Fluid-mediated carbon release by infiltration of serpentinite dehydration fluids during subduction:

Insights from thermodynamic models of serpentinite-hosted carbonate rocks

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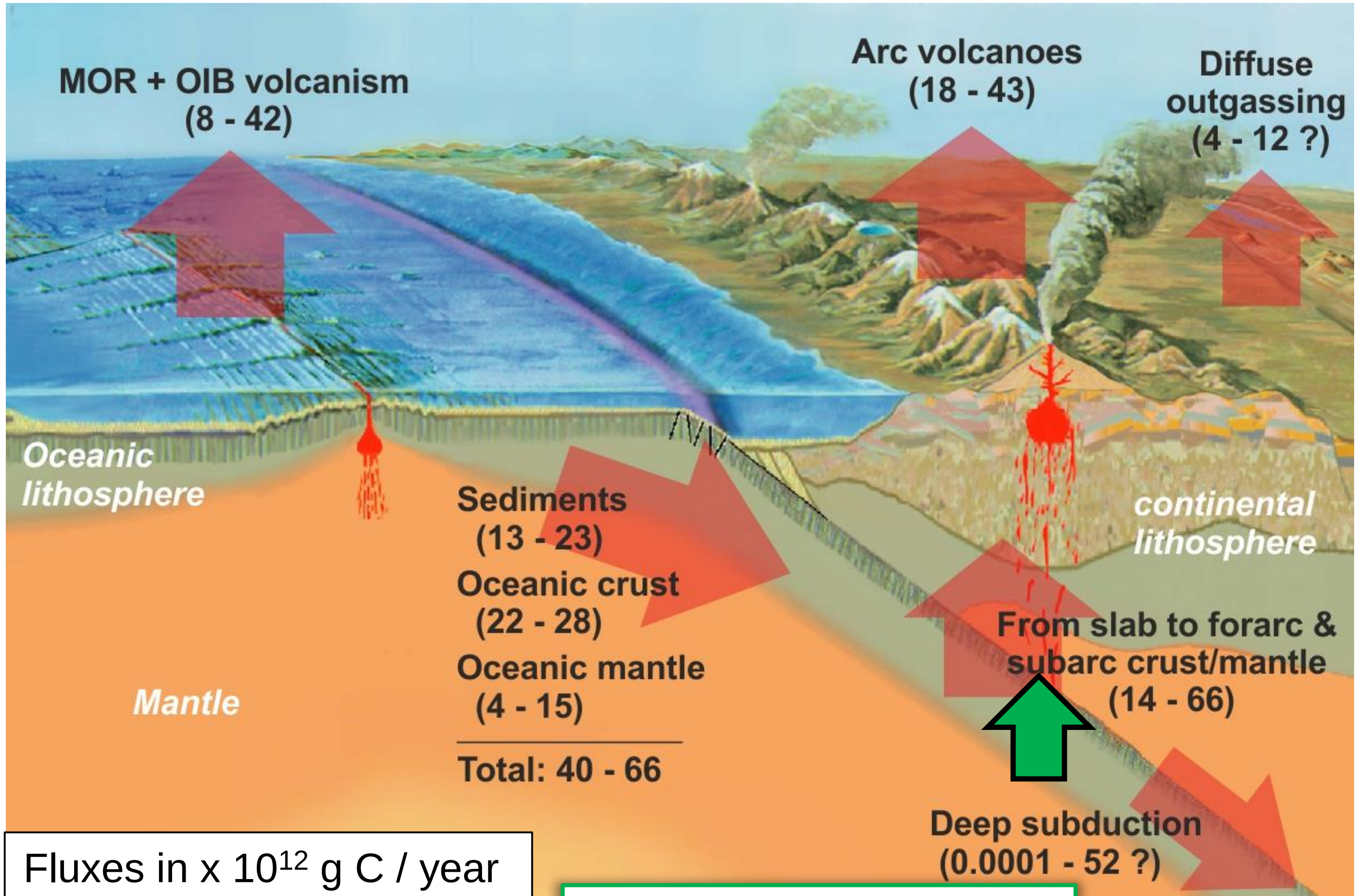
Carbon fluxes in subduction zones



Carbon fluxes after
Kelemen & Manning (2015)

Serpentinite dehydration
(6 – 11 wt% H_2O)

Atg = Ol + Opx + fluid
(Chl-harzburgite)

- *C recycling beyond subarc is controlled by prograde and infiltration-driven devolatilization.*
- *What is the C solubility in serpentinite dehydration fluids?*

Aims

- *What are the effects of electrolytic fluids and open system fluid flux on the stability of serpentinite-hosted carbonate rocks during antigorite dehydration in subduction zones, and their implications for deep carbon fluxes?*
- *Understanding open system fluid–rock interactions in subduction zones in a chemically simple system, by modelling of fluid compositions and speciation, and the time-integrated fluid flux required for complete carbonate dissolution*
- *Improved mass-balance estimates of carbon fluxes from these lithologies during serpentinite dehydration in different thermal regimes of subduction zones*

→ *(Menzel et al., 2020)*

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Fluid-mediated carbon release from serpentinite-hosted carbonates during dehydration of antigorite-serpentinite in subduction zones

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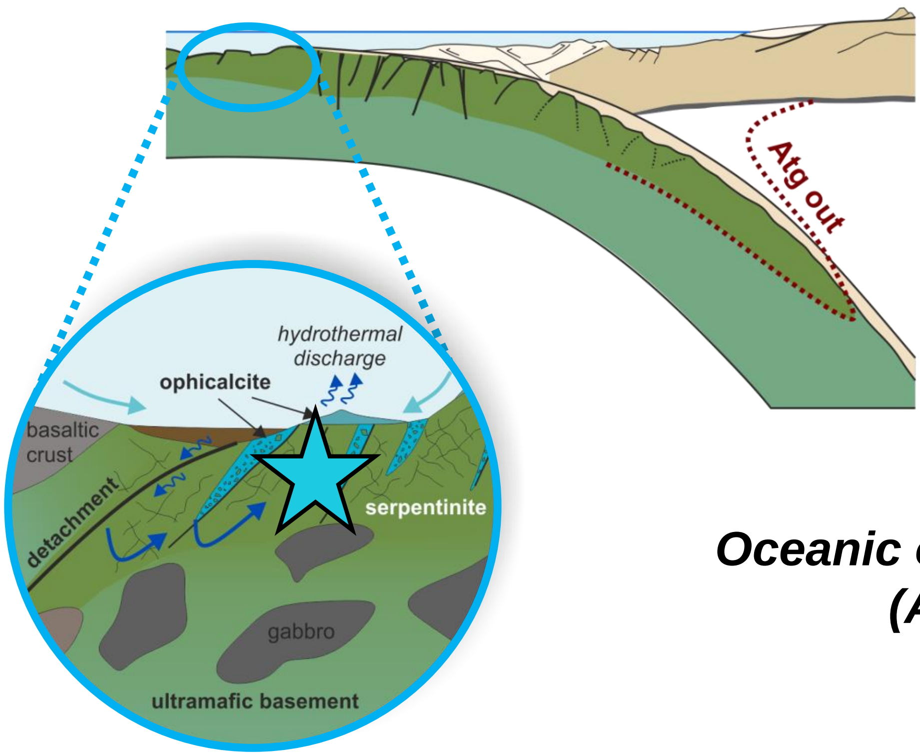
Subduction of serpentinite-hosted carbonates



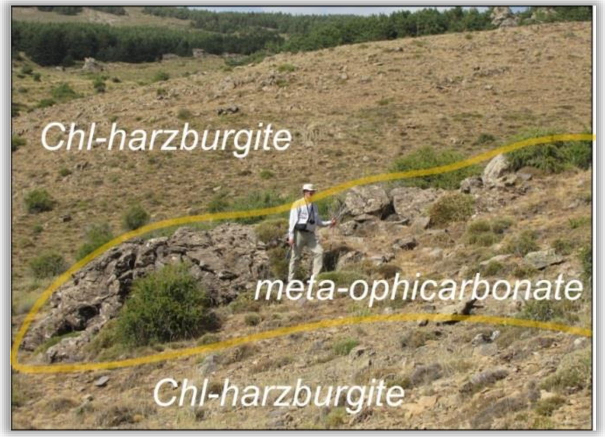
after Lafay et al. (2017)

Meta-ophicalcite

(Serpentine + $CaCO_3$)

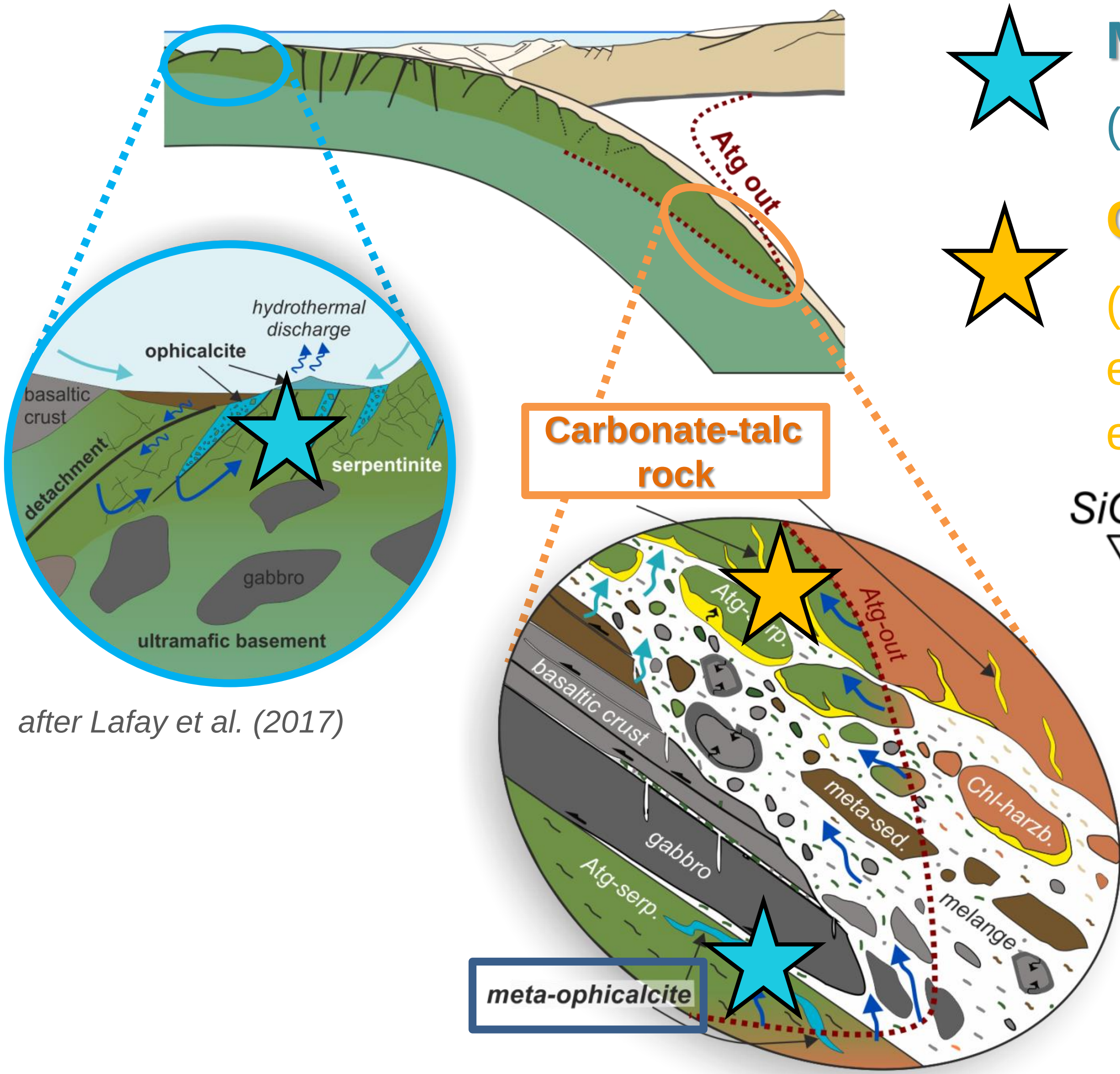
Oceanic ophicalcite (Apennines)

Subducted meta-ophicalcite (Betic Cordillera, Spain) (Menzel et al., 2019, JMG)



- *Serpentinites can store high amounts of C during the formation of ophicalcite at the seafloor*

Subduction of serpentinite-hosted carbonates



after Lafay et al. (2017)

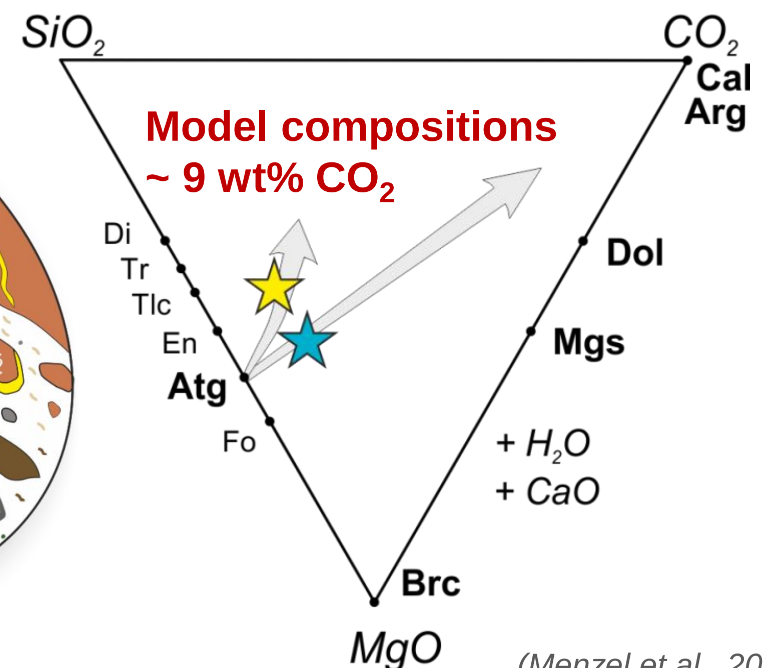
(Menzel et al., 2020; mod. after Bebout & Penniston-Dorland, 2016)

Meta-ophicalcite

(Serpentine + $CaCO_3$)

Carbonate-talc rock

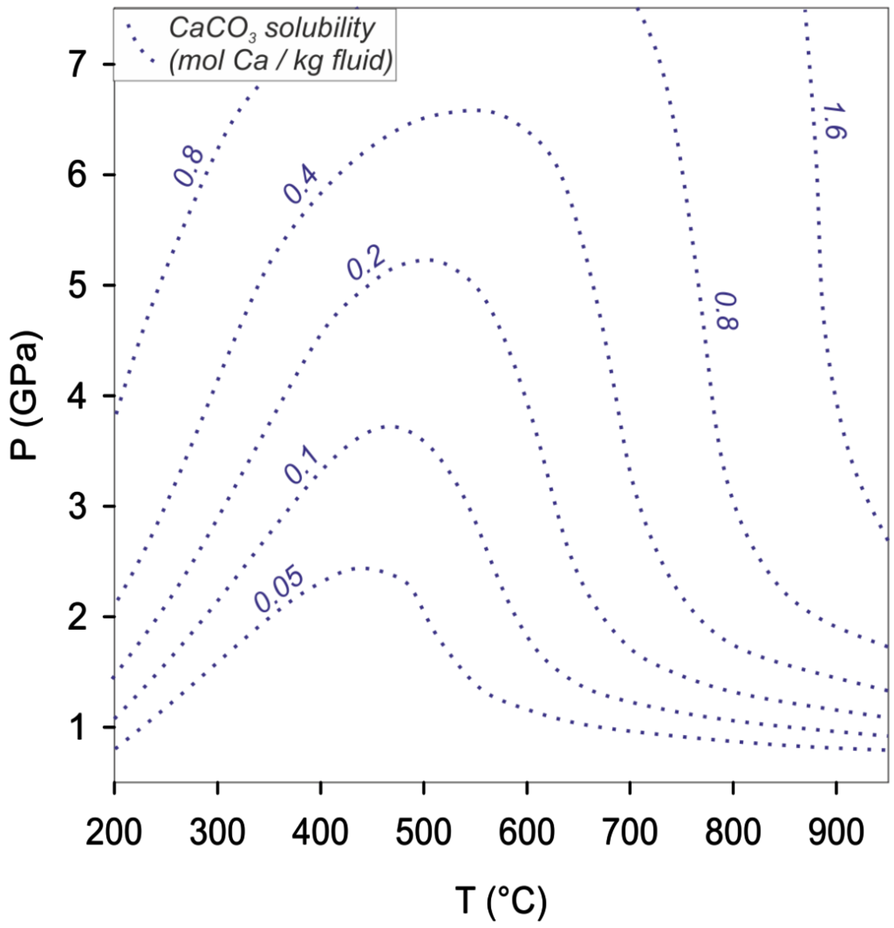
(Dol-Atg-Tlc schist; New Caledonia eglocite-facies melange; Spandler et al. 2008)



(Menzel et al., 2020)

➢ *Serpentinites in forearc mantle wedge trap C from subduction fluids as carbonate-talc rocks.*

What controls fluid-mediated C release in subduction zones



Congruent CaCO$_3$ solubility in the Ca-COH system. (Menzel et al., 2020; cf. Kelemen & Manning, 2015)

Congruent dissolution:

aragonite + H_2O = Ca^{2+} + $CO_{2,aq}$ + $CaHCO_3^+$ + HCO_3^- + CO_3^{2-}

1. Prograde devolatilization:

carbonate + silicate = silicates + fluid

2. Infiltration-driven devolatilization:

carbonate + silicate + infiltrated fluid = silicates + outflow fluid

Devolatilization modelling approach

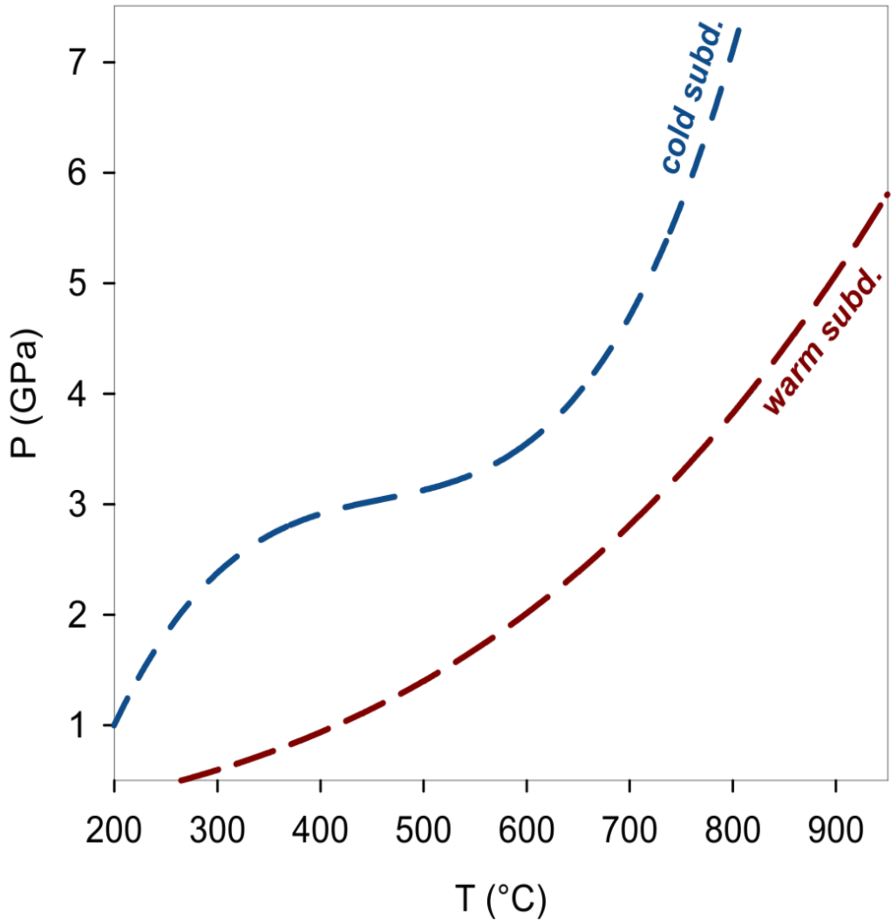
- **Deep Earth Water (DEW) model**
  (Sverjensky et al., 2014)
- **Perple_X**
  (Galvez et al., 2015; Connolly & Galvez, 2018)
- **Chemical system:**
  Ca-Fe-Mg-Al-Si-C-O-H

Model compositions

	Serpentinite	Ophicalcite	Carbonate-talc-rock
oxides (wt%)	AL98-4b	(synthetic)	Spandler-2814
SiO_2	39.33	31.46	45.5
Al_2O_3	3.29	2.63	0.9
Fe_2O_3 (total)	8.34	6.67	4.78
MgO	37.58	30.06	28.5
CaO	0.28	11.44	5.88
CO_2		8.89	9.67
H_2O	11.60	8.99	4.89
elements (mol/kg)			
Si	6.5185	5.2287	7.5637
Al	0.6426	0.5155	0.1763
Fe	1.0402	0.8344	0.5980
Mg	9.2851	7.4479	7.0628
Ca	0.0497	2.0368	1.0473
C		2.0176	2.1946
H_2	6.4121	4.9820	2.7112
O_2	15.5423	15.4023	15.6450
Fe^{3+}/Fe_{total}	*0.57*	*0.57*	*0.3*

(Menzel et al., 2020)

Devolatilization modelling approach



Subduction geotherms:

warm: Penniston-Dorland et al. (2015)

cold: Connolly & Galvez (2018)

1. Prograde devolatilization

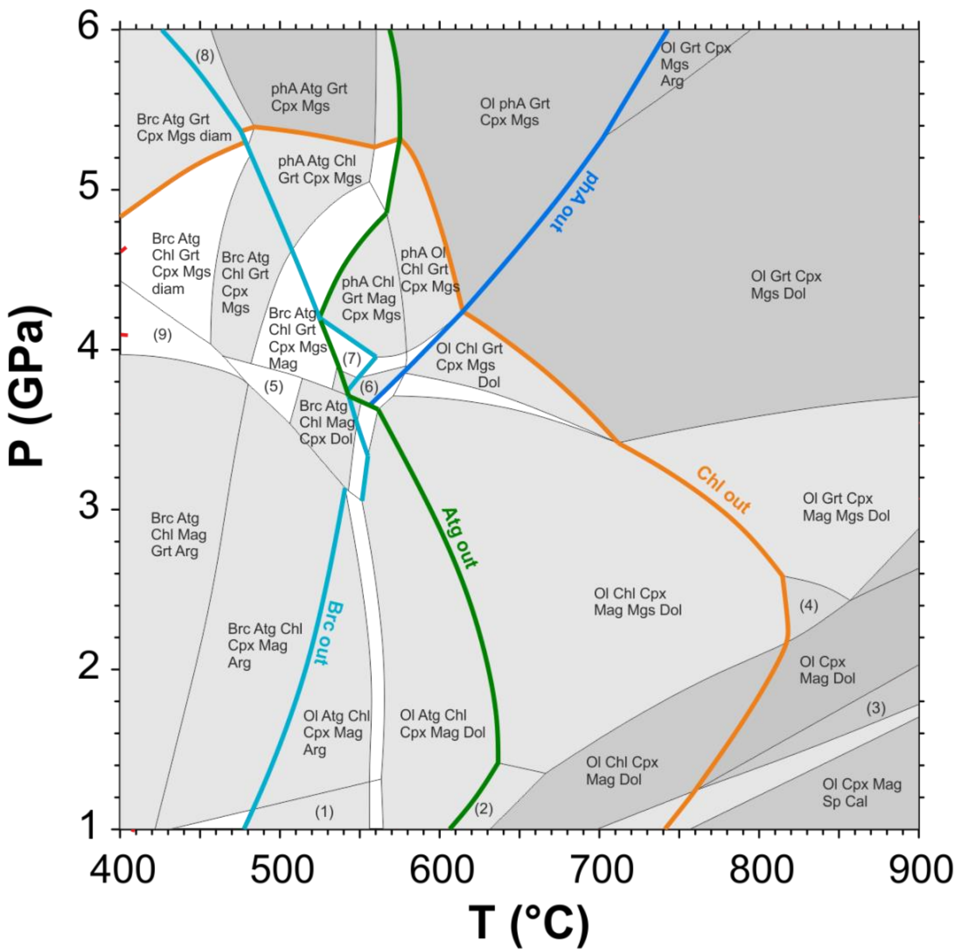
(variable P and T):

carbonate + silicate

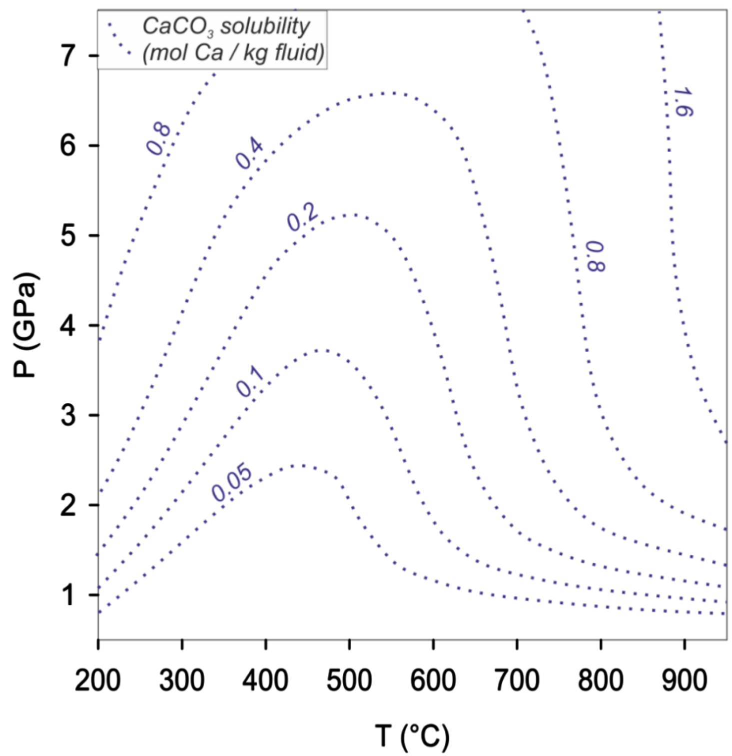
= silicates + fluid

Prograde Devolatilization

Meta-ophicalcite



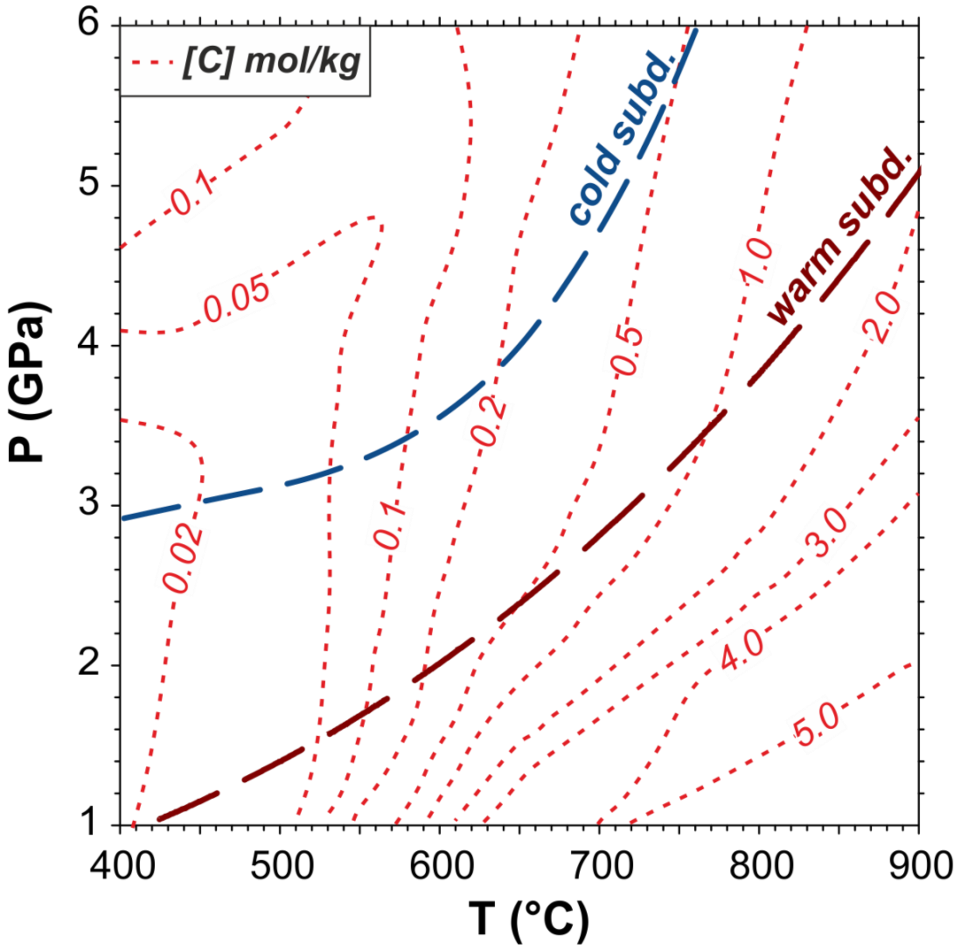
P-T pseudosection of meta-ophicalcite with main devolatilization reactions (Menzel et al., 2020)

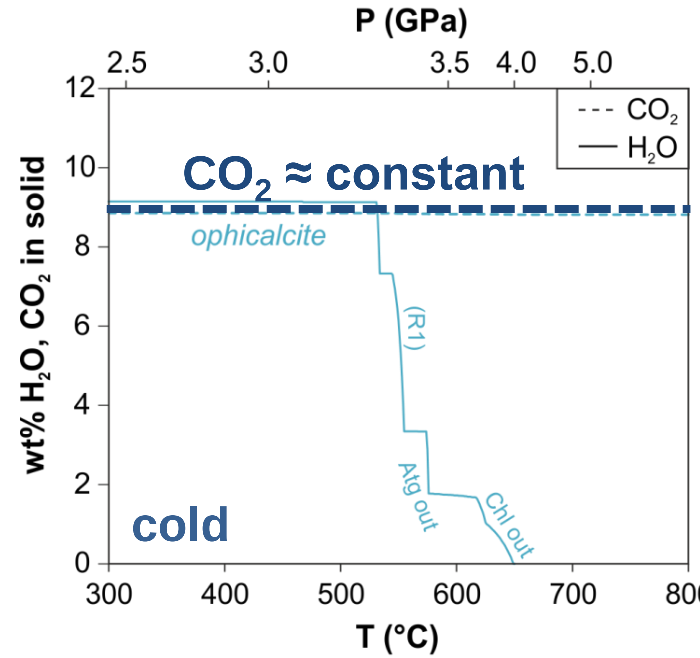


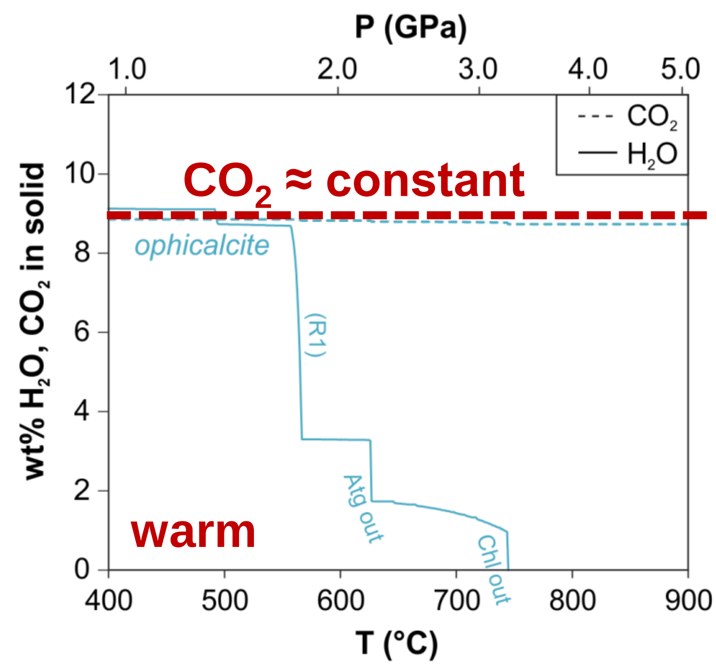
Congruent $CaCO_3$ solubility in the Ca-COH system. (Menzel et al., 2020; cf. Kelemen & Manning, 2015)

Prograde Devolatilization

Meta-ophicalcite

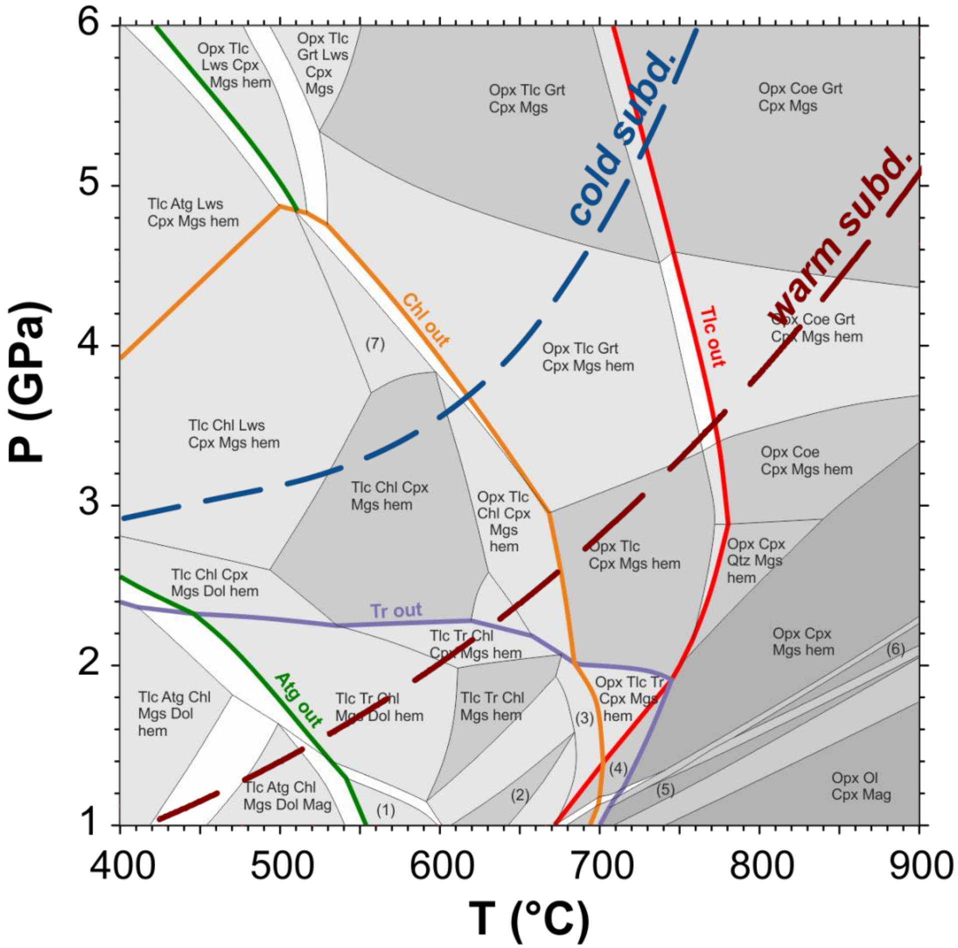






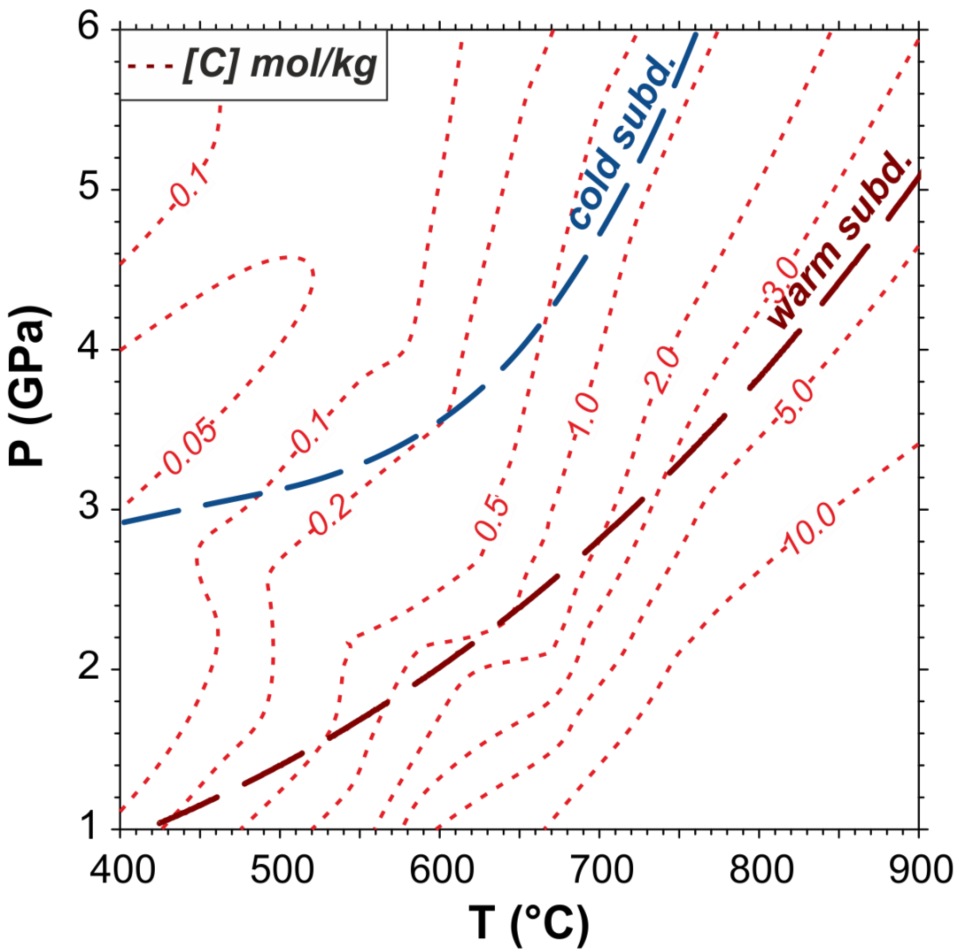
top: C solubility with P-T in fluids in equilibrium with meta-ophicalcite; right: C and H2O loss into fluid during prograde devolatilization (Menzel et al., 2020)

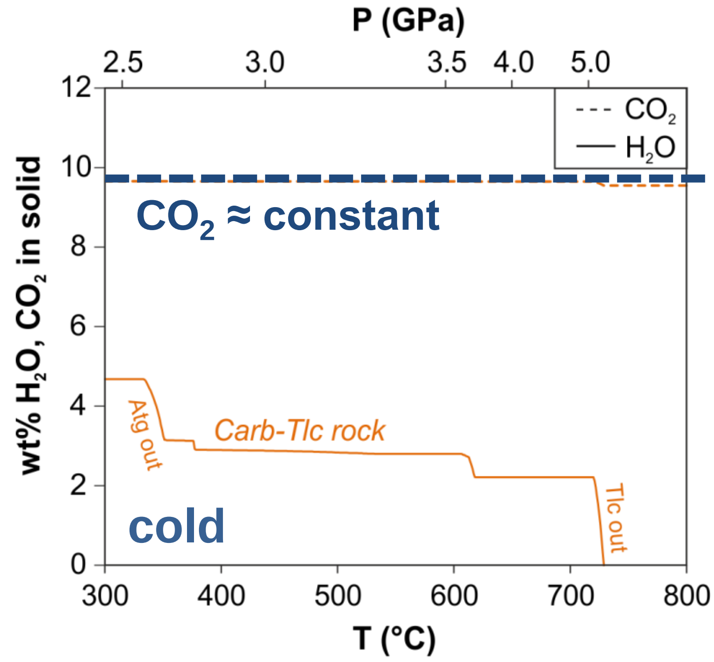
Prograde Devolatilization
Carbonate-talc rock

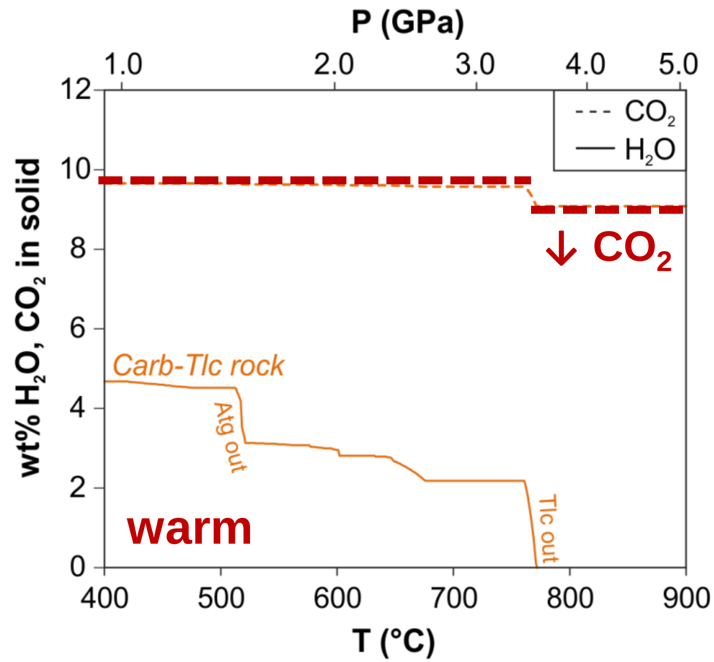


P-T pseudosection of carbonate-talc rock with main devolatilization reactions (Menzel et al., 2020)

Prograde Devolatilization
Carbonate-talc rock

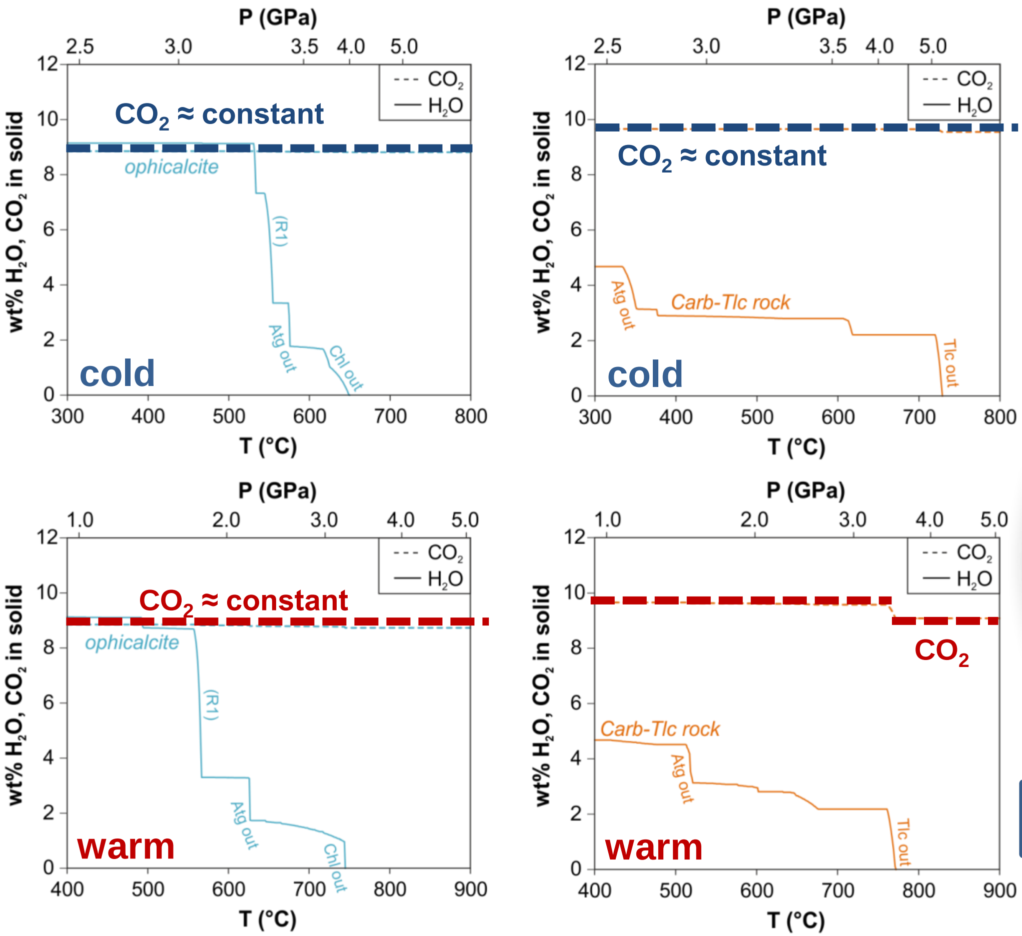


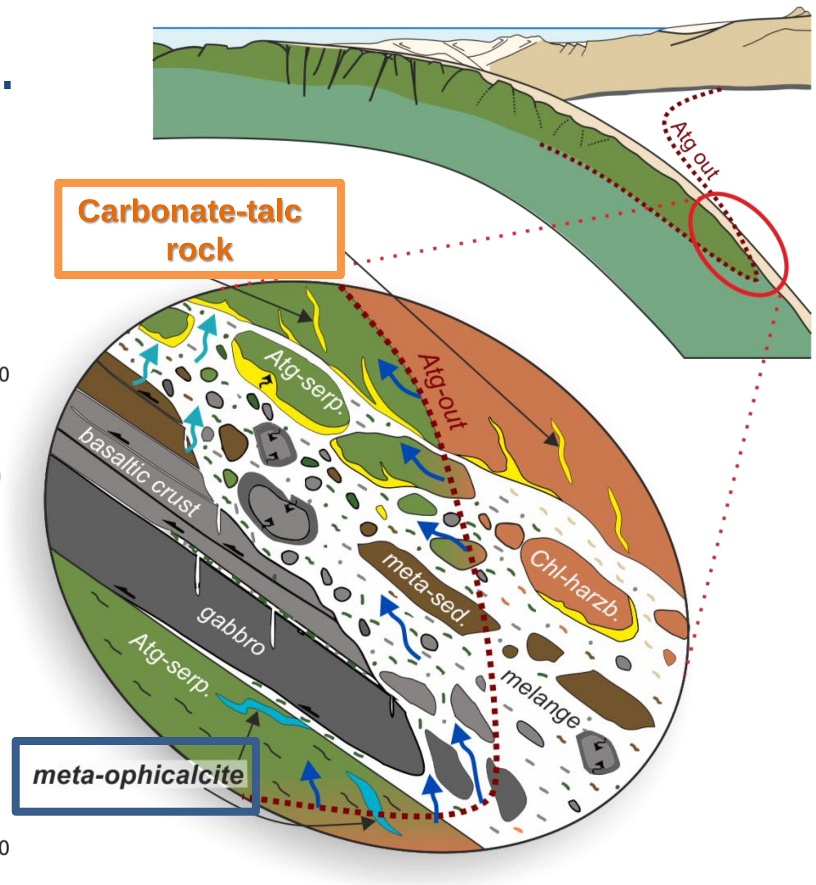




top: C solubility with P-T in fluids in equilibrium with carbonate-talc rock; right: C and H2O loss into fluid during prograde devolatilization (Menzel et al., 2020)

Prograde Devolatilization is not efficient for C release from Meta-ophicalcite & Carbonate-talc rock

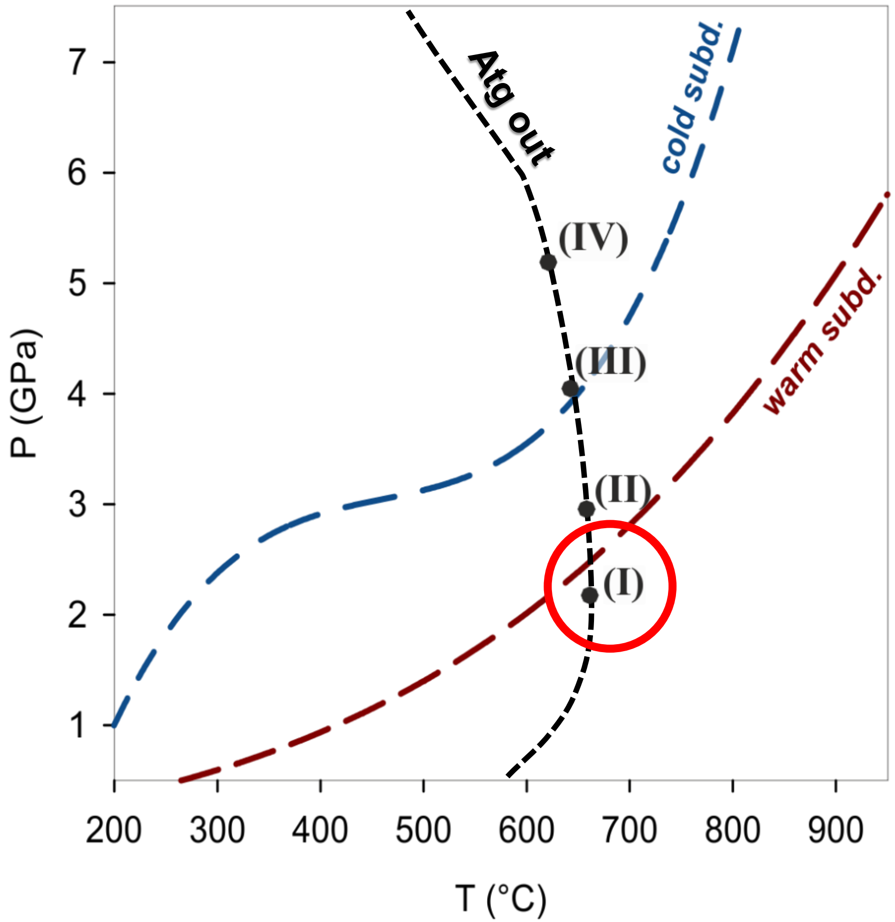




- Serpentinite-hosted carbonate rocks will be preserved to the conditions of Atg-serpentinite dehydration

(Menzel et al., 2020)

Infiltration-driven devolatilization



warm geotherm: Penniston-Dorland et al. (2015)

cold geotherm: Connolly & Galvez (2018)

2. Infiltration-driven devolatilization

(P-T conditions along Atg-serpentinite dehydration):

carbonate + silicate

+ infiltrated fluid

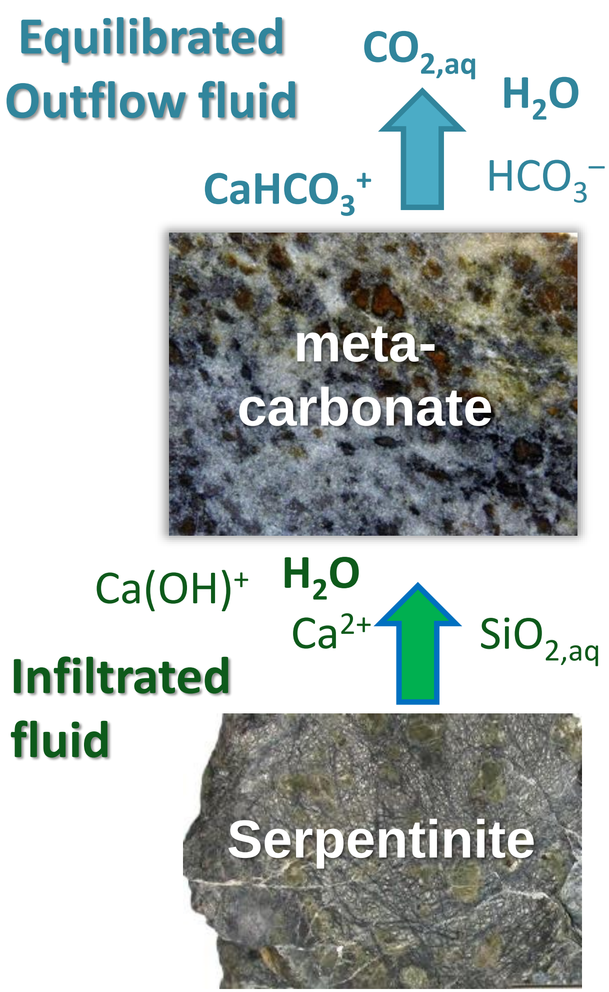
= silicates + outflow fluid

Most important source of H_2O-rich fluids in subduction zones: Serpentinite dehydration ("Atg-out")

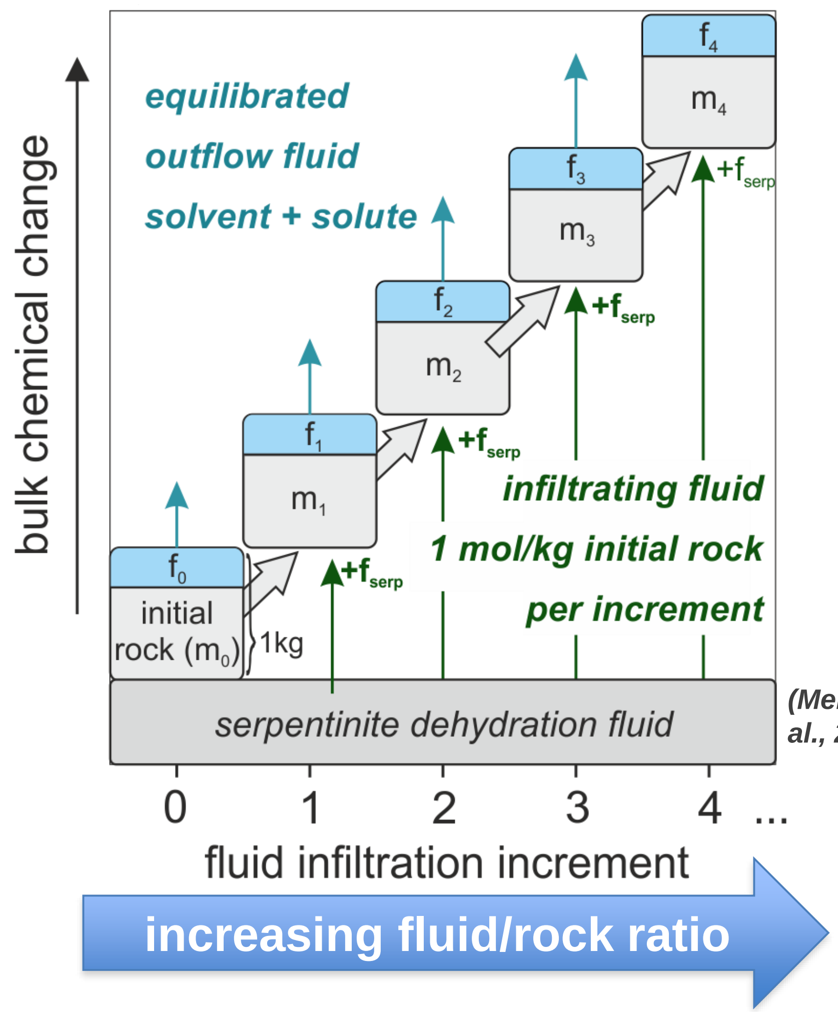
- *C release estimated for ophicalcite and carbonate-talc rock at P-T conditions of serpentinite dehydration*
- *P-T of hot subduction zones (**I**) yield maximum C removal by open system fluid flux.*

Modelling infiltration-driven devolatilization

carbonate + silicate + infiltrated fluid
= silicates + outflow fluid



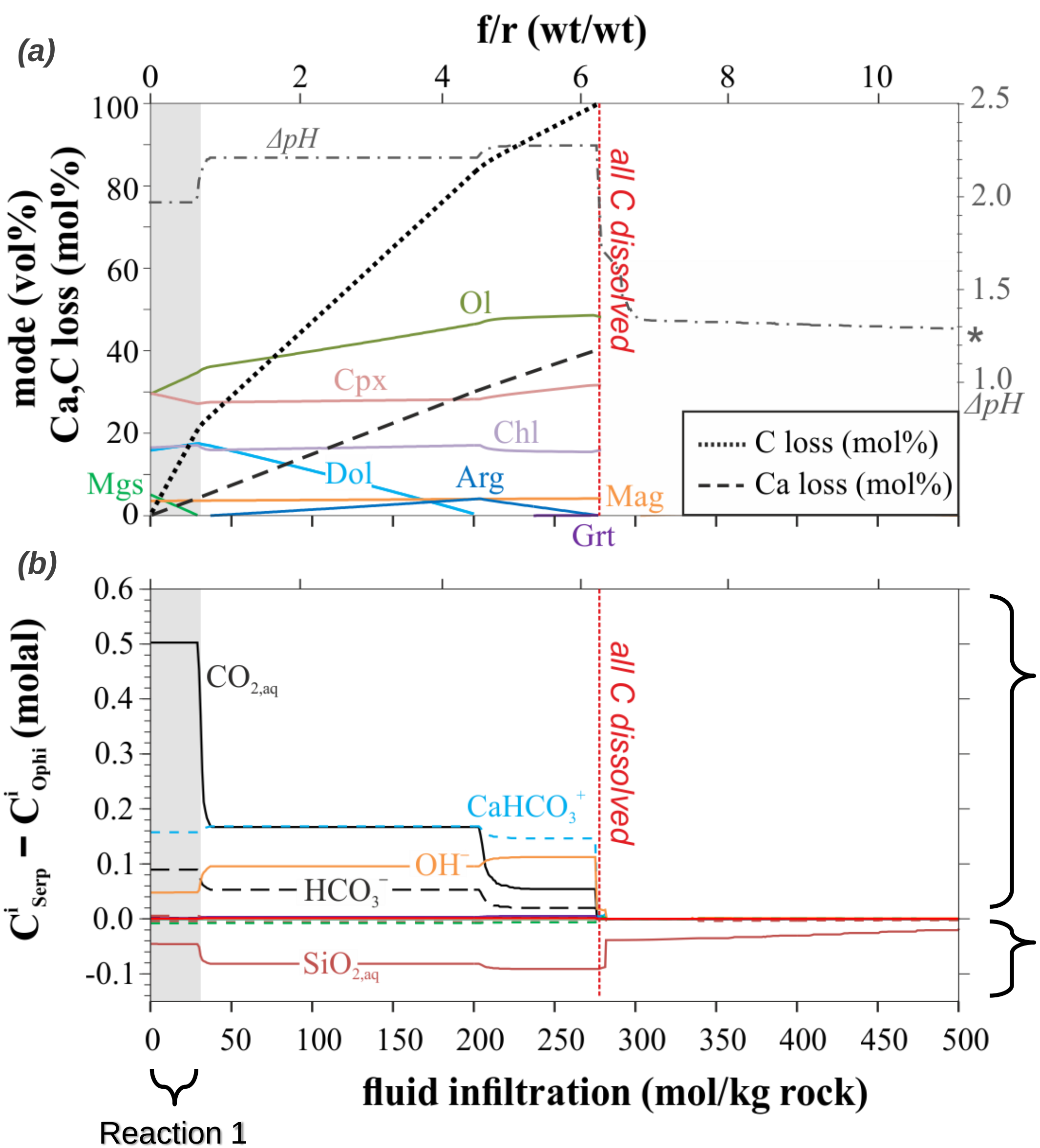
(I) P = 2.2 GPa, T = 663 °C



(Menzel et al., 2020)

Model setup: incremental fluid infiltration & fractionation (Perple_X). The composition of the infiltrated fluid at each increment is constant, while the composition of the solid and the outflow fluid change with increasing f/r ratio

Infiltration-driven devolatilization of meta-ophicalcite



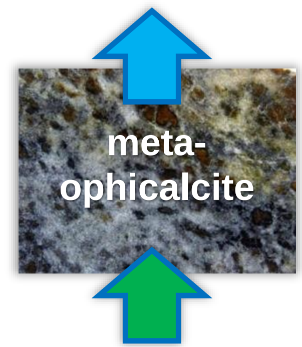
(Menzel et al., 2020)

(I) P = 2.2 GPa, T = 663 °C

Reaction 1:

$$19\ \textit{magnesite} + 5\ \textit{diopside} + SiO_{2,aq} + 3\ H_2O = 2\ \textit{dolomite} + 11\ \textit{olivine} + 10\ CO_{2,aq} + 3\ CaHCO_3^+ + 2\ HCO_3^- + OH^-$$

enriched in outflow fluid

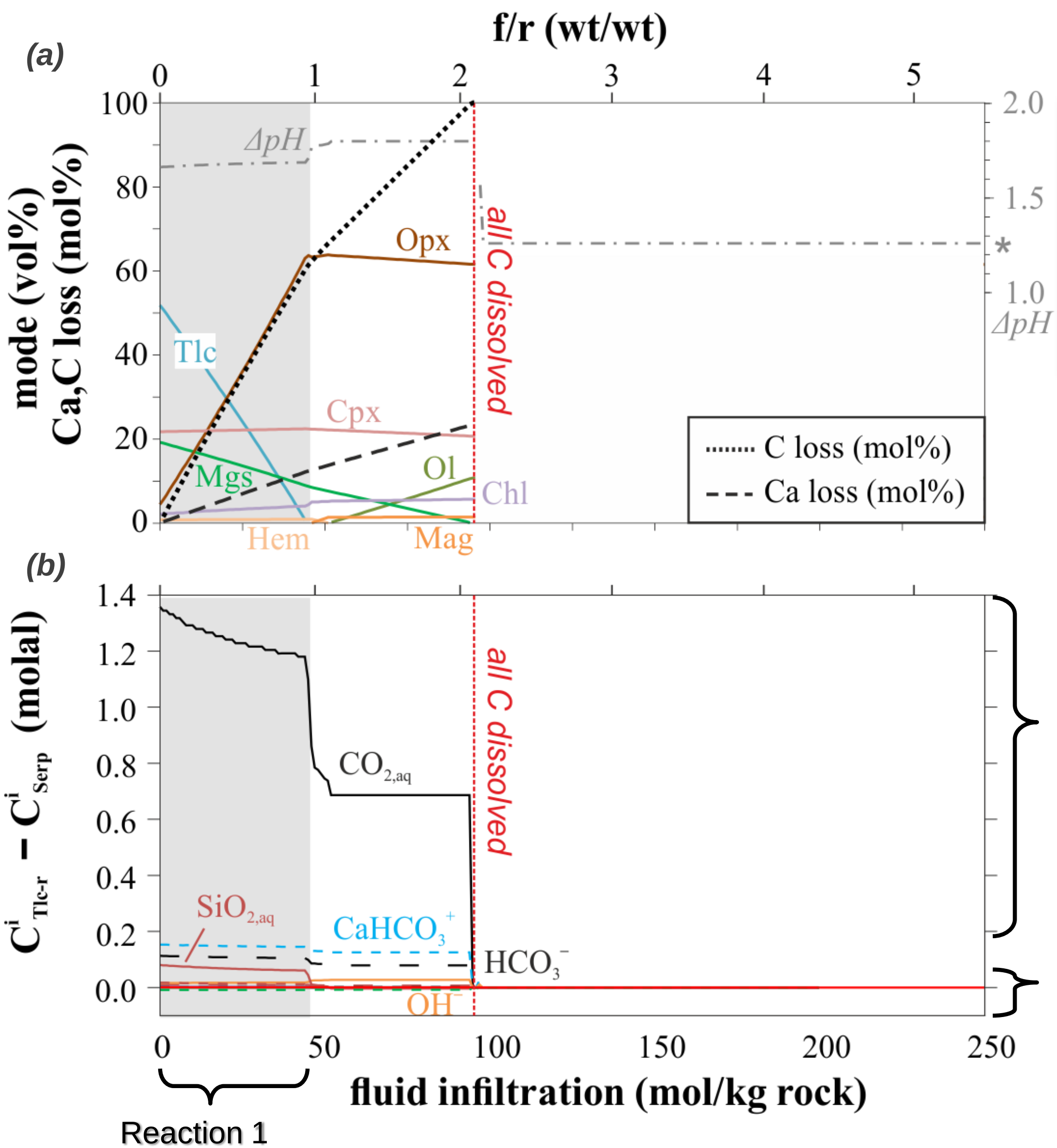


enriched in infiltrated fluid

Serpentinite dehydration fluid

(a) Changes in phase assemblages, ΔpH, and C and Ca contents in the residual rock as a function of the amount of fluid infiltration, and (b) corresponding changes in the difference between infiltrated (serpentinite derived) fluid and outflow fluid.

Infiltration-driven devolatilization of carbonate-talc rock



(Menzel et al., 2020)

(I) P = 2.2 GPa, T = 663 °C

Reaction 1:

25 magnesite + 23 *talc* + 6 *diopside*

=

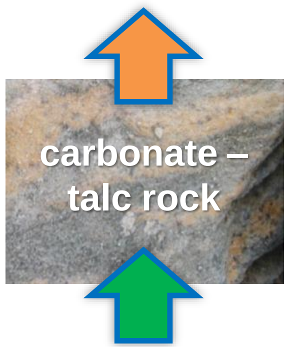
50 orthopyroxene + 16 $CO_{2,aq}$ + 17 H_2O

+ 6 $CaHCO_3^+$ + 3 HCO_3^- + 4 $SiO_{2,aq}$ + 3 OH^-

(stoichiometries derive from the model)

enriched in outflow fluid

enriched in infiltrated fluid



Serpentinite dehydration fluid

(a) Changes in phase assemblages, ΔpH, and C and Ca contents in the residual rock as a function of the amount of fluid infiltration, and (b) corresponding changes in the difference between infiltrated (serpentinite derived) fluid and outflow fluid.

Conclusions

- The carbon solubility of serpentinite-hosted carbonates is higher than that of pure aragonite due to open-system reactions involving carbonates, silicates, and fluid.
- Prograde devolatilization is not an efficient mechanism to release carbon from serpentinite-hosted carbonates. Therefore, they are subducted to subarc depths without substantial carbon loss.
- Infiltration-driven devolatilization during antigorite dehydration is the most efficient mechanism for carbon release from serpentinite-hosted carbonates.
- The subduction of oceanic meta-ophicalcite will preserve carbonate beyond subarc depths, and will recycle carbonate-garnet-clinopyroxene-olivine rocks into the deep mantle even in hot subduction zones, where they may be related to the formation of deep diamonds, carbonatites and kimberlites.
- Serpentinite-derived dehydration fluids infiltrating at subarc depths readily dissolve carbonate–talc rocks and transform them into orthopyroxenite in most subduction thermal regimes

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