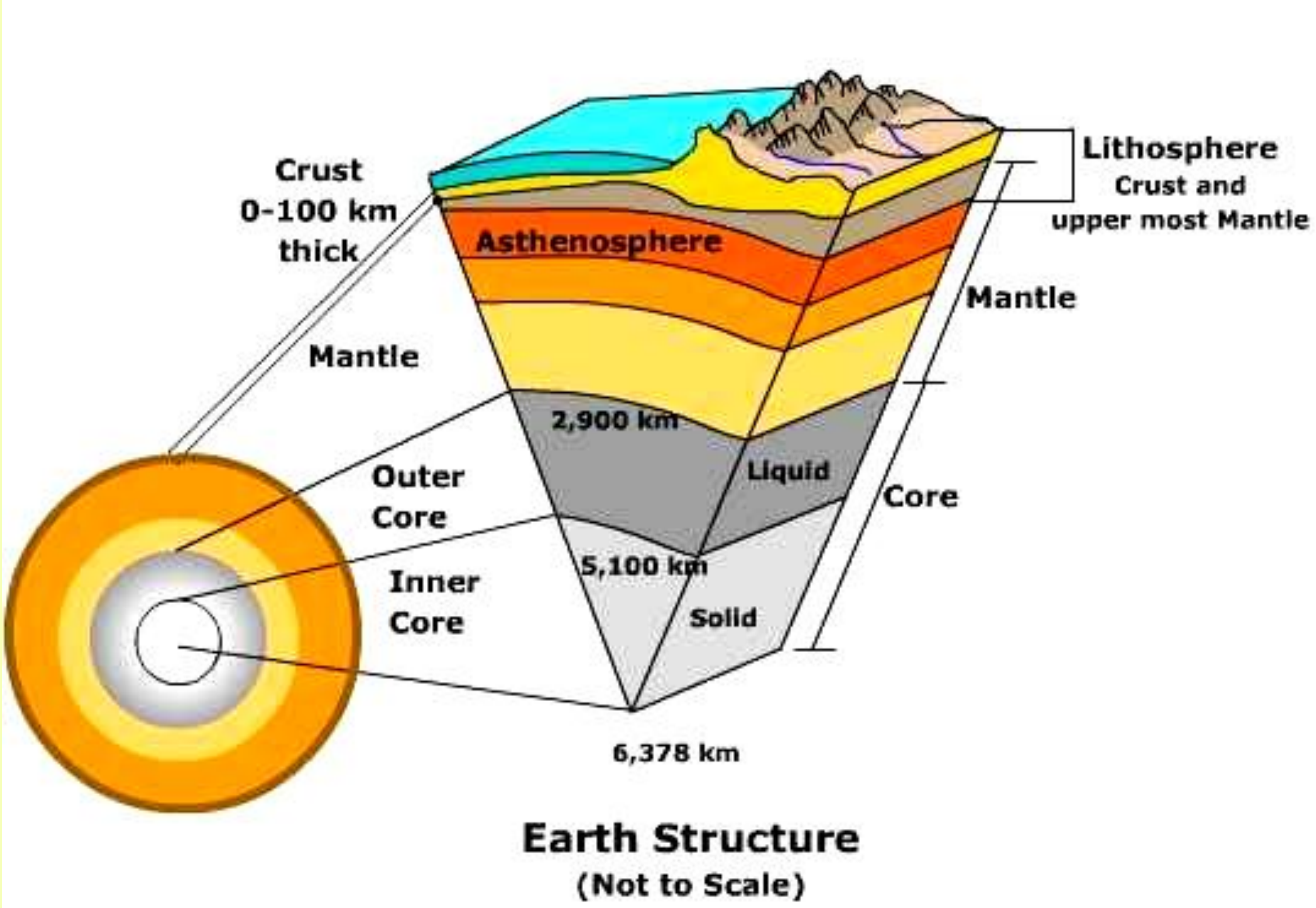
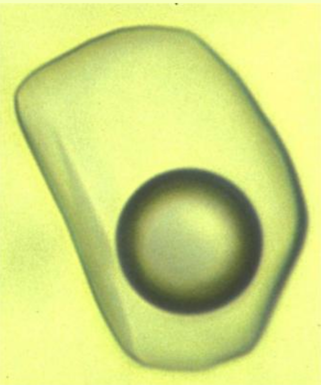
Fluid and Melt Inclusion Evidence for the Distribution and Speciation of Carbon in the Earth

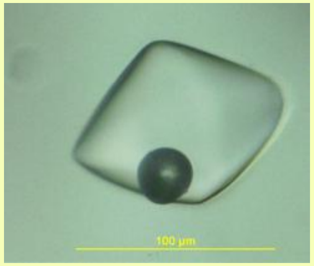


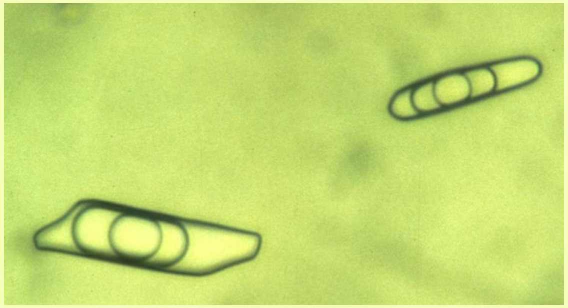
Earth Structure
(Not to Scale)

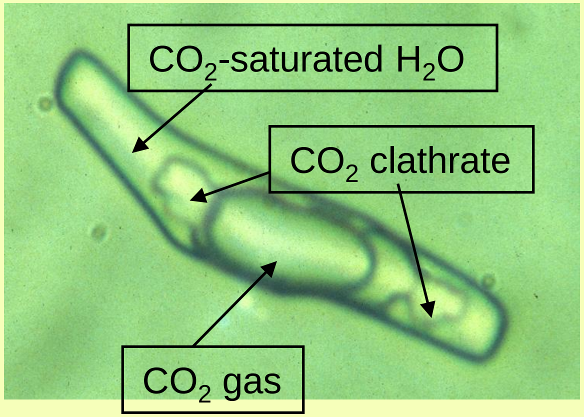
Fluid and melt inclusions provide the most direct evidence for the nature of fluids in the lithosphere.

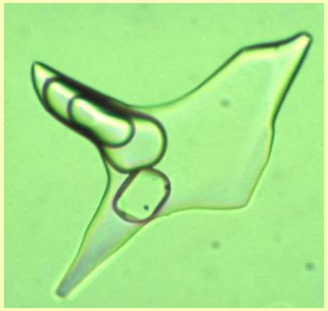
- *FI in sedimentary (diagenetic) environments*
- *FI in metamorphic environments*
- *FI & MI in shallow crustal magmatic environments*
- *FI & MI in upper mantle environments*
- *FI in diamonds*
- *FI in deeper mantle minerals (nano- to pico-scale FI)*











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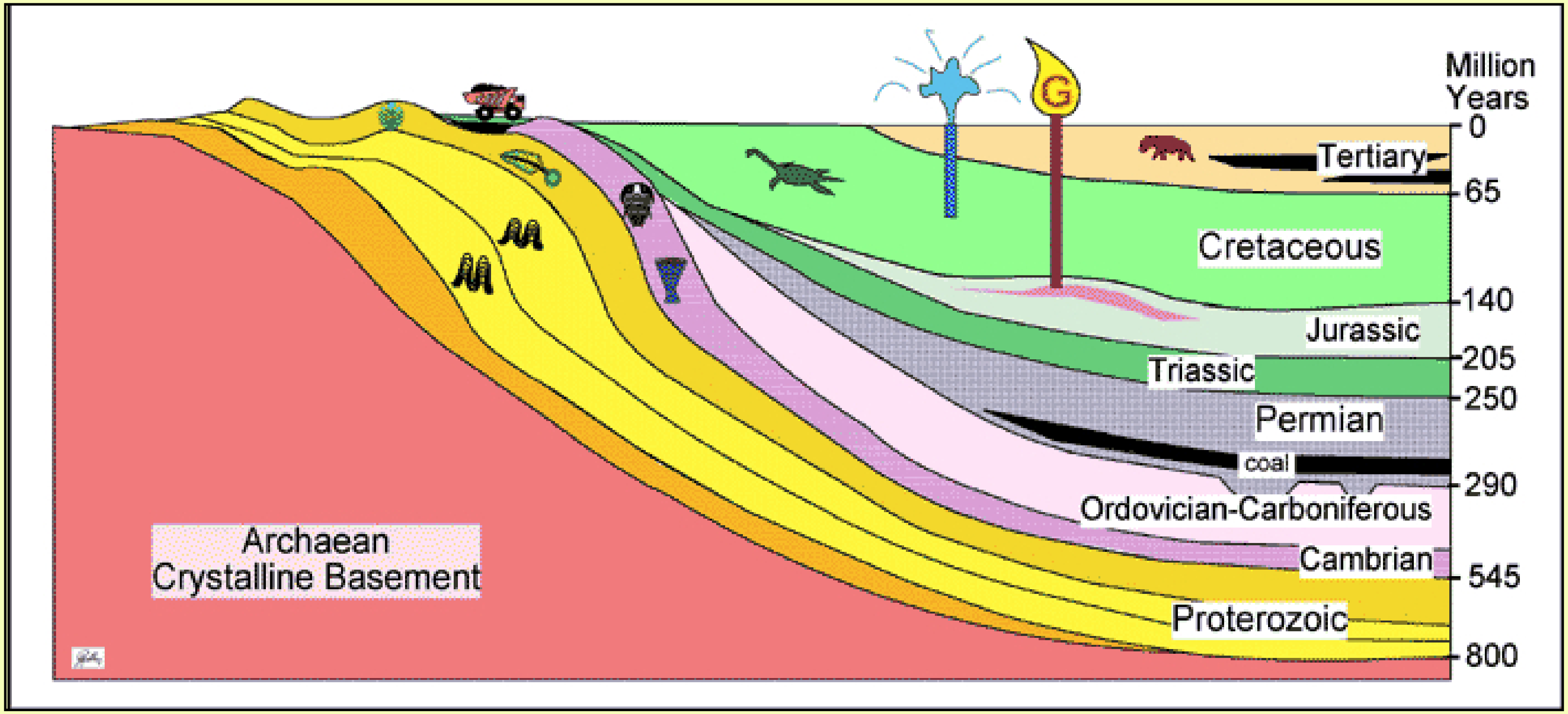
During the burial and diagenesis of organic-rich sediments the organic matter undergoes systematic changes with increasing depth of burial (temperature).



At the shallowest depths biogenic CH_4 is produced as organic material starts to breakdown. The methane dissolves in pore waters which can be trapped to produce CH_4-bearing aqueous fluid inclusions. In submarine areas near continental margins and in permafrost regions the CH_4 can react with H_2O to produce methane hydrate (clathrate)

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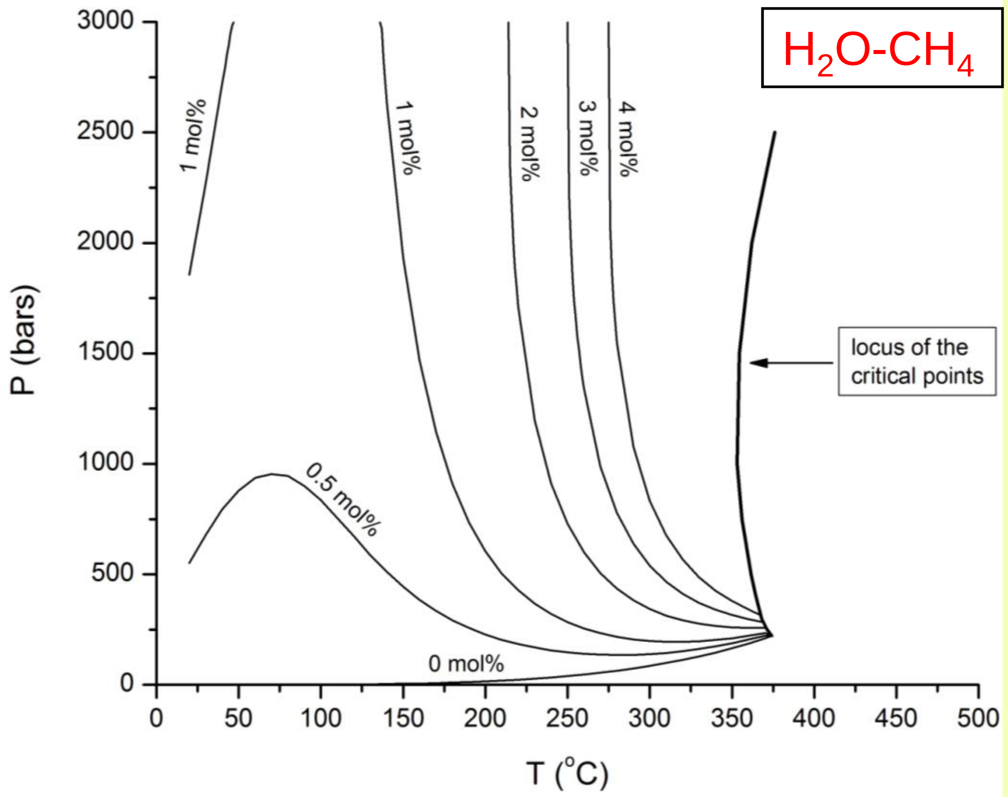
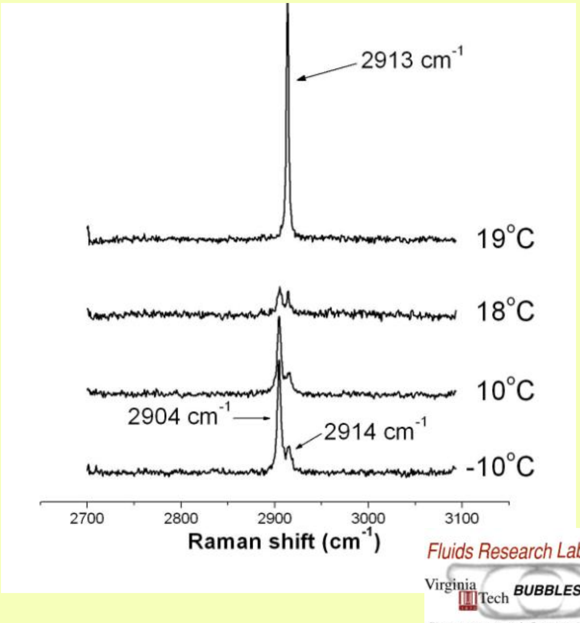
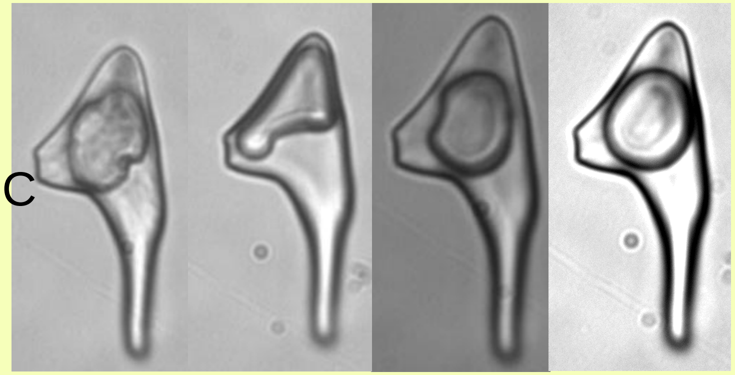


At low temperature (≈<30° C) and high pressure, methane hydrate (clathrate) is stable and occurs naturally in the sub-seafloor near continental margins and in permafrost regions. It is estimated that worldwide more methane exists in hydrate deposits (≈10^{17} - 10^{20} cubic feet!) than in all the other fossil energy (coal, oil, natural gas) deposits combined.



≈-40° C



≈22° C

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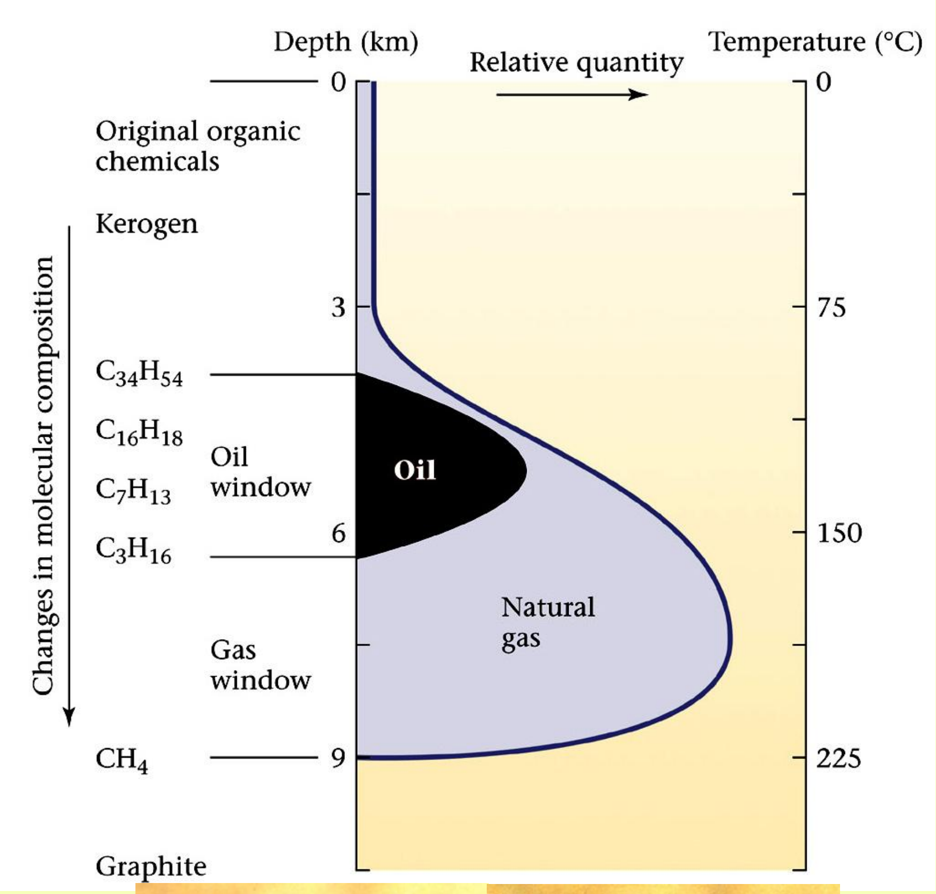
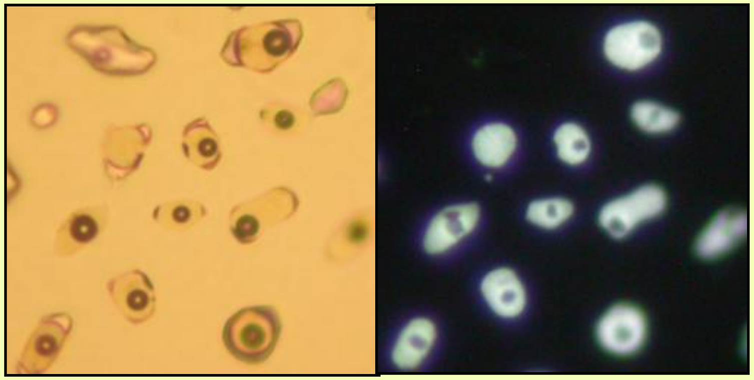
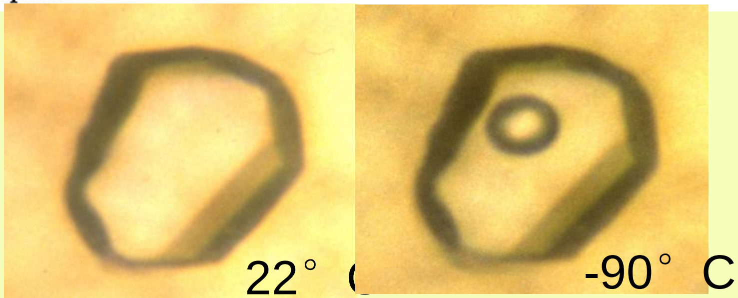
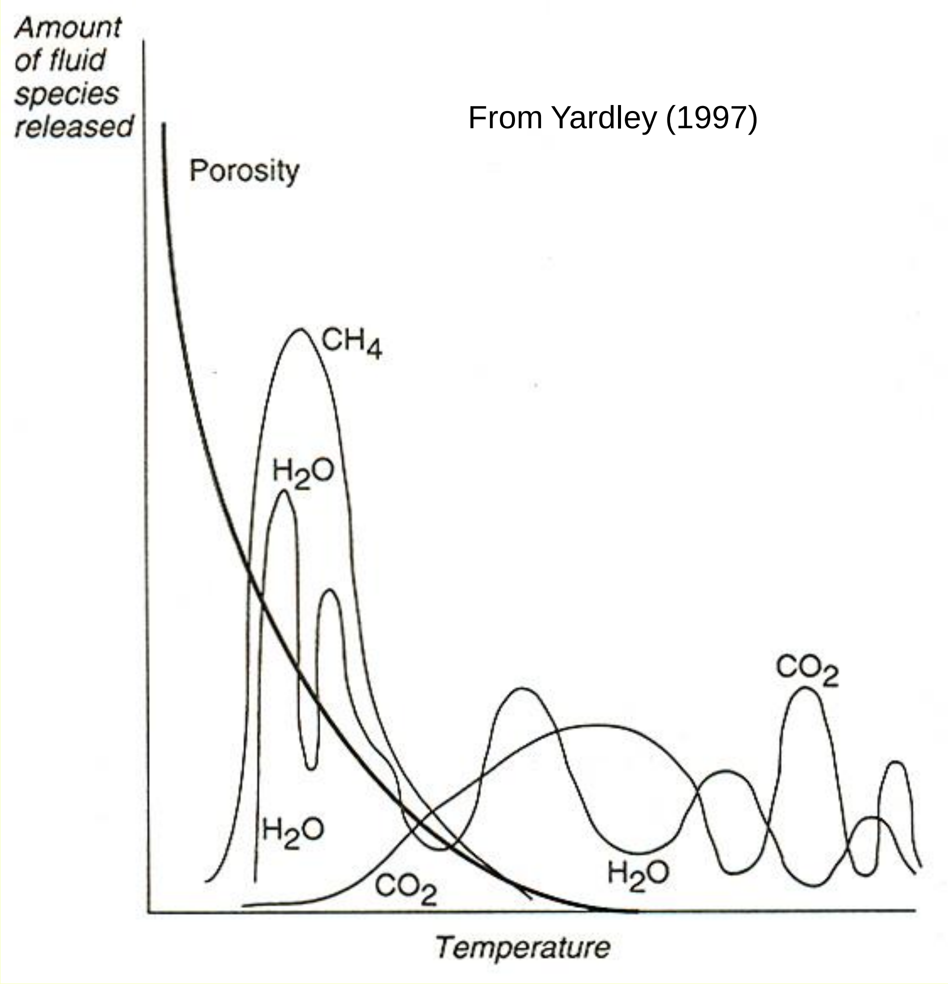


With continued burial the sediments enter the “oil window” where liquid hydrocarbons are generated. When the sediments are buried to depths greater than the “oil window” and enter the anchimetamorphic zone, liquid hydrocarbons become unstable and break down to produce mostly methane gas, with lesser amounts of ethane, propane, butane and non-hydrocarbon gases (N_2, H_2S, etc.).

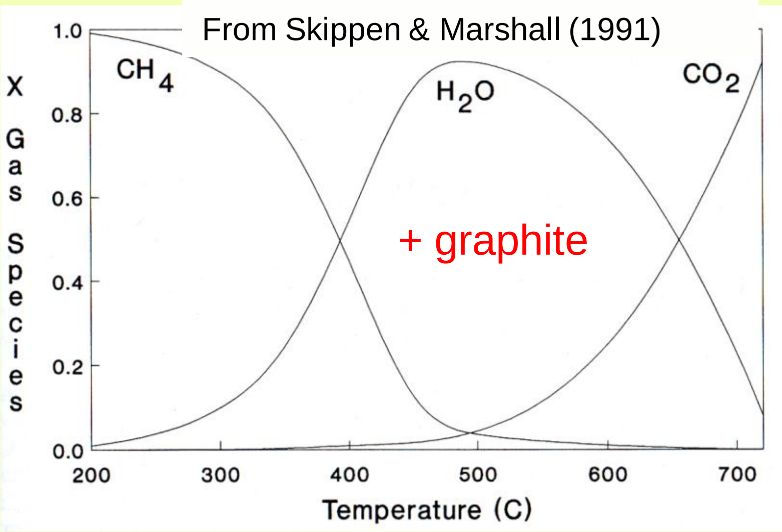




Most metamorphic fluids are approximated by the C-H-O-S-(salt) system. The composition of metamorphic fluids varies systematically with changing f_{O2}, temperature and pressure.



From Yardley (1997)



From Skippen & Marshall (1991)

The relative proportions of fluid species vs. T for QFM-1 is shown above. As noted by Yardley (1997), the actual proportions of different fluid species will be controlled by fluid-mineral reactions and will involve pulses of CH_4, H_2O or CO_2-rich fluids as organic matter, hydrous phases and carbonate minerals, respectively, break down at different temperatures.

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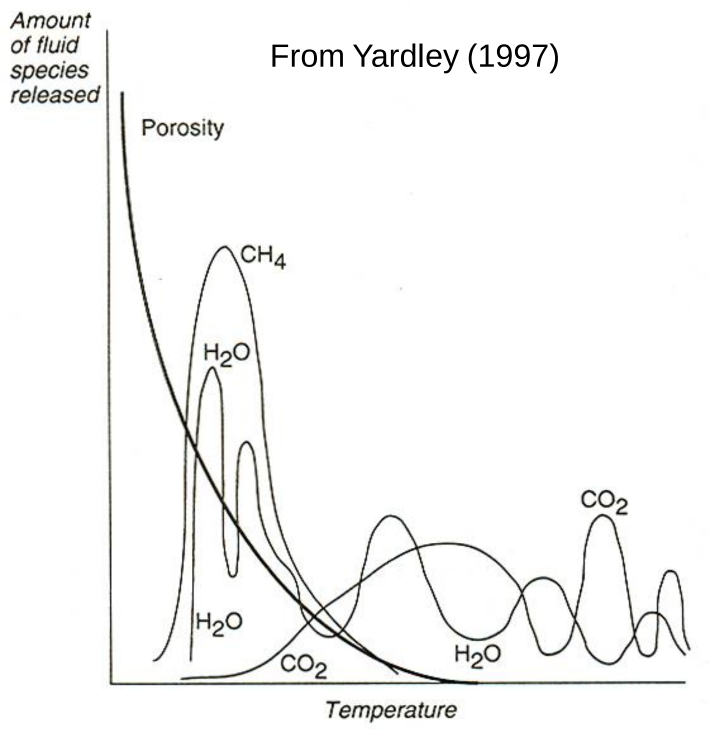
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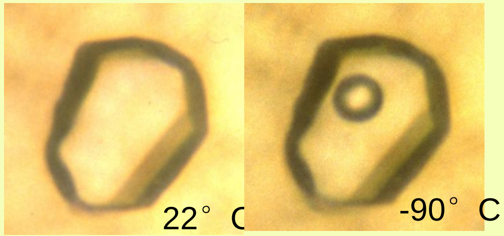

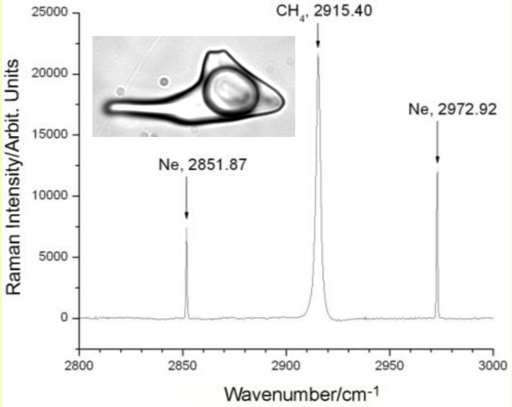

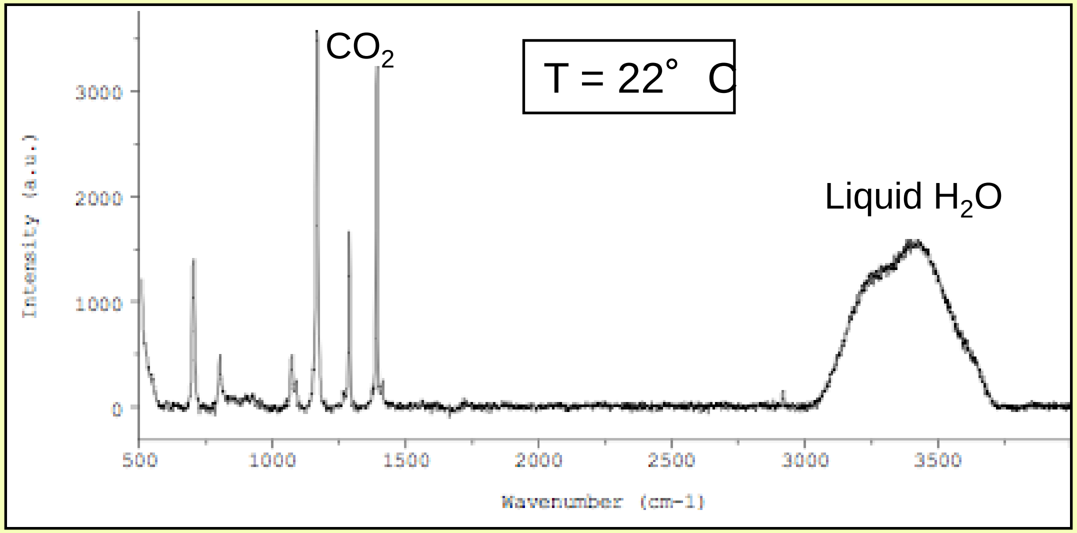

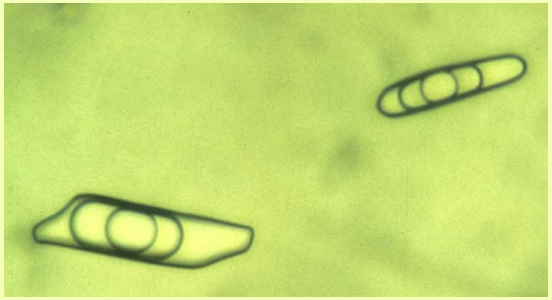

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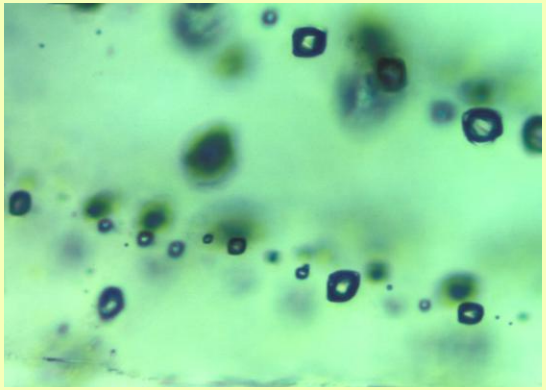
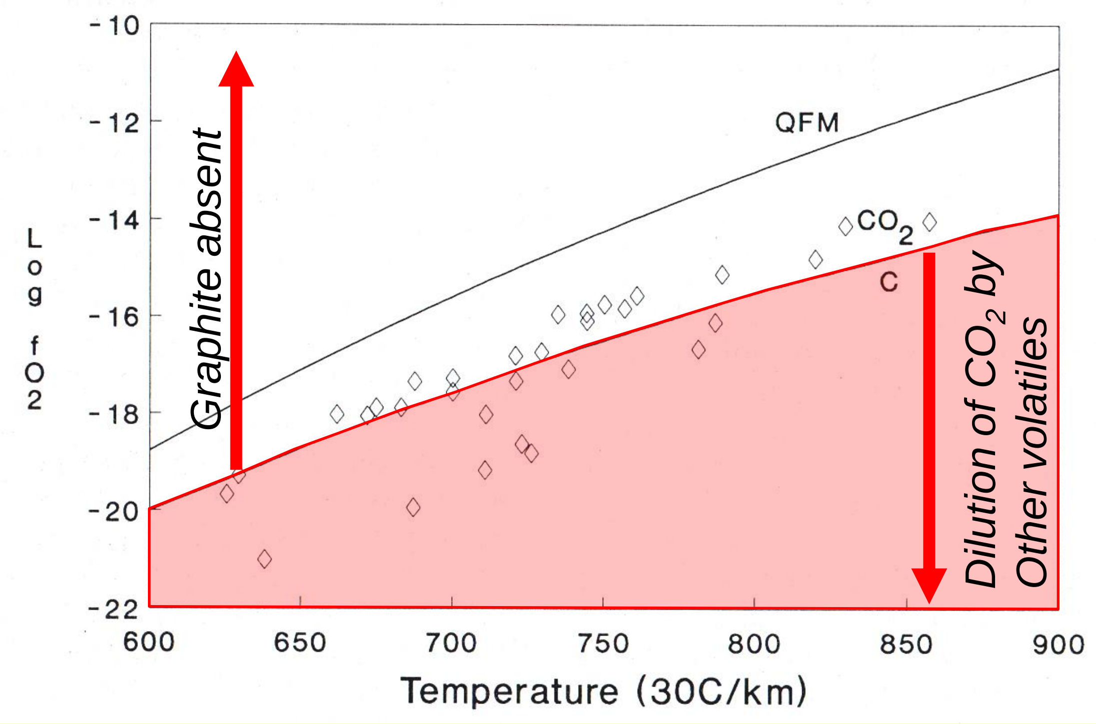
Mineral equilibria for granulite grade metamorphic rocks indicate that the oxygen fugacity of the lower continental crust is ≈QFM - 1.



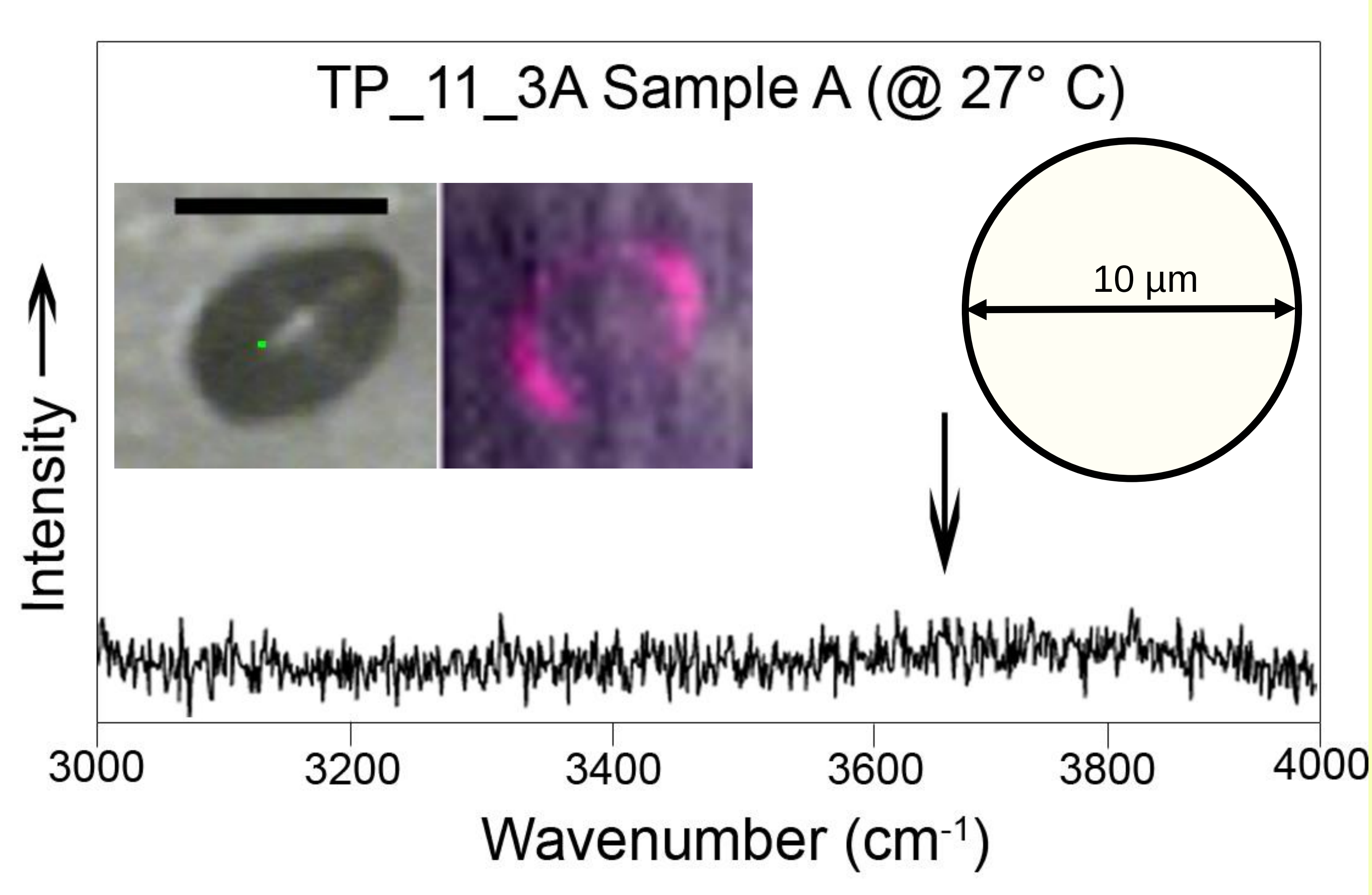


From Skippen & Marshall, 1991, Canadian Mineralogist

QFM - 1 for lower crustal rocks is consistent with the fact that most granulites are at (or close to) saturation in graphite and that nearly pure CO_2 fluid inclusions are ubiquitous in granulites.

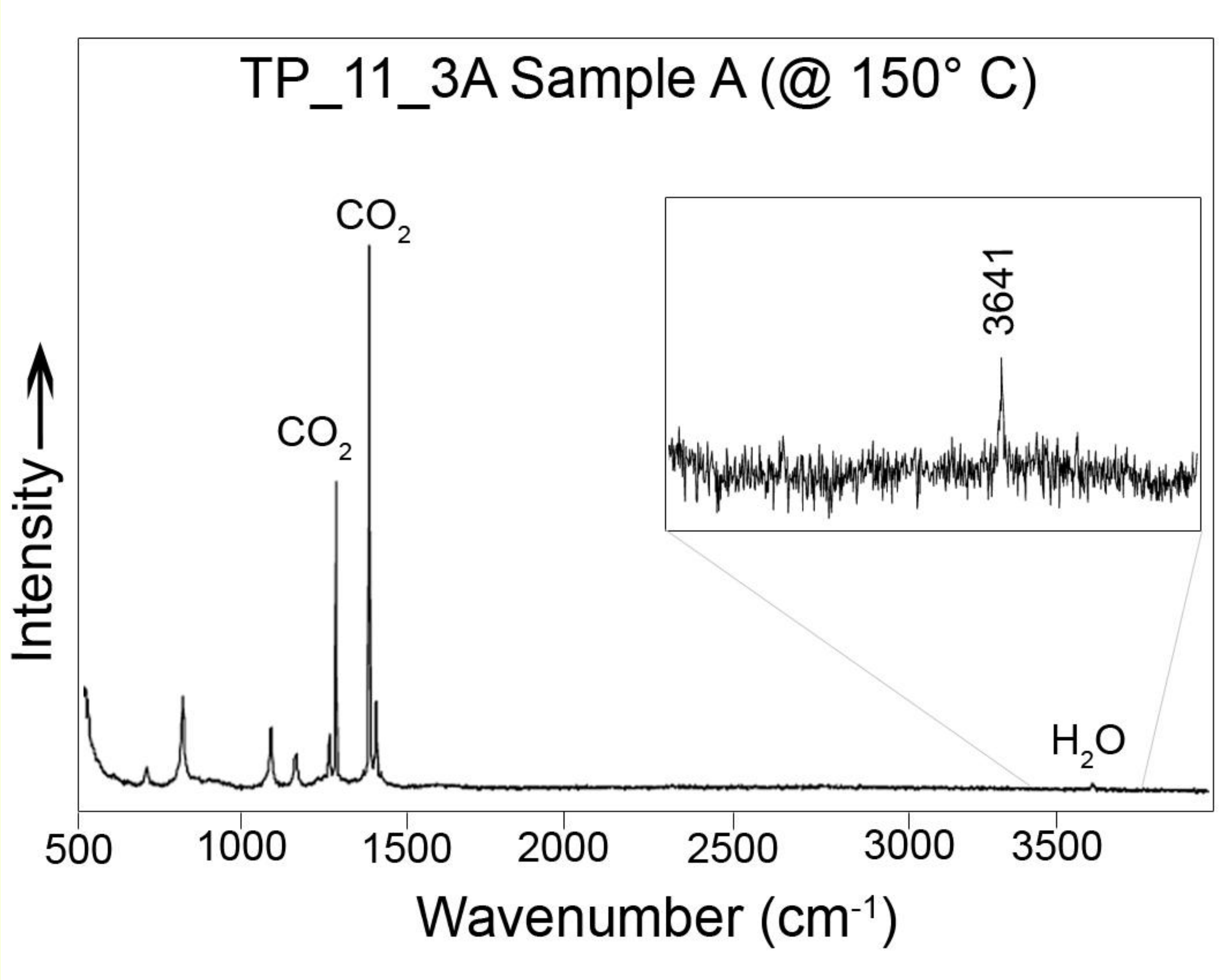
Diamonds above represent oxygen fugacities based on oxide barometry from Lamb & Valley (1984) and assuming a 30° C/km geotherm.

H_2O is not detected during room temperature Raman analysis of “single” phase fluid inclusions in granulites from the Adirondack Mtns.



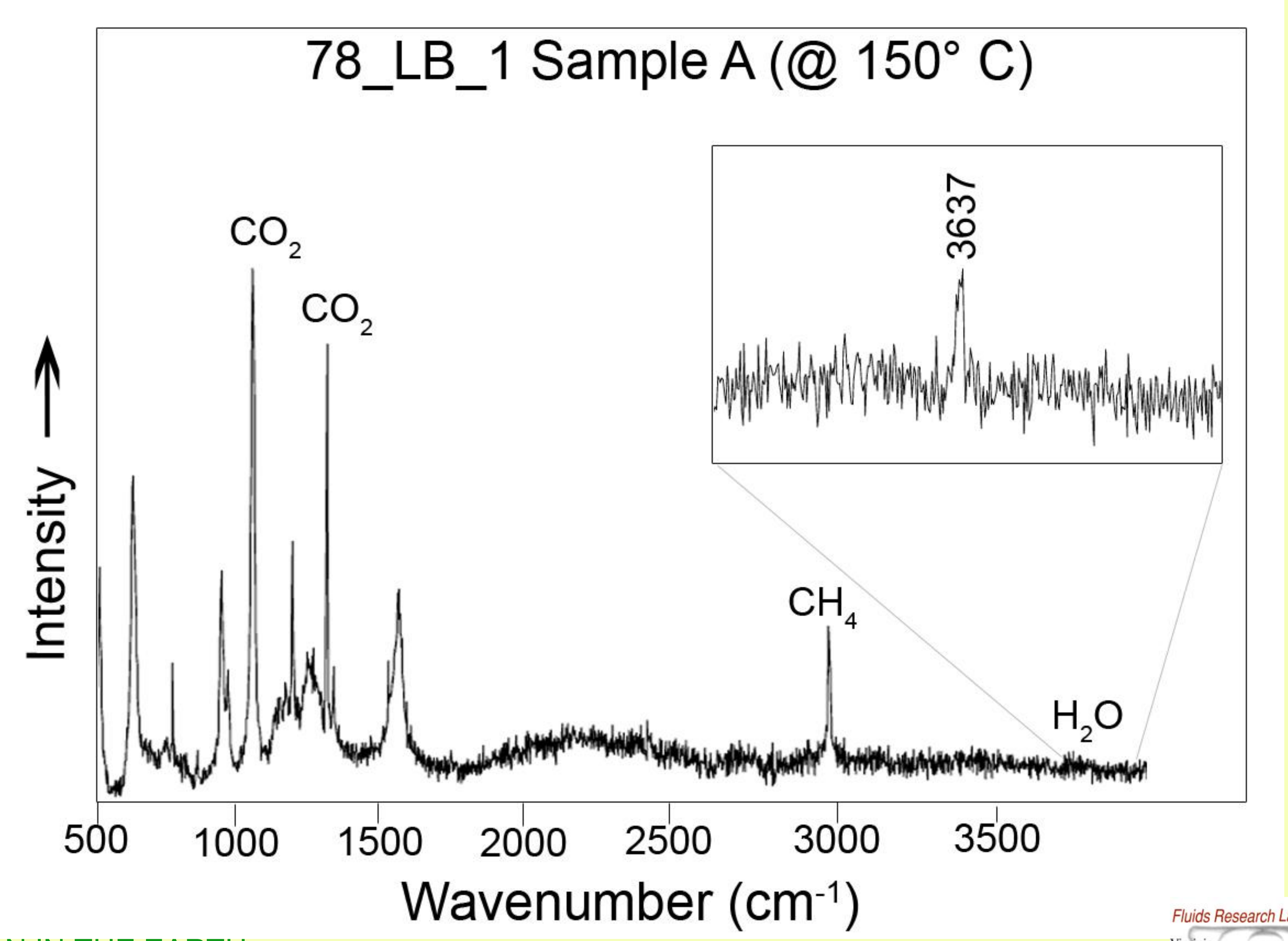
If a 10 µm spherical FI contains 90 mol% CO_2 with a density of 0.7 g/cc, and 10 mol% H_2O with a density of 1 g/cc, the H_2O phase will occur as a 0.05 µm (50 nanometer) film on the FI walls!

When the same FI is analyzed at 150° C, a small but distinct peak characteristic of H_2O is observed. Results suggest a few mole% H_2O in the inclusion.



When the inclusion is heated, the small film of H_2O that occurs wetting the walls at room temperature evaporates into the CO_2-rich fluid phase to produce a homogeneous H_2O-CO_2 fluid. Evaporation of the H_2O into the CO_2 produces a larger analytical volume containing H_2O, and the H_2O peak becomes sharper and more intense with increasing temperature.

In some fluid inclusions from granulites, a small amount of CH_4, in addition to the more abundant CO_2, is also detected.



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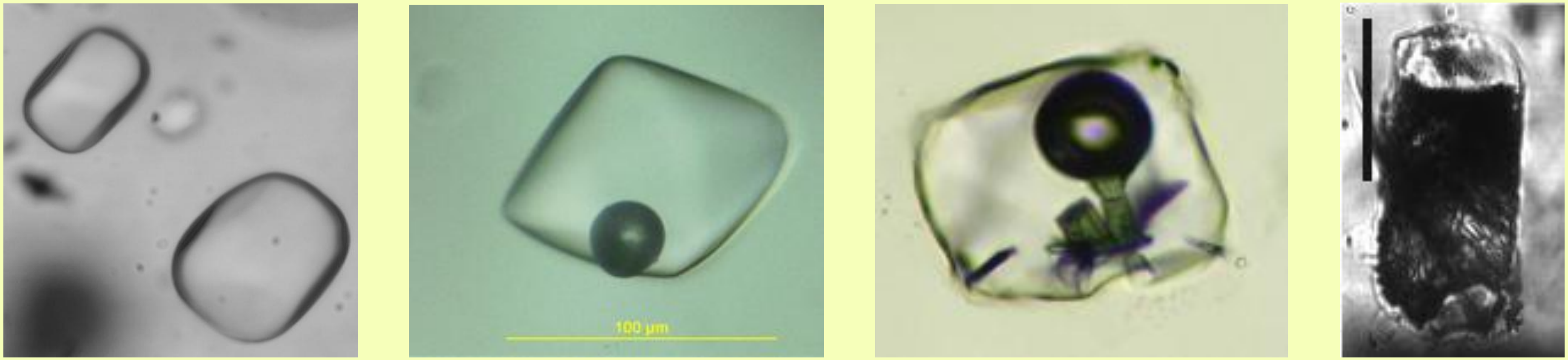
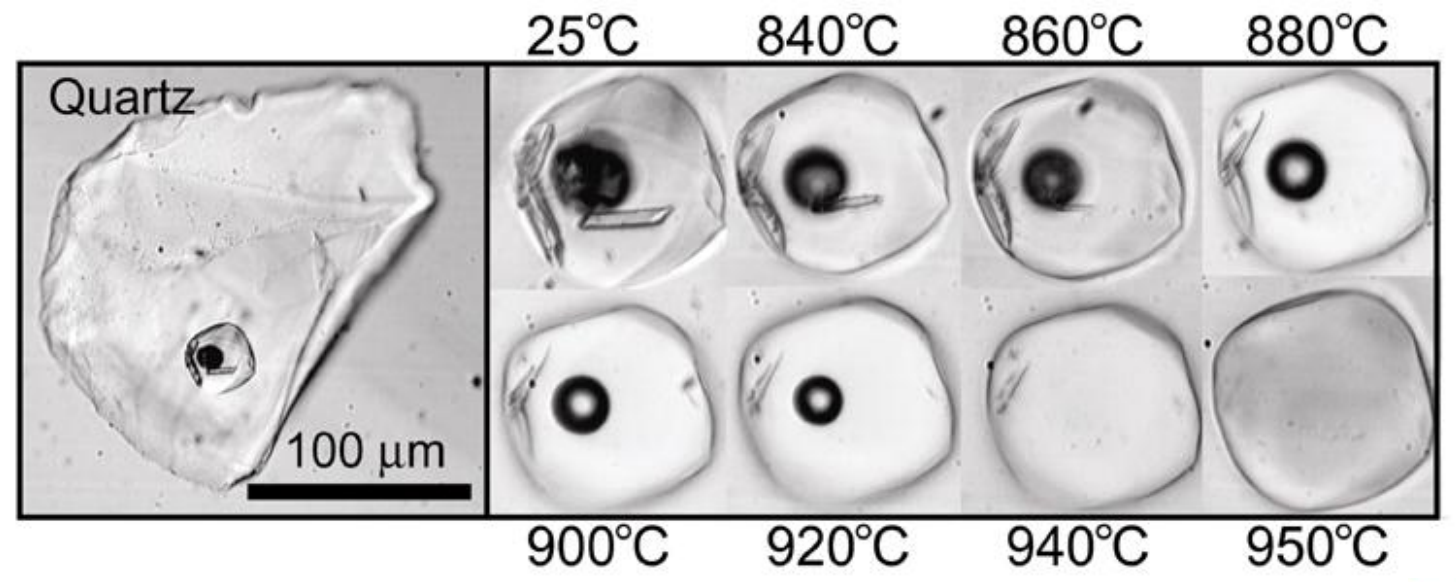
Melt inclusions trapped in phenocrysts in magmatic systems provide the best and most direct evidence for volatile abundances and speciation in lithospheric magmas.





From Bodnar & Student, MAC Short Course, 2006

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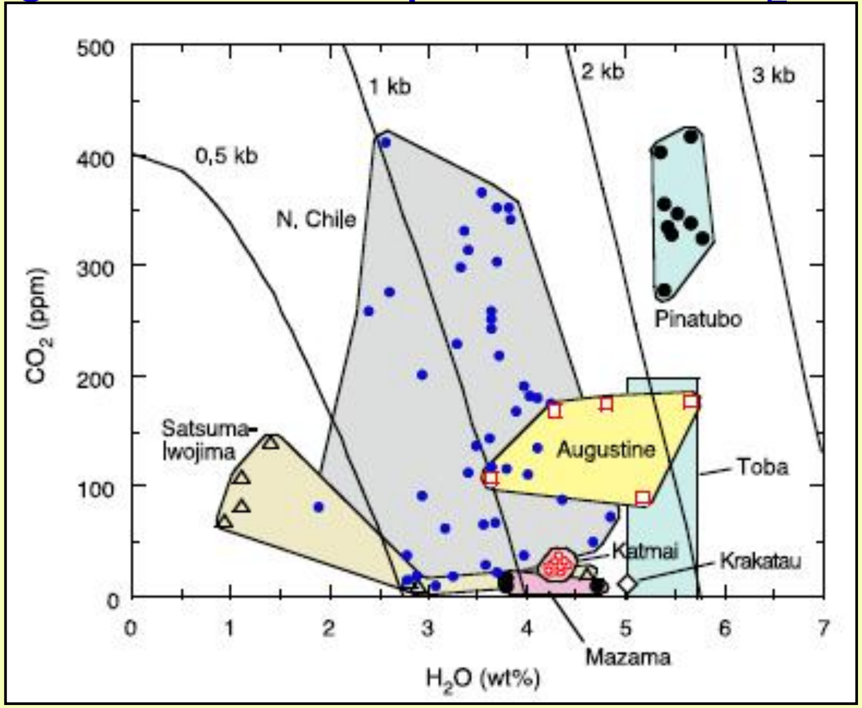
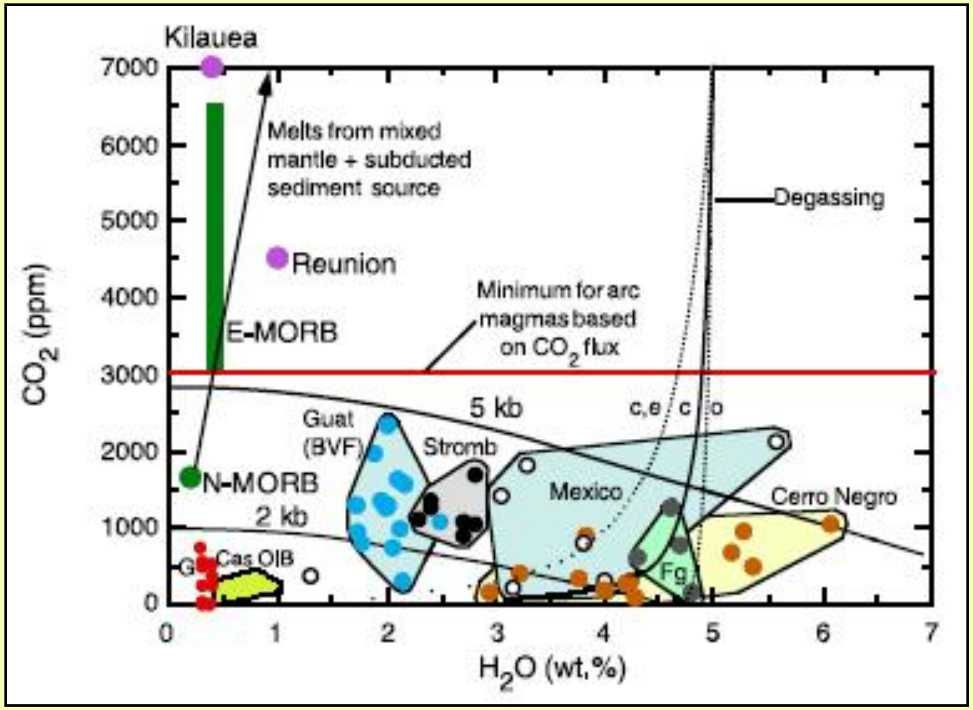
Carbon dioxide contents of melt inclusions from arc basalts (MI mostly in olivine) are significantly higher than CO_2 content of MI from arc dacites and rhyolites (MI mostly in quartz). The differences in CO_2 content largely reflect differences in magma generation depths and CO_2 solubilities in mafic vs. felsic melts.



Arc dacites and rhyolites



Arc basalts

From Wallace, 2005, JVGR

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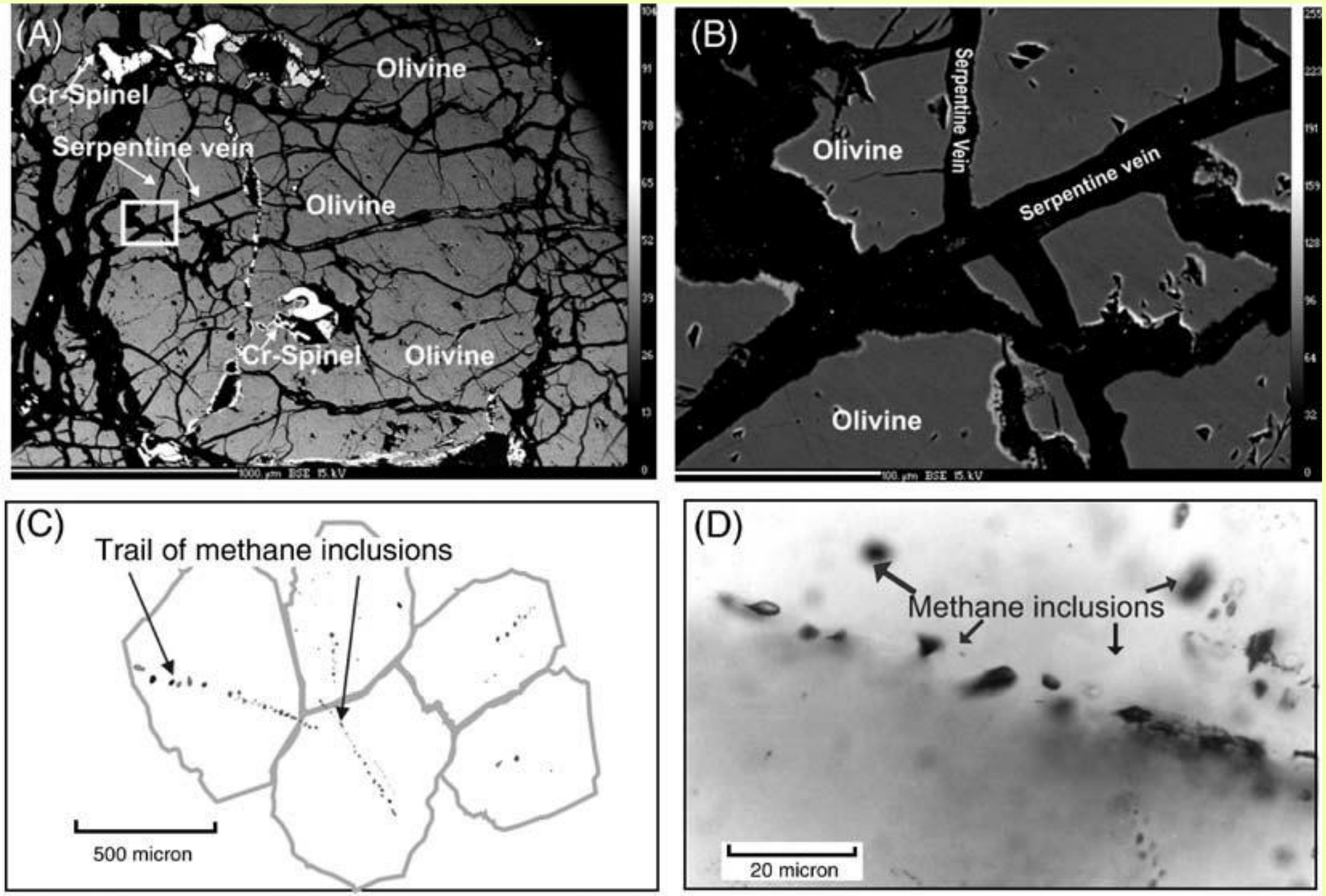
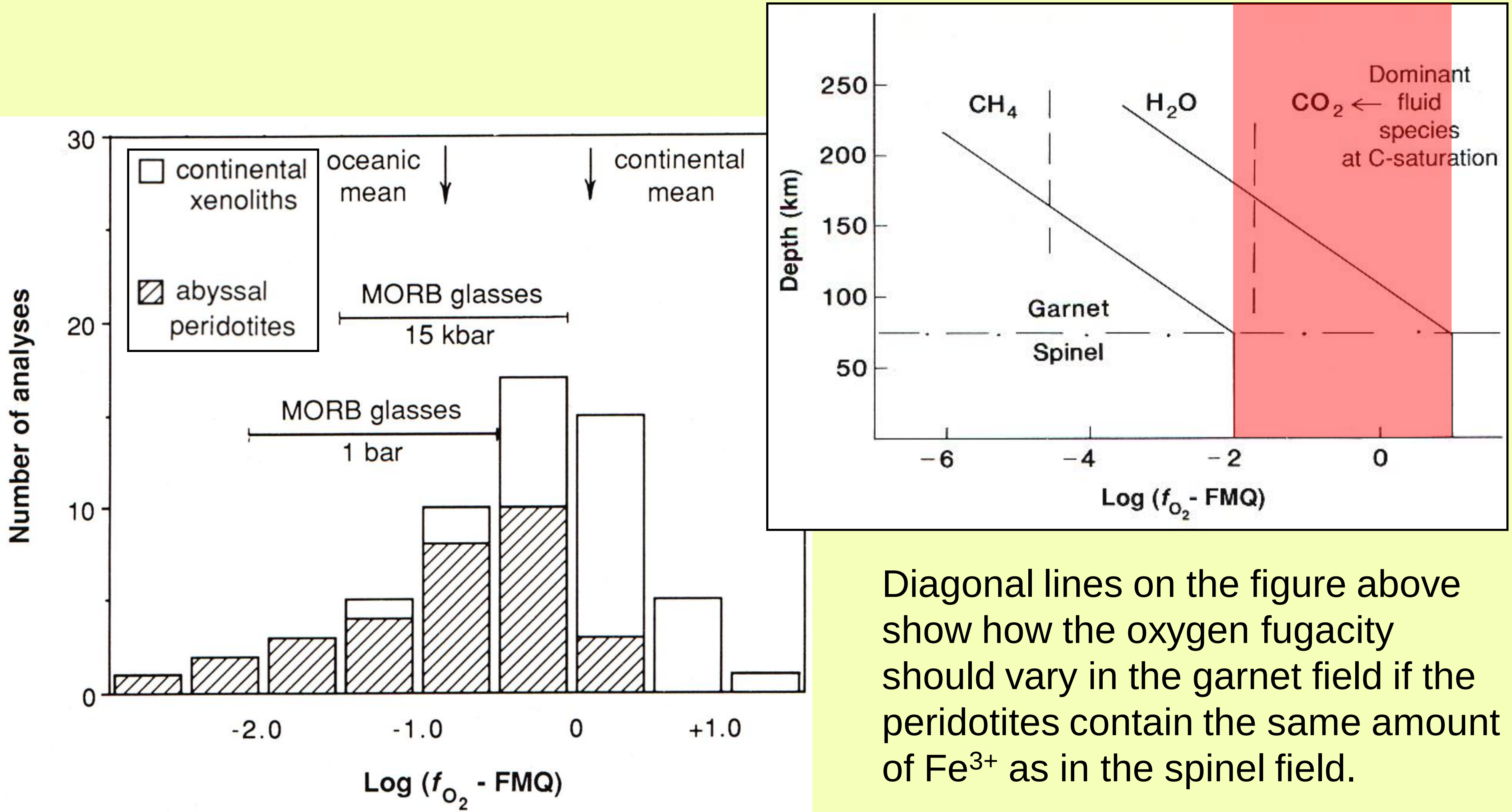
In submarine hydrothermal systems CH_4 is generated during the serpentinization of olivine. Sometimes CH_4 produced during serpentinization is preserved in secondary inclusions in rocks that have experienced rapid burial and uplift.



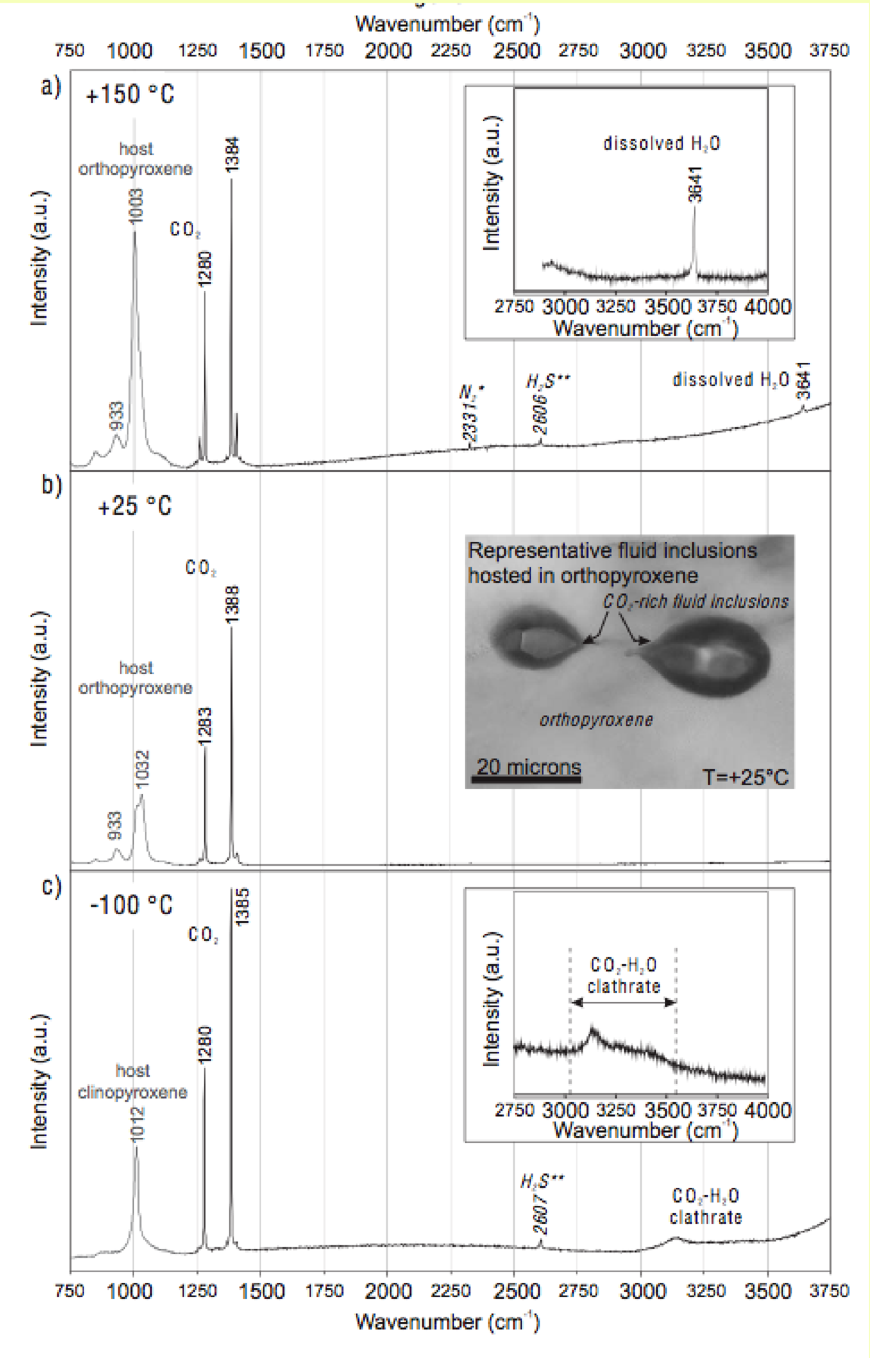
From Sachan et. al., EPSL, 2007

Mantle xenoliths indicate that the oxygen fugacity in the upper mantle is within one order of magnitude of QFM and that at mantle PT conditions $CO_2 \pm H_2O$ should be the stable fluid species.



Diagonal lines on the figure above show how the oxygen fugacity should vary in the garnet field if the peridotites contain the same amount of Fe^{3+} as in the spinel field.

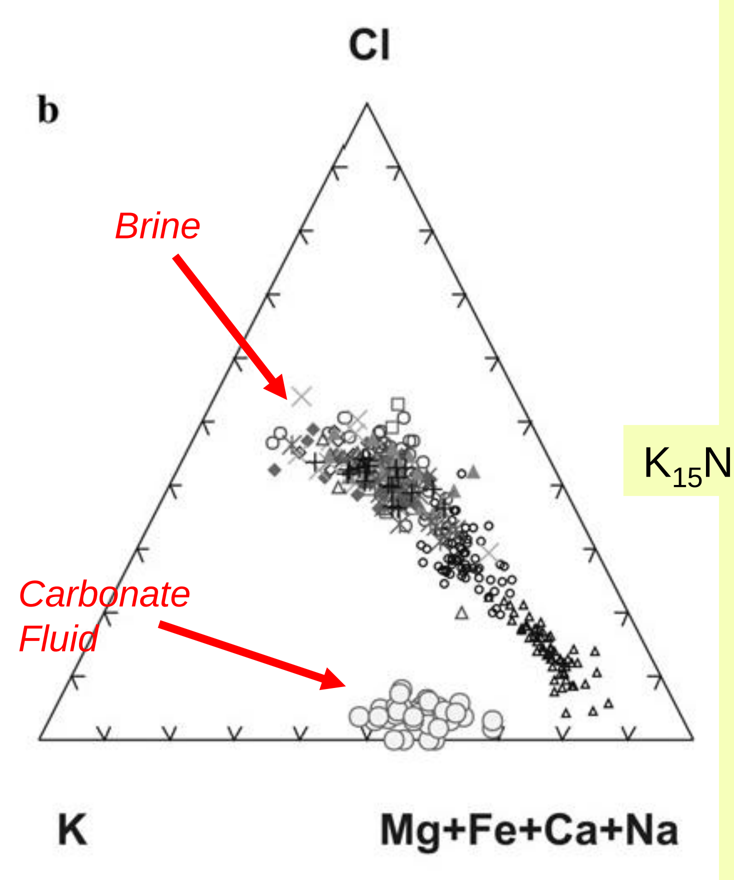
From Wood, 1990, Science, vol. 248



Peridotitic mantle xenoliths often appear contain “pure” CO$_2$ fluid inclusions. However, when analyzed by Raman spectroscopy at either low (-100° C) or elevated (+150° C) temperature, a distinct peak for H$_2$O is observed. The H$_2$O peak is not present when the same inclusion is analyzed at room temperature. Work in progress suggests that the presence of small amounts of H$_2$O in CO$_2$-rich FI from upper mantle environments is common.

From Berkesi et al., J. Raman Spec., 2009

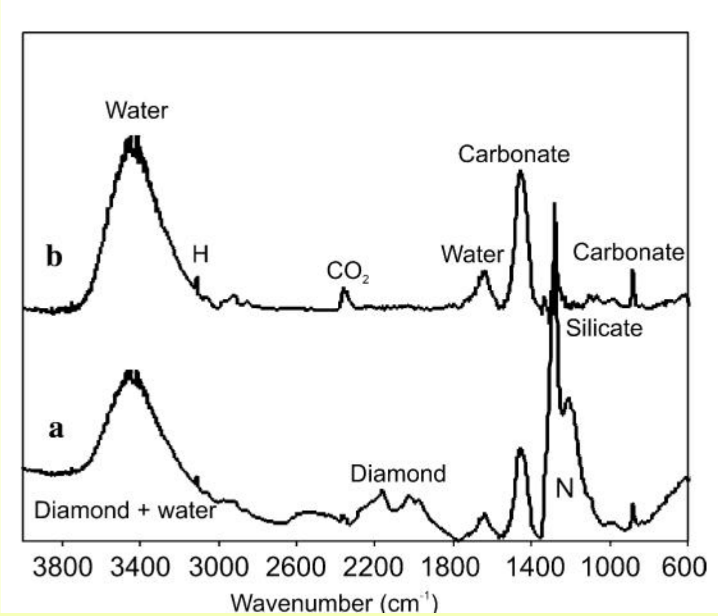
Analyses of fluid inclusions in diamond suggests the presence of carbonate-rich fluids and CO_2 in the source region.



From Klein-BenDavid et al., GCA 71 (2007)

Diamond from the Diavik Mine, Canada, contains brine and carbonate inclusions. The two fluids are thought to represent immiscibility of an original high-density carbonatitic melt to produce one fluid rich in Si, H_2O and Cl, and another carbonate-rich fluid. The carbonate end-member composition is approximately:

$K_{15}Na_{21}Ca_{6.7}Mg_{8.1}Fe_{6.2}Ba_{5.7}Si_{4.8}Ti_{1.4}Al_{1.9}O_{17}Cl_{29}(CO_3)_{29}(H_2O)_{29}$

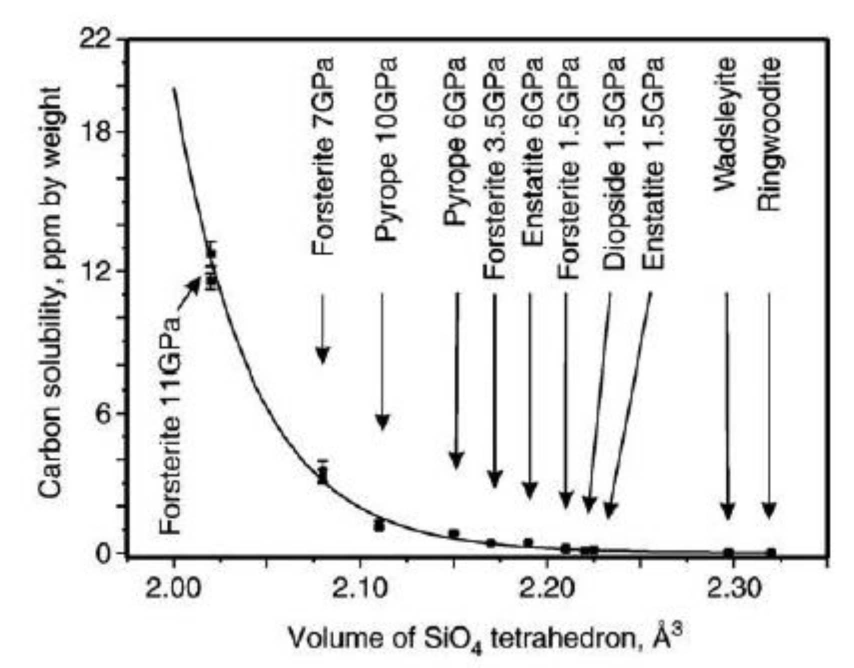


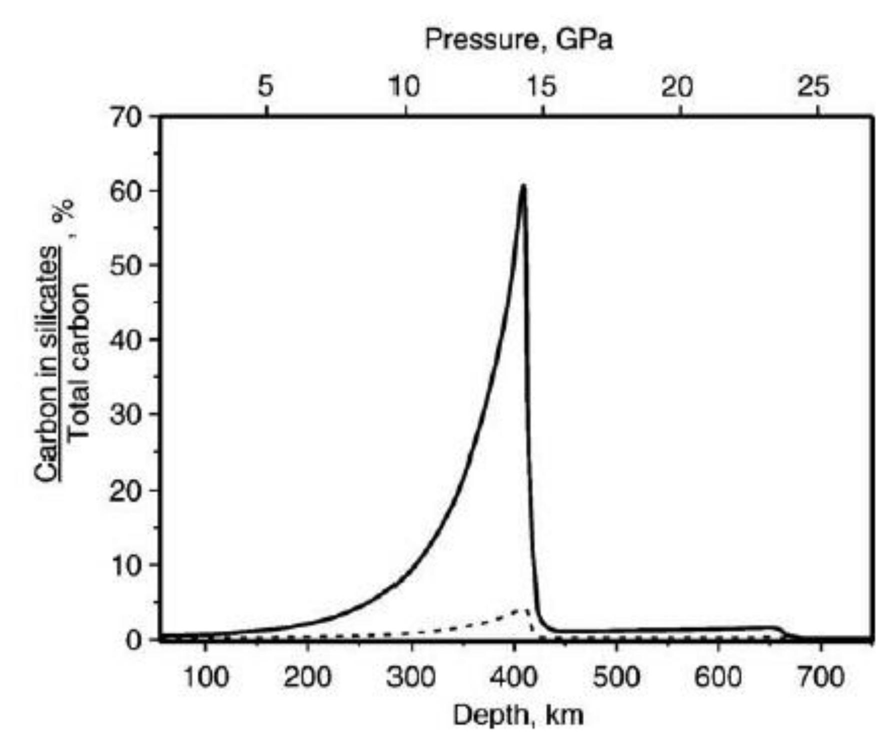
FTIR spectrum of inclusions in diamond.

(Top) After subtraction of the diamond and nitrogen peaks.

Recent work suggests that in the deeper mantle most carbon is present as defects (nano- to pico-scale FI?) in volatile-free minerals.

Carbon dissolved in volatile-free minerals can exsolve as the minerals are exposed to lower pressure conditions as a result of mantle convection.

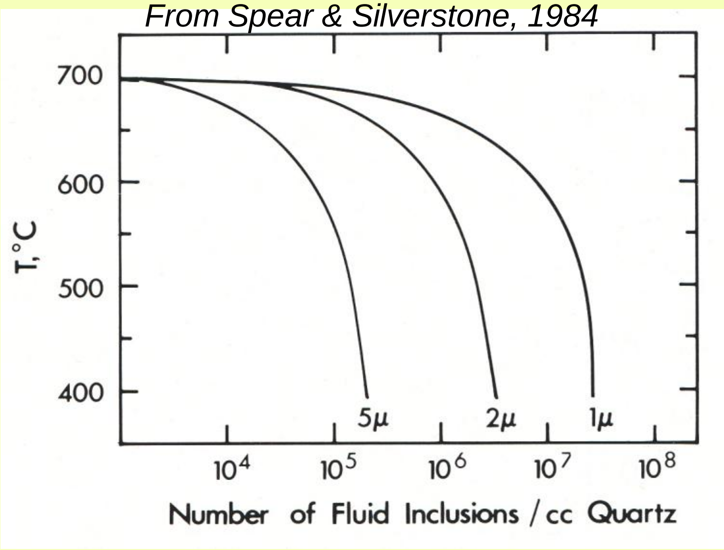




The highest proportion of carbon dissolved in volatile-free minerals is expected to occur in a thin zone of the upper mantle just above the transition zone.

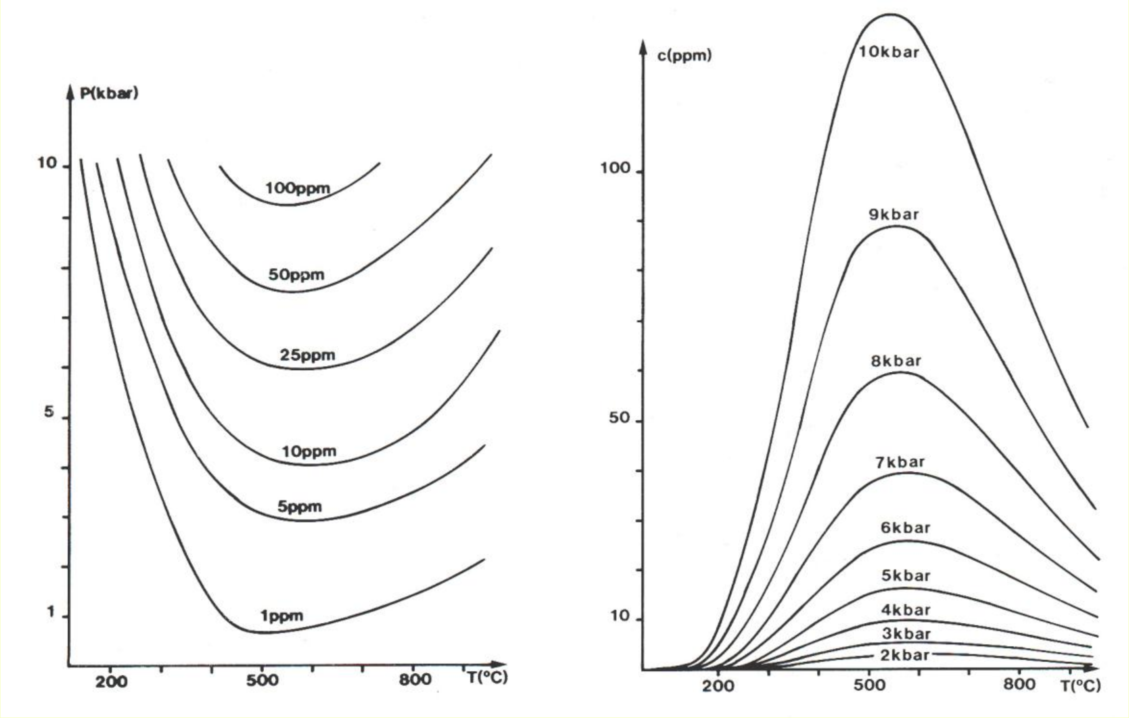
From Shcheka et al., EPSL, 2006

From Spear & Silverstone, 1984



If water is dissolved in quartz at high temperature and pressure as an OH defect, how much fluid can be generated if the H_2O exsolves during uplift?

≈ 10^7 kg H_2O per km^3 rock!



From Doukhan & Paterson,

Several tens of ppm H_2O can dissolve in quartz at high temperature and pressure. When this quartz is uplifted to the surface water may exsolve from the quartz structure to produce tiny, uniformly distributed fluid inclusions that give quartz a milky texture.

Summary

- Fluid and melt inclusions provide the most direct evidence for the composition and distribution of carbon in the Earth.
- Carbon speciation is controlled by the oxidation state of the system, which in turn depends on solid phases present.
- In organic-rich sedimentary environments and the anchi-metamorphic zone the dominant carbon species is CH_4.
- In metamorphic environments fluids evolve from being CH_4-rich to CO_2-rich with increasing metamorphic grade.
- Silicate melts contain from a few 100 (felsic) to a few 1000 (mafic) ppm CO_2.
- In the deeper upper mantle most carbon is likely present as nano- to pico-scale FI (defects) in volatile-free minerals. The dissolved C can exsolve during mantle convection to produce CO_2-rich FI that are ubiquitous in upper mantle xenoliths.

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