

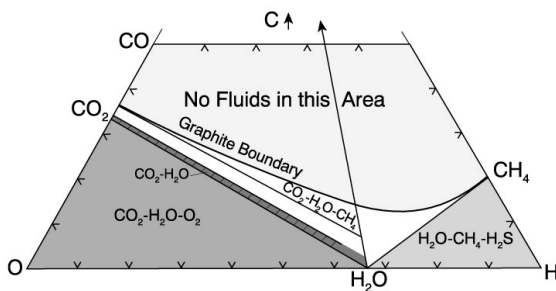
Metasomatism

Reading: Winter, Chapter 30

Volatile Species

- O, H, C, & S, N
- Behave as supercritical fluids
- At high P volatile density is similar to water at STP
- Volatile phase may have 4-5 components!
- Large degree of freedom without buffering

C-O-H-S System



Fluid speciation at 1100°C and 0.5 Gpa. After Holloway (1981) and Winter (2001)

Metasomatism Model

- Obvious in rocks with contrasting mineral layers
- Related to unequal partitioning of elements between solid phases and fluids
- Model uses ion-exchange reactions

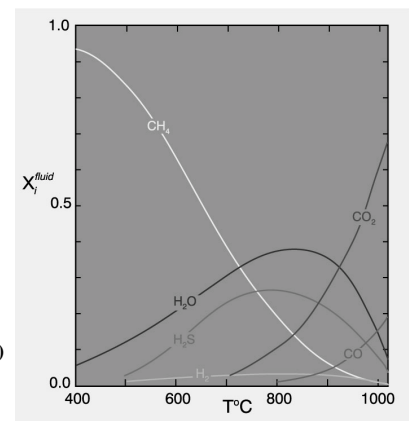
Fluid Buffers

- Graphite acts as a buffer for S
- O_2 is buffered to a low value by magnetite/hematite
- This prevents extremely large concentrations of CO

Speciation in C-O-H-S fluids

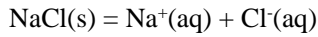
Mole fraction of each species in fluids coexisting with graphite at 0.2 GPa with f_{O_2} buffered by quartz-fayalite-magnetite.

From Holloway (1981) and Winter (2001).



Non-volatile Solutes

- Solids approach equilibrium with fluids
- Solubility product of NaCl



$$K_{sp} = \alpha_{\text{Na}^+} * \alpha_{\text{Cl}^-}$$

Fick's Law

- Flux (J) is proportional to concentration (C) gradient

$$J = -D * dC/dx$$

D is the diffusion gradient

- Mean displacement (\bar{x})

$$\bar{x} = (D*t)^{0.5}$$

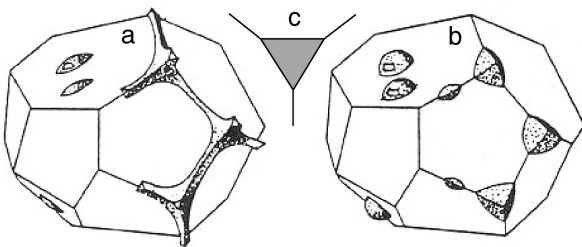
Diffusion

- Diffusion in solids
 - Very slow
- Diffusion in liquids
 - Rapid
 - Depends on interconnectivity

Diffusion Rates

- Diffusion of a few cm through solids (rocks and minerals) takes hundreds of millions of years
- Diffusion through a fluid can occur at a rate of a few meters per year
- Therefore, migration of elements through metasomatism requires a continuous fluid phase

Distribution of Fluids



Three-dimensional distribution of fluid about a single grain at $\theta < 60^\circ$ (left) and $\theta > 60^\circ$ (right). In the center is a cross section through a fluid tube at the intersection of three mineral grains for which $\theta = 60^\circ$. After Brennan (1991)

Amphibolite Facies Metasomatism

- Alternating sedimentary layers with more and less calcite
- Leads to slightly different plagioclase composition in metamorphic bands
- Ion exchange produces plagioclase and K-spar bands

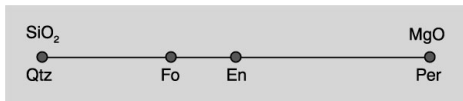
Potassium Migration

- K^+ is concentrated relative to Na^+ in chloride fluids
- In fractured rock under a T gradient K^+ moves toward higher temperature regions
- K-spar is replaced by Na-spar in low temperature regions
- This could explain large K-spar megacrysts

Local Equilibrium

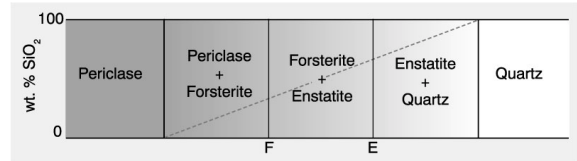
- Disequilibrium exists along surfaces D and F in the previous diagram
- Incompatible phases are in contact
 - enstatite + periclase = forsterite
 - forsterite + quartz = enstatite
- These reactions create monomineralic layers

SiO₂-MgO chemographic diagram assuming only Qtz, Fo, En, and Per are stable. Winter (2001)



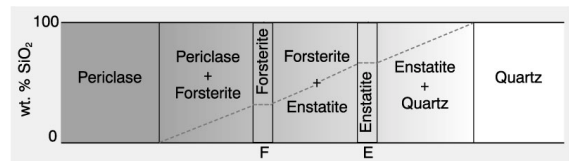
- Triangular diagrams assume that all components are mobile, hence 3 stable phases
- If water is mobile, the MgO-SiO₂ diagrams shows that two phases are more common.
- Single phase bands are rare

Thompson's Rock Column



Hypothetical rock column proposed by J. B. Thompson (1959). The left end is pure periclase and the right end pure quartz. Between these ends the bulk composition varies continuously so that the wt. % SiO₂ increases linearly from left to right (dashed line). Winter (2001)

Thompson's Rock Column

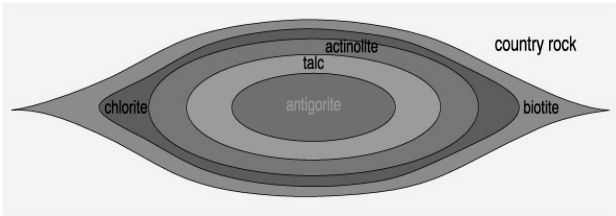


The hypothetical rock column of J. B. Thompson (1959) after reactions form monomineralic layers of pure forsterite and enstatite. After Winter (2001)

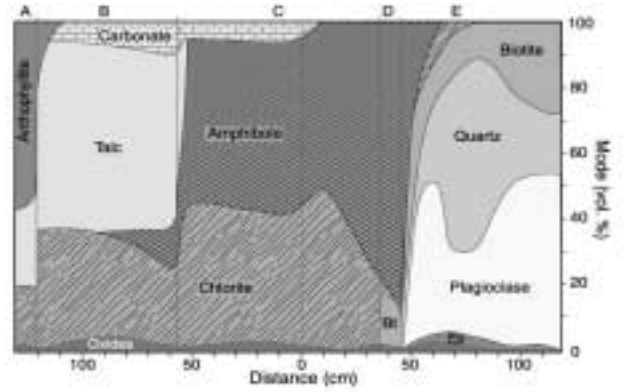
UM Metasomatic Zonation

Antigorite	$Mg_6Si_4O_{10}(OH)_8$
Talc	$Mg_3Si_4O_{10}(OH)_2$
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Chlorite	$(Mg,Fe)_6Si_4O_{10}(OH)_8$
Biotite	$K(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2$

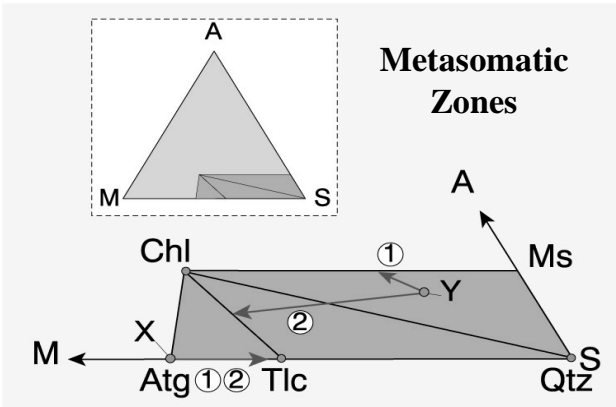
Ultramafic Metasomatism



“Ideal” mineral zonation due to metasomatism in < 3-m long ultramafic pods in low-grade regionally metamorphosed pelites at Unst, Shetland Islands. After Read (1934)

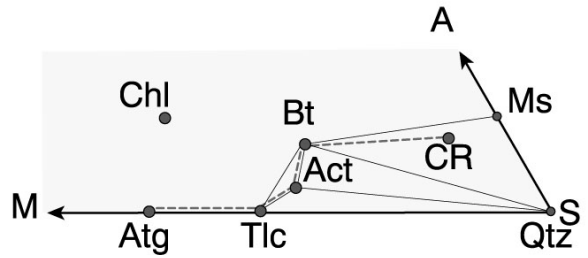


Mineral proportions across the zones between the ultramafic and quartzo-feldspathic gneiss contact at Grafton, Vermont, after Sanford (1982). A = Tlc + Ath, B = Tlc, C = Act + Chl, D = transitional, E = quartzo-feldspathic country rock. After Sanford (1982)

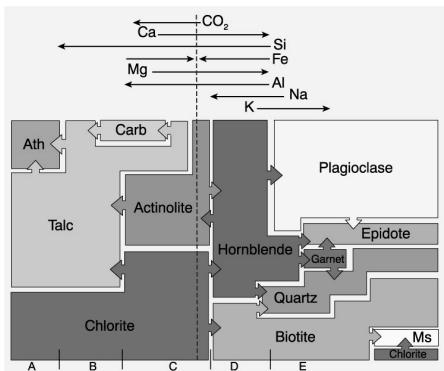


AMS diagram (A = Al₂O₃, M = MgO + FeO, and S = SiO₂) for ideal lower-temperature metasomatic zones around ultramafic bodies. After Brady (1977) and Winter (2001)

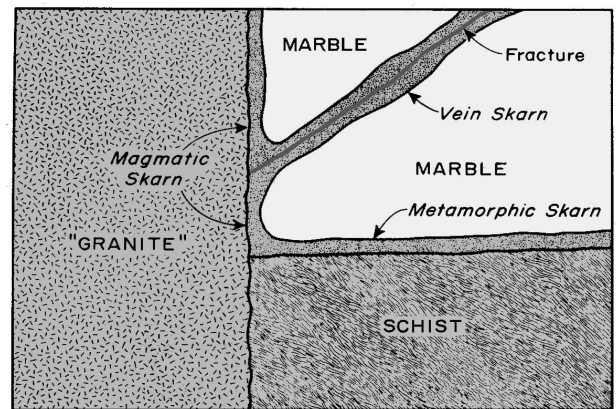
Metasomatized Ultramafic Rocks



The same portion of the AMS diagram, projected from K₂O and CaO, with the locations of analyzed rocks from the metasomatized zones of Read (1934), reported by Curtis and Brown (1969). The dashed curve represents a path through the zonal sequence. After Brady (1977)



Schematic representation of major silicate mineral reactions and component fluxes associated with metasomatism of the ultramafic body at Grafton, Vt. Elemental fluxes across various zones are indicated by the arrows at the top. Arrows between mineral boxes indicate reactions. When horizontal, these arrows involve metasomatic reactions; when vertical they are approximately isochemical. After Sanford (1982)



Three principle types of skarns

Skarns (Calc-silicate)

- Skarns contain Ca-Fe-Mg silicates formed by strong migration of fluids and cations
- Endo skarns develop within a plutonic rock
- Exoskarns develop in the carbonate rocks outside the contact

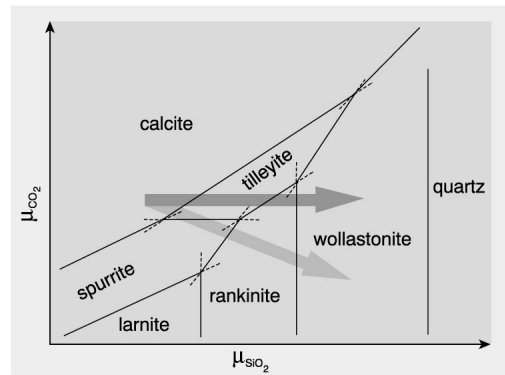


Chert nodule in carbonate with layer sequence: calcite | tilleyite | wollastonite | quartz. Christmas Mts., Texas. From Joesten and Fisher (1988)

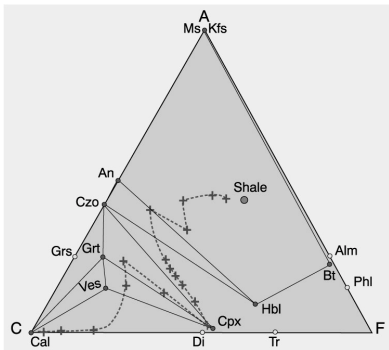
Ca-Si Index Minerals

Tilleyite	$\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$
Spurrite	$\text{Ca}_5\text{Si}_2\text{O}_8\text{CO}_3$
Rankinite	$\text{Ca}_3\text{Si}_2\text{O}_7$
Wollastonite	CaSiO_3

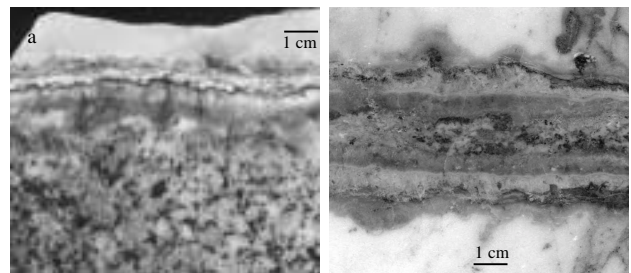
CaO-SiO₂-H₂O System



Schematic isothermal isobaric μ_{CO_2} - μ_{SiO_2} diagram for fluids in the CaO-SiO₂-H₂O system at high temperatures. After Joesten (1974)



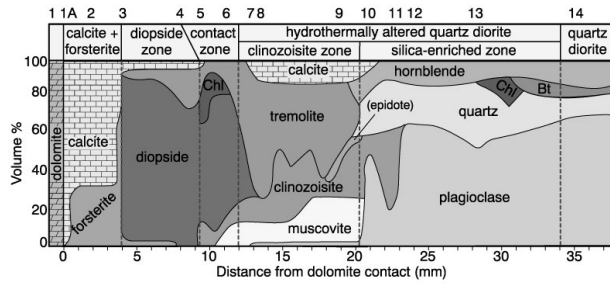
Al₂O₃-CaO-(FeO+MgO) diagram showing mineral phases and calculated bulk compositional path for metasomatic zones that develop at the contact between pelitic and carbonate layers near Lake Willoughby, VT. Ideal mineral compositions are in gray, real ones in black. After A. B. Thompson (1975)



a. Metasomatic zones separating quartz diorite (bottom) from marble (top).

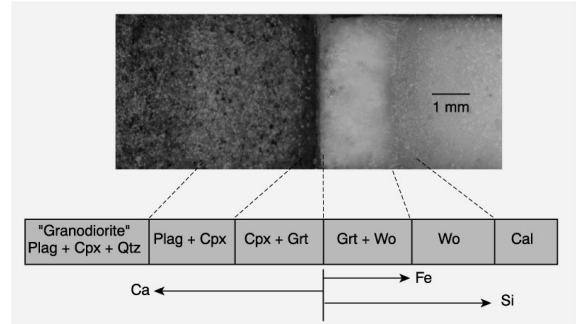
b. Symmetric metasomatic vein in dolomite, Adamello Alps.

After Frisch and Helgeson (1984) and Winter (2001)



Mineral zones and modes developed at the contact between quartz diorite and dolomitic marble. Initial contact may be at either side of the contact zone. Index numbers at the top indicate the locations of bulk chemical analyses. After Frisch and Helgeson (1984) and Winter (2001)

Experimental Skarn



Zonation in an experimental skarn formed at the contact between granodiorite and limestone at 600°C, $P_{fluid} = 0.1$ GPa ($X_{CO_2} = 0.07$). After Zharikov, V.A. and G.P. Zharaisky (1991). Photo courtesy G. Zharaisky in Winter (2001).