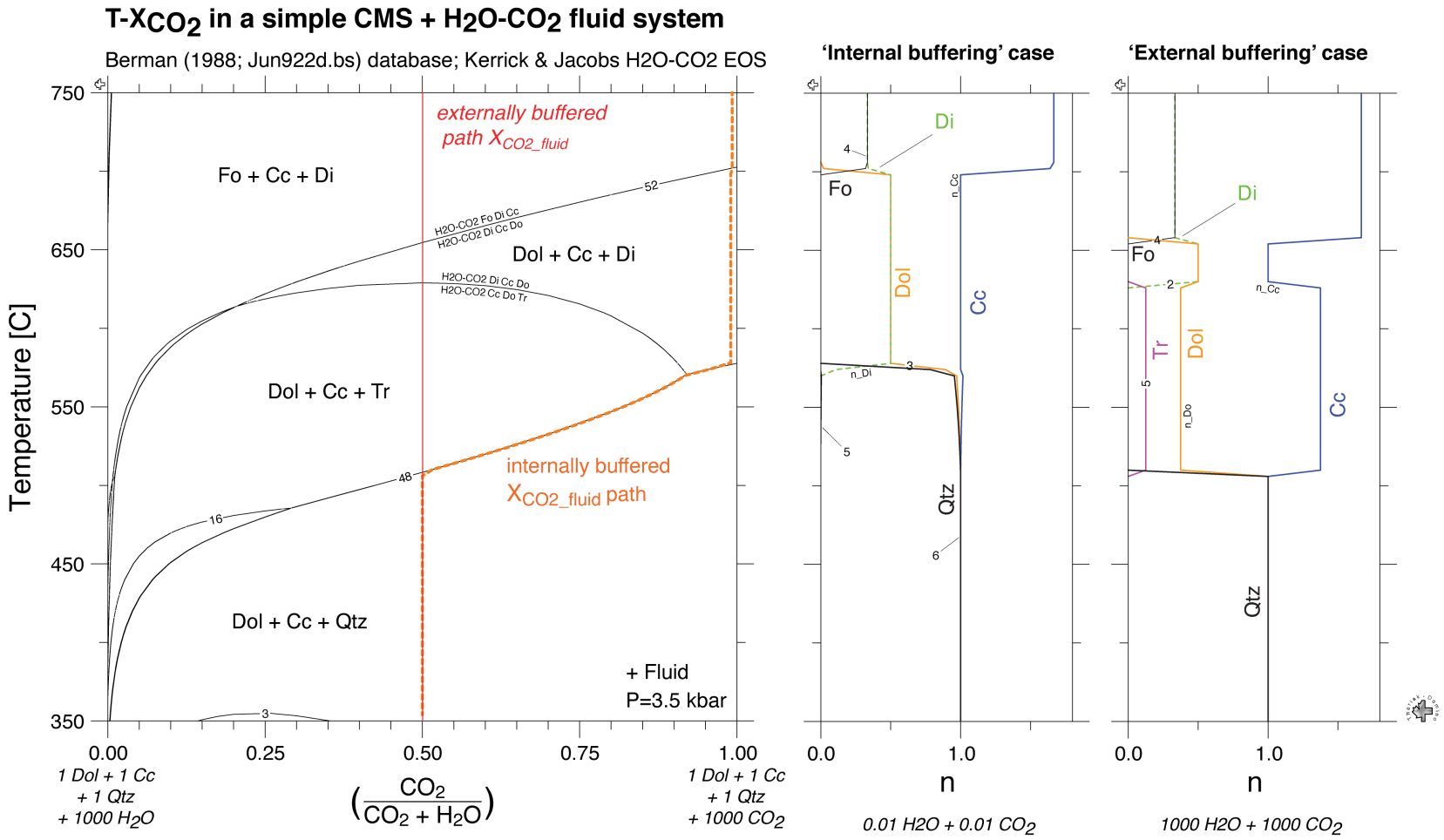


example modified after de Capitani (2010), U. Calgary short course on Theriak-Domino

Internal vs external buffering in a simple system

Internally vs. Externally buffered, classic example:

- Same starting composition at 350 °C
- Note the difference in $X_{CO2,fluid}$ above 575 °C
- Note the ending proportions of Fo, Di & Cc are identical
- You can determine the reactions occurring (and visualize them to the right) in each case



example modified after de Capitani (2010), U. Calgary short course on Theriak-Domino

4. Dealing with more complicated fluids

- Evans, Powell & Holland (2010) added sulfides and Sulfur fluid species to the Holland & Powell (1998; ds5.5S) dataset, and subsequently to the Holland & Powell (2011; ds6)
- Modelling with COH & COHS fluids in the presence of sulfides is now feasible in large chemical systems used in mainstream metamorphic studies
- Interplay between Fe-S-O can be investigated in modelling studies

Journal of
METAMORPHIC GEOLOGY

J. metamorphic Geol., 2010, **28**, 667–687 doi:10.1111/j.1525-1314.2010.00890.x

Internally consistent data for sulphur-bearing phases and application to the construction of pseudosections for mafic greenschist facies rocks in Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–CO_2–O–S–H_2O

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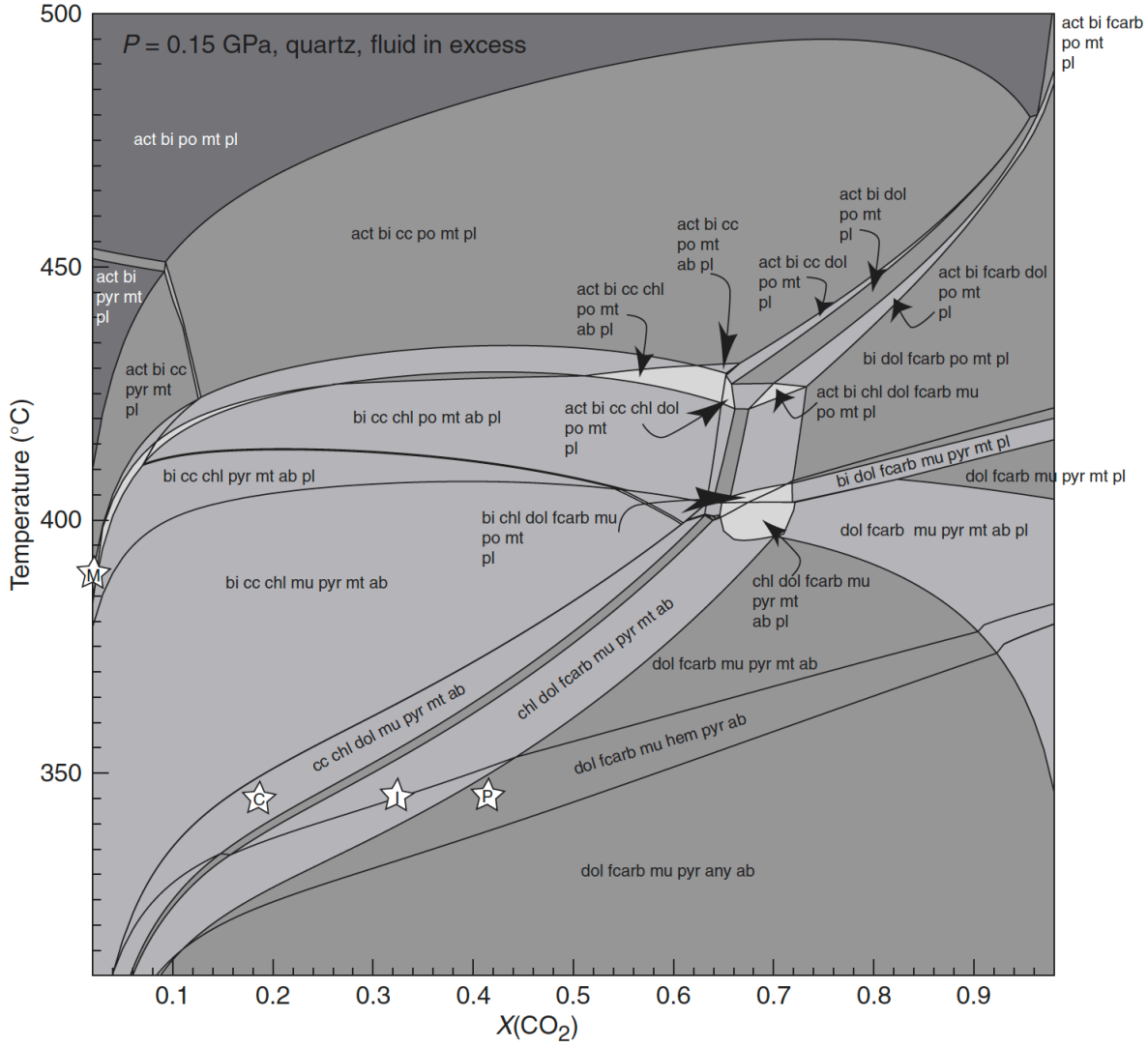
NCKFMASH-COS T-XCO2 equilibrium assemblage diagram (Fig. 9 of Evans, Powell & Holland, 2010)



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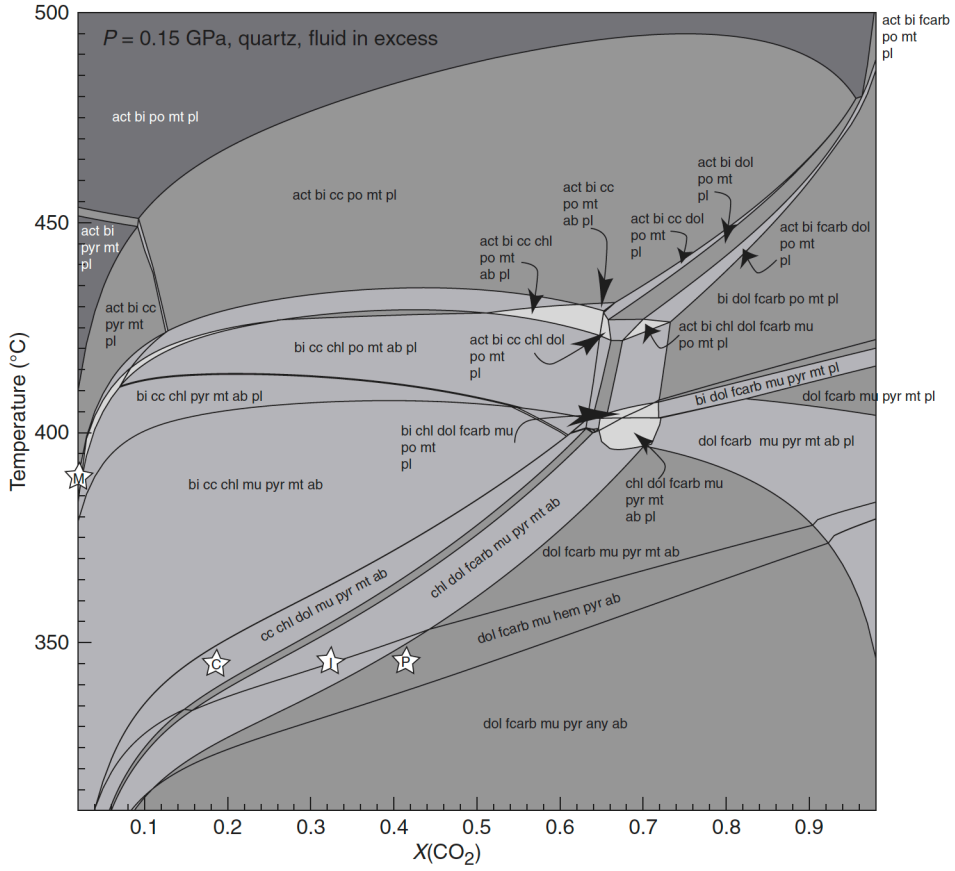
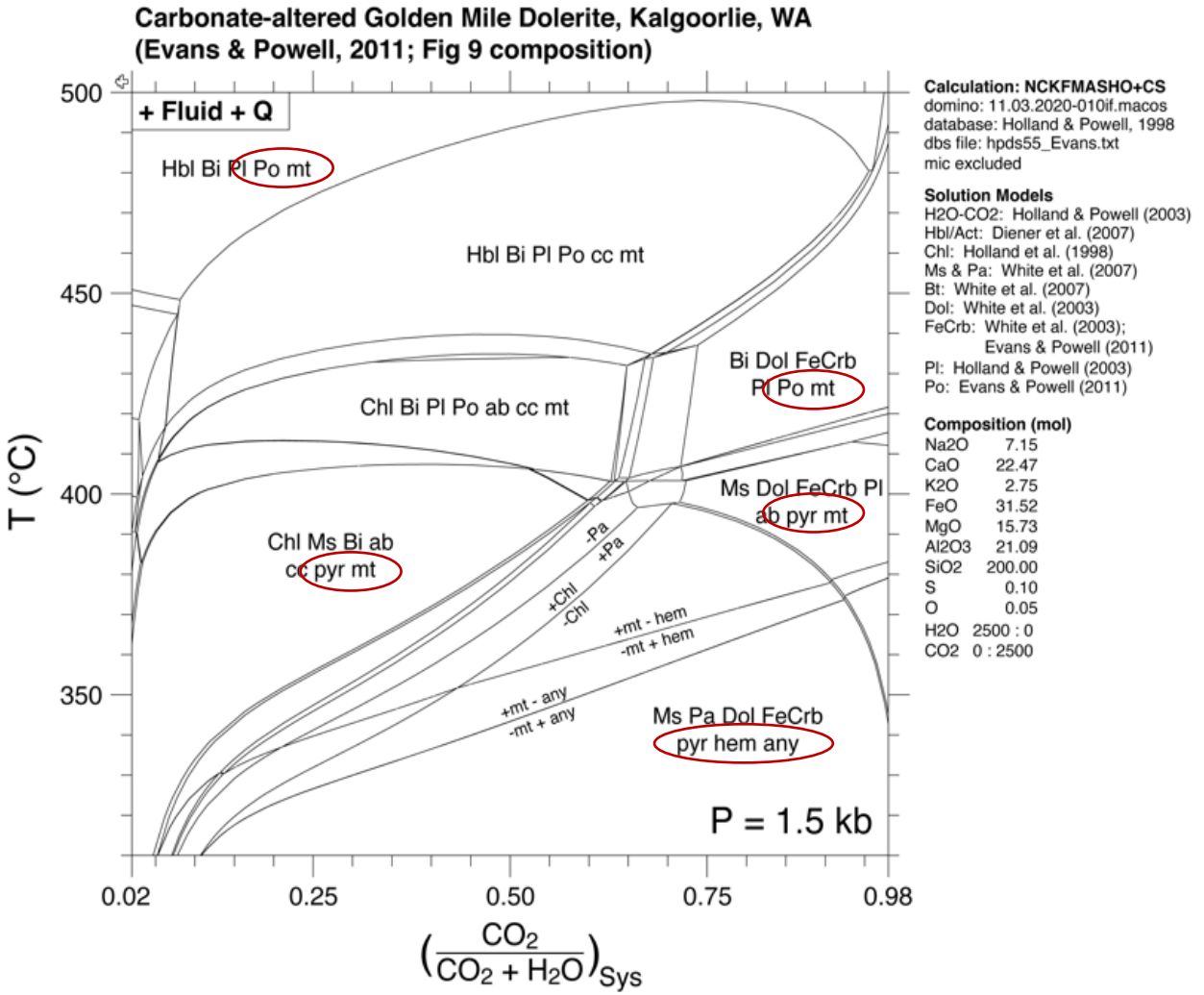
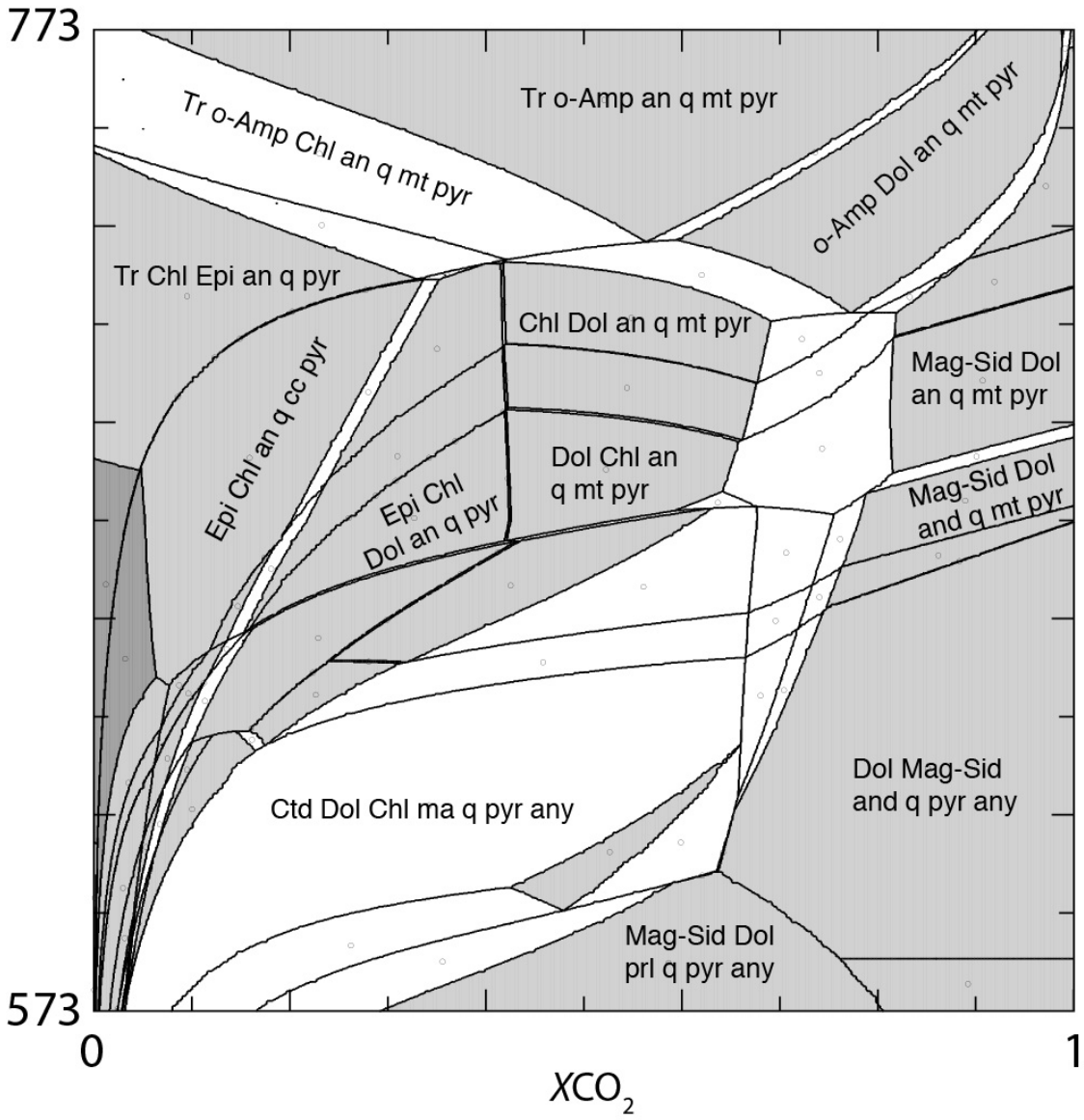
THERMOCALC NCKFMASH-COS T-XCO2 diagram (Fig. 9 of Evans, Powell & Holland, 2010)



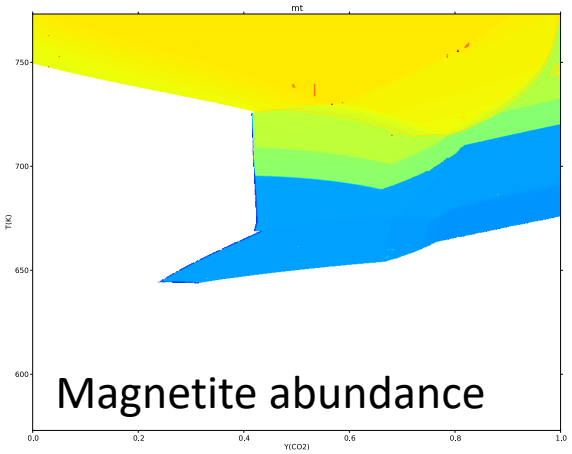
Theriak-Domino constructed equivalent

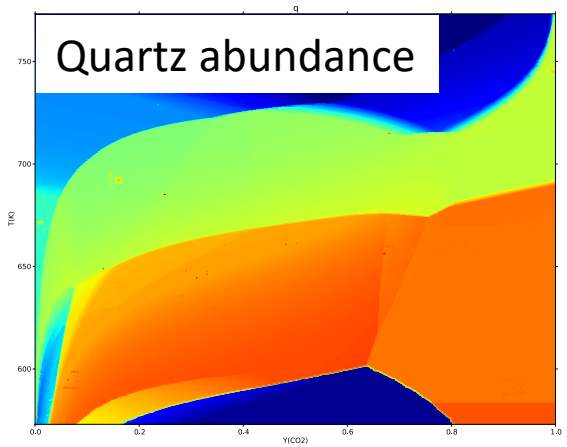


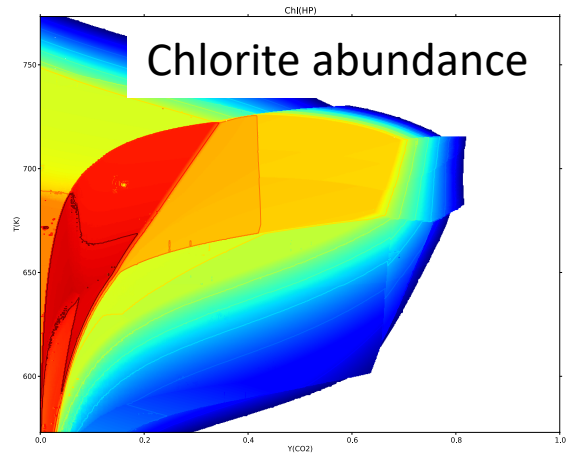
The Evans et al. (2010) COHS fluid model is working in Theriak-Domino

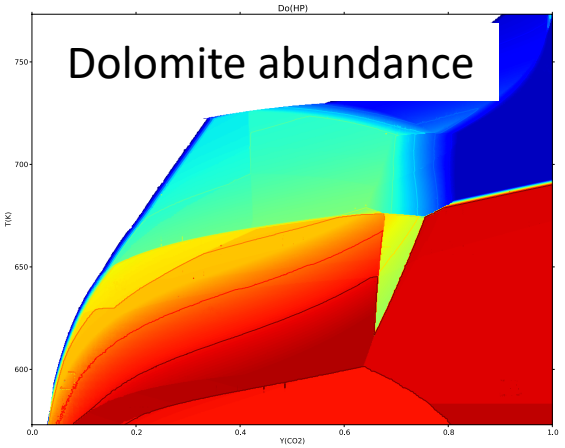


Similar diagrams can now be calculated with each of the three programs we discussed this week

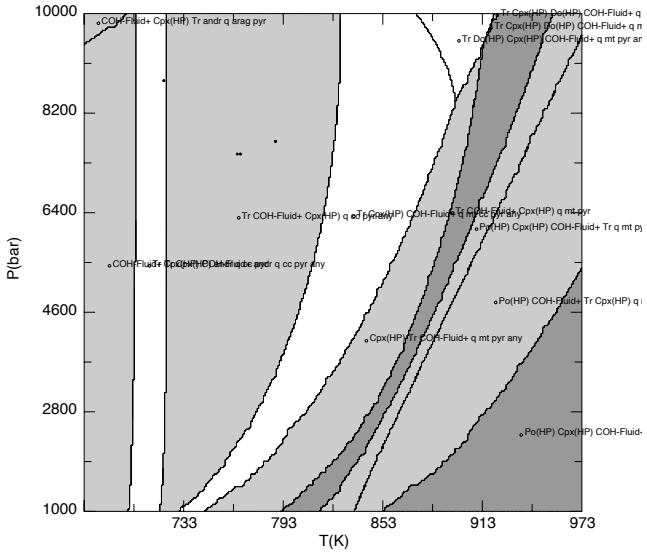


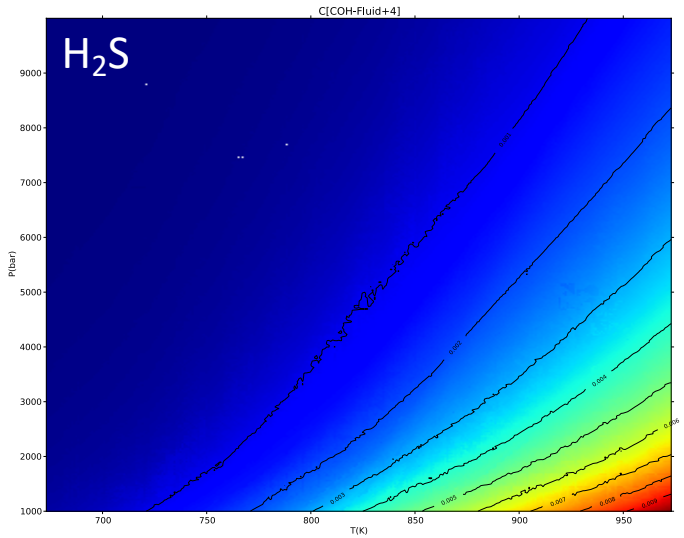


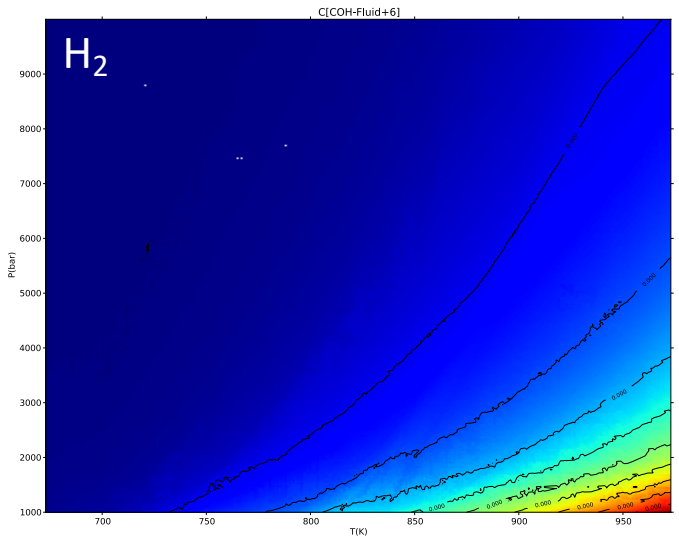


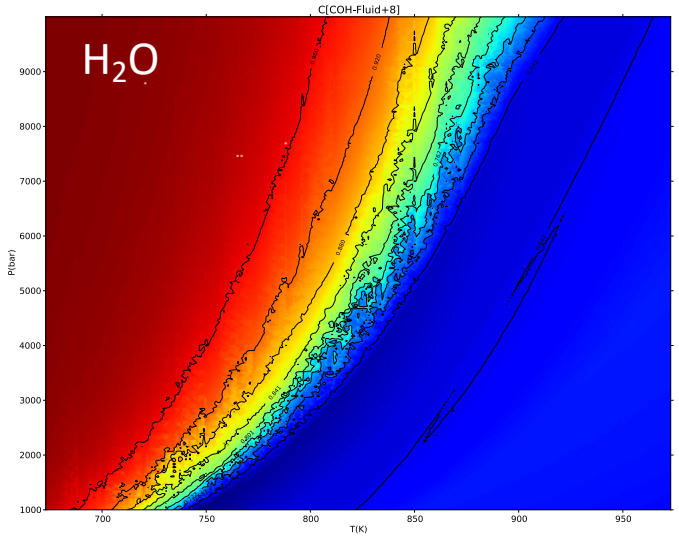


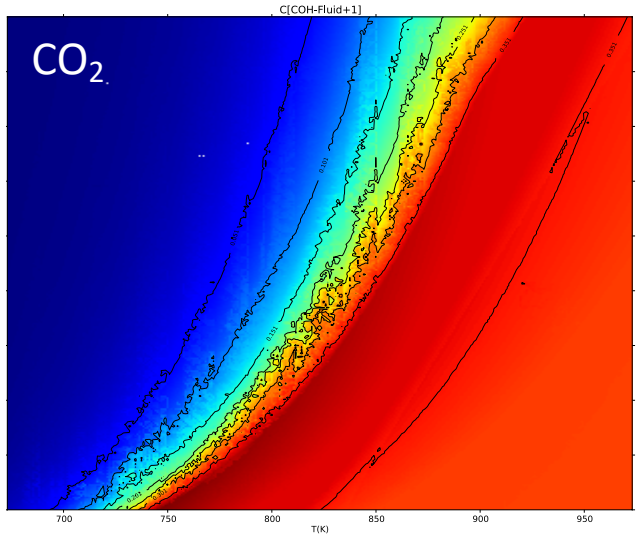
We might want to expand beyond simple H_2O:CO_2

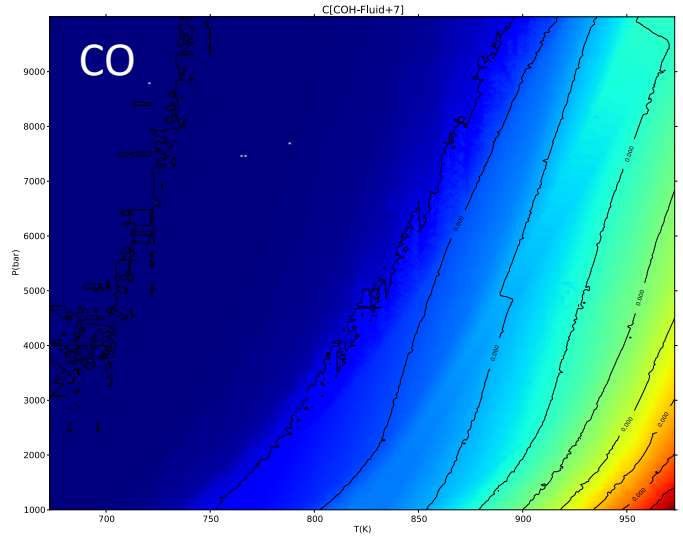




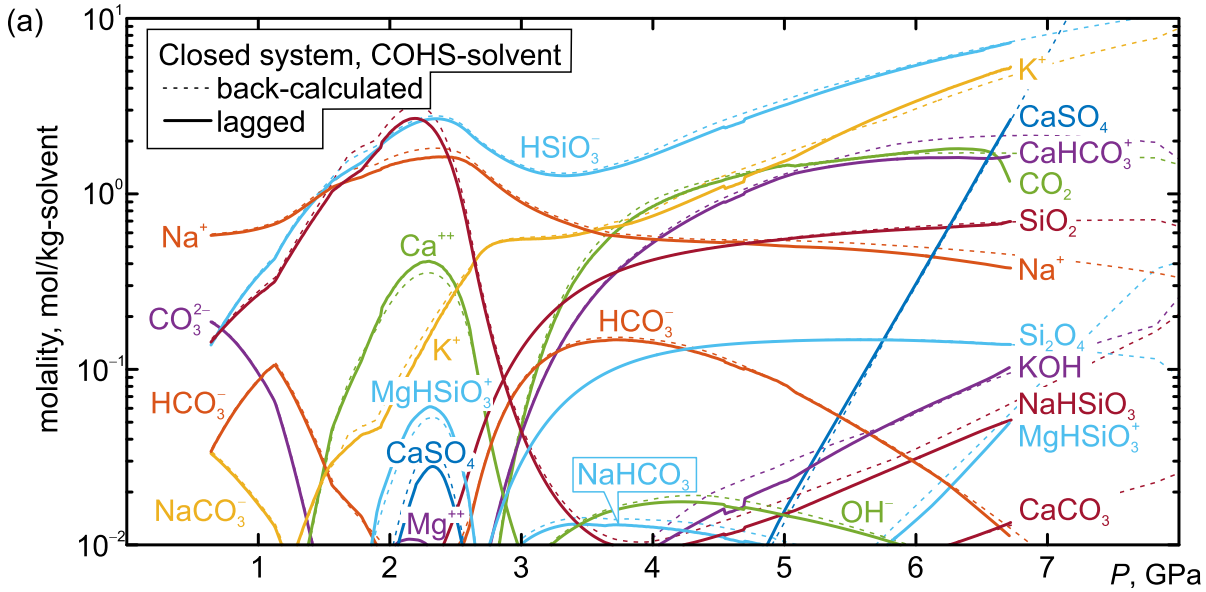








True reactive transport modeling is getting closer…



Connolly & Galvez (2018)

This problem has been made tractable by implementation of the Deep Earth Water (DEW) model for electrolytic fluids (Sverjensky et al., 2014), which extends the Helgeson–Kirkham–Flowers (HKF) formulation (Shock et al., 1992) for aqueous species to high pressure conditions.

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