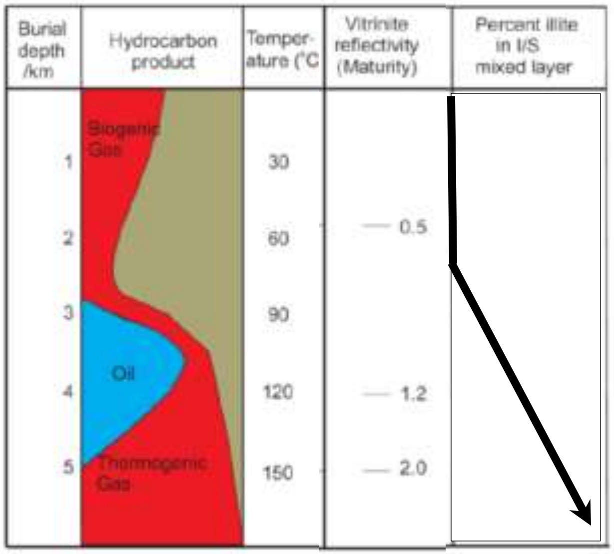
Thermodynamics of low-temperature phyllosilicates

Gaz de schiste (Fontaine ardente de Gua dans le Dauphiné)

ISTerre
Institut des Sciences de la Terre

O. Vidal

From Jiang (2012)



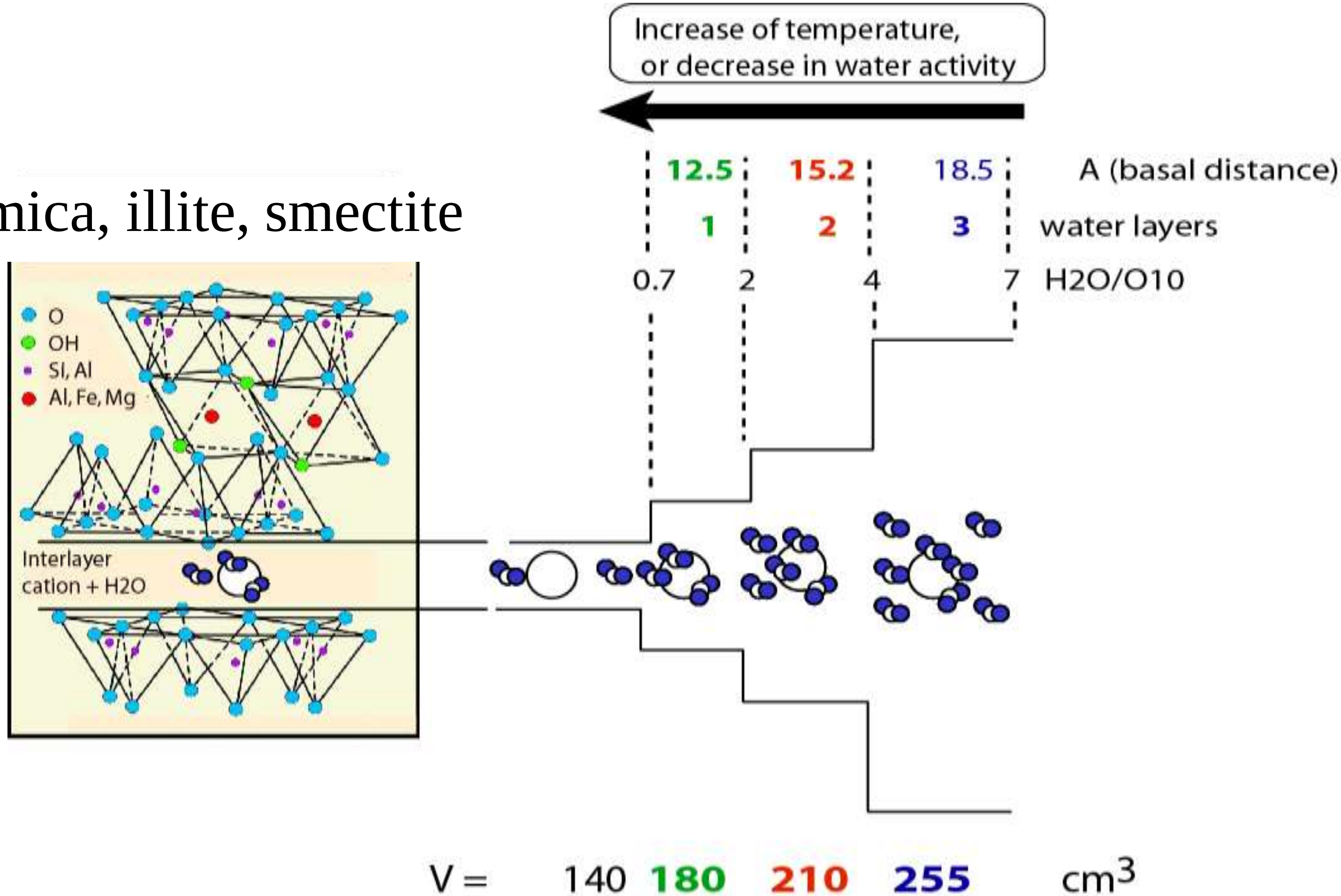
Smectite

I/S

Smectite, I/S +- kaolinite, chlorite

- Empirical thermometer and indicators of thermal maturity of hydrocarbon
- Basin tectonic evolution
- Hydrocarbon generation, migration and accumulation processes
- Diagenetic history and reservoir quality prediction

mica, illite, smectite



ΔVsolid = -20 to 30 %

150kg of water is generated per m3 of rock

Smectite dehydration or breakdown is accompanied by large variations of volume and free water production

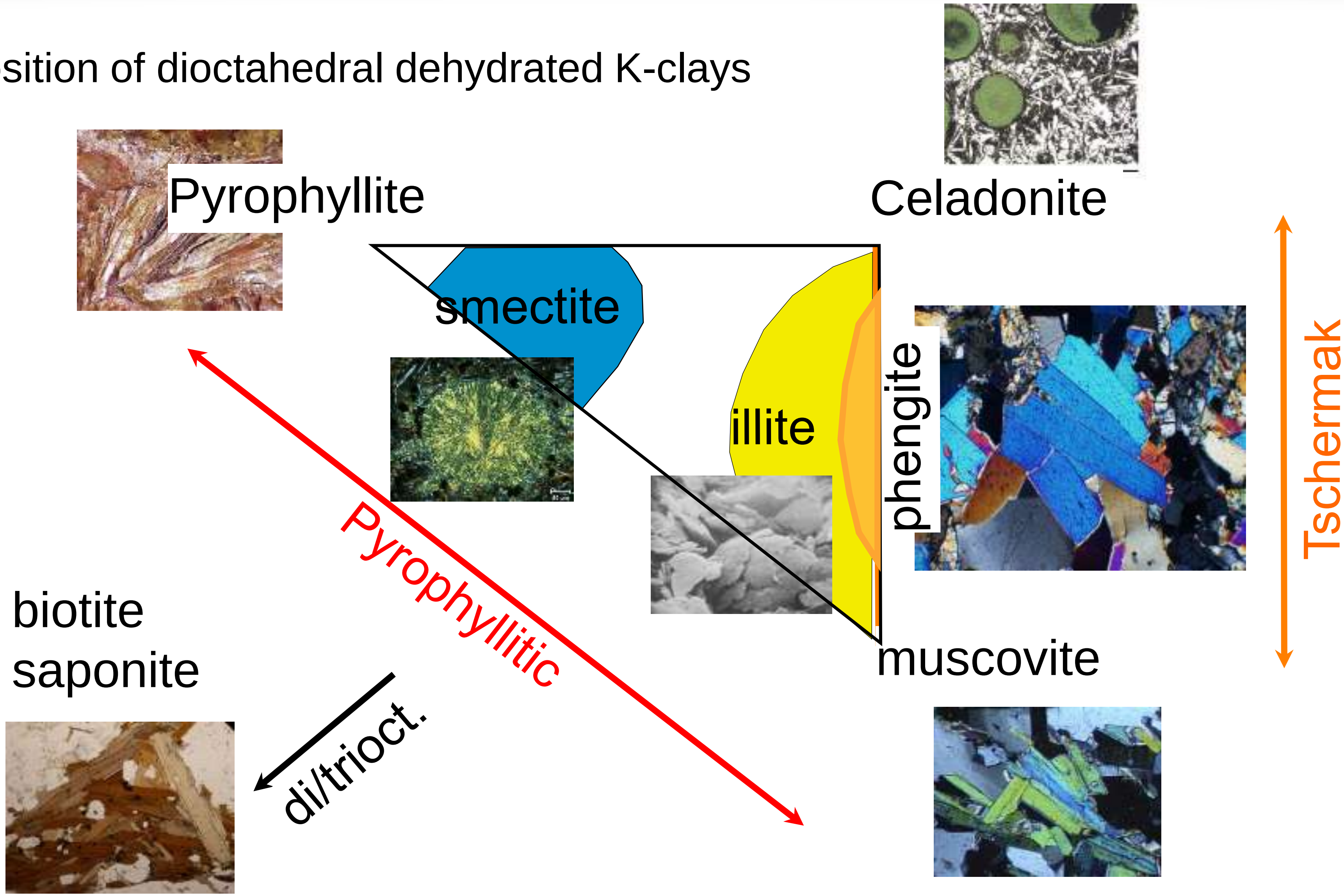
- Land subsidence (Bethke, 1986; Liu et al., 2001; Liu and Lin, 2005),
- Fracturation, variation of rock porosity and permeability
- Sediment overpressuring (Bethke, 1986; Audet, 1995) and
- Petroleum migration (Bruce, 1984)
- The formation of mudvolcanoes
- LF earthquake in subduction zones

Modeling these processes requires knowledge of the various phyllosilcates stability as a function of pressure, temperature, rock and fluid composition (water activity).

=>Thermodynamics

Main challenge of clay thermodynamics : dealing with small size (µm) minerals that present a large range of composition

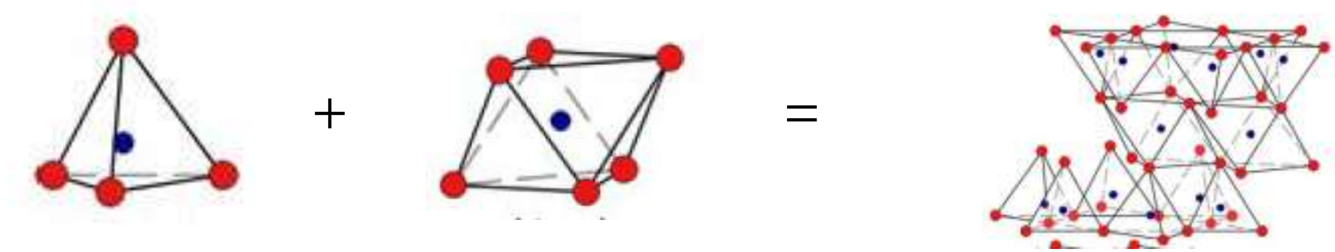
composition of dioctahedral dehydrated K-clays



Thermodynamics of clays

1. «Classical» thermodynamic databases -> thermodynamic properties of discrete (dehydrated) compositions estimated by oxide summation

Phase	Formula	$\Delta G_f°$ (cal/mol)	S° (cal/mol-K)	V° (cm^3/mol)	Heat Capacity Coefficients* a (cal/mol-K)	b x 10^3 (cal/mol-K^2)	c x 10^{-5} (cal-K/mol)
Ca-Beidellite	$Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1280912.557	58.345	129.766	82.1908	37.1515	18.0311
Ca-Montmorillonite	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	-1272306.883	59.845	133.070	80.1811	39.5011	16.6451
Ca-Nontronite	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1079810.475	67.549	135.850	78.1908	52.9315	13.2011
Ca-Saponite	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$	-1345103.557	62.328	134.359	85.2388	39.5475	14.0891

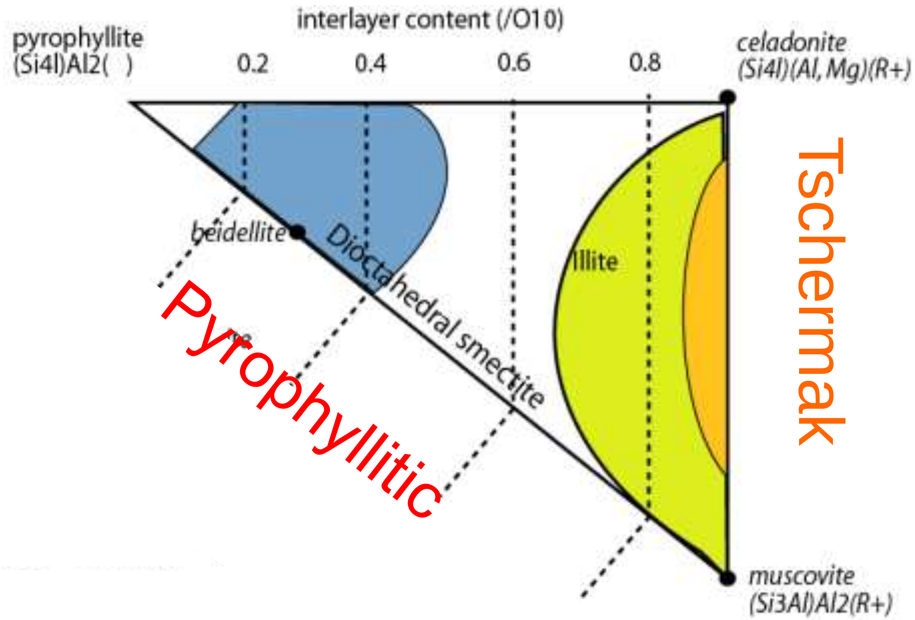


- The energetic contribution of interlayer water and solid solution are not taken into account
- Very weak experimental constraints

=> poor reliability of the results

Thermodynamics of clays

2. Solid solution approach (only the well constrained thermodynamic properties of the end-members are required).

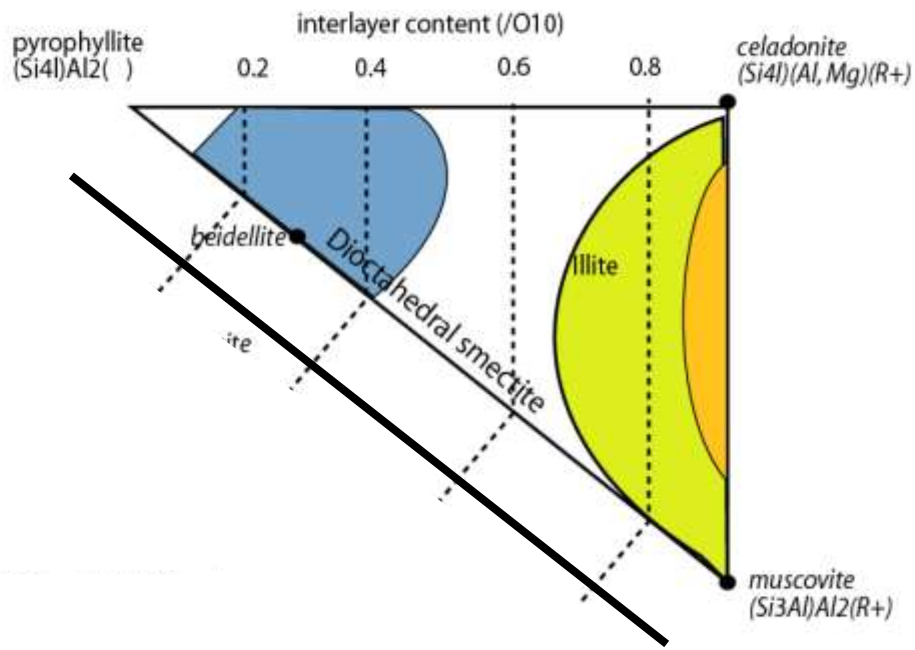


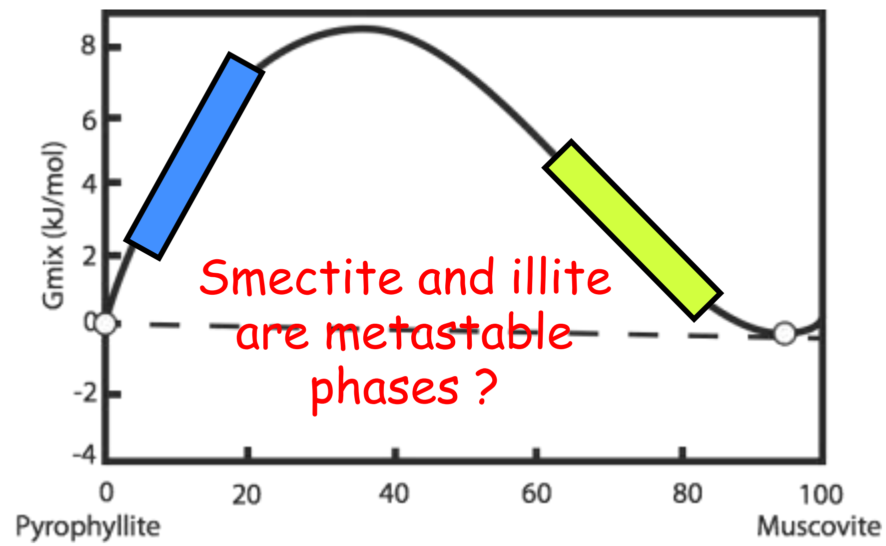
$$Gmix = X_{Prl}\mu_{Prl} + X_{Msc}\mu_{Msc} + X_{Cel}\mu_{Cel} \ldots$$

... ideal mixing

Thermodynamics of clays

2. Solid solution approach (only the well constrained thermodynamic properties of end-members are required).



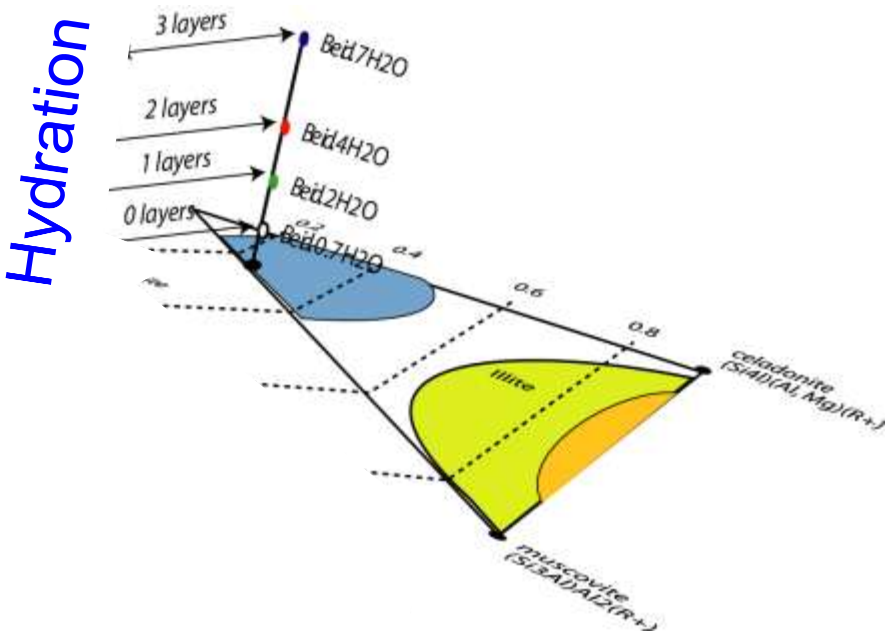


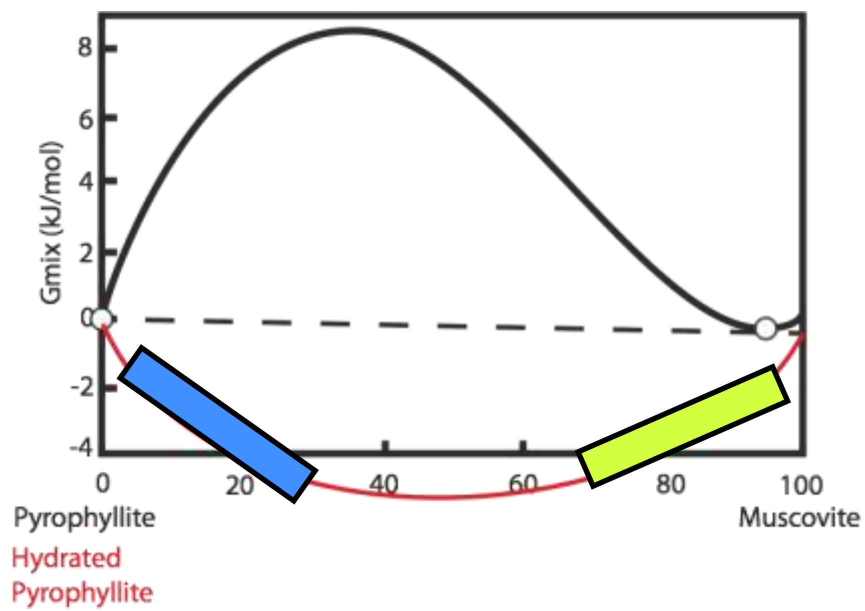
$$Gmix = X_{Prl}\mu_{Prl} + X_{Msc}\mu_{Msc} + X_{Cel}\mu_{Cel} \ldots$$

... ~~ideal mixing~~

Thermodynamics of clays

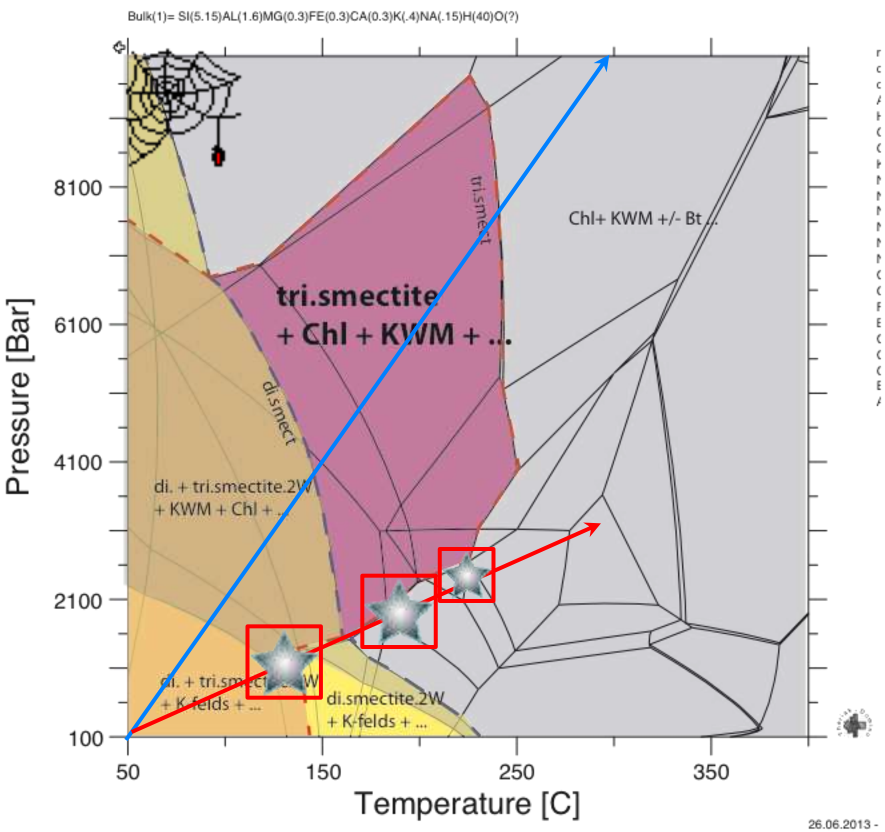
3. hybrid approach : oxide summation with hydration and full description of mixing properties (Vidal et al., 2009; Dubacq et al., 2010)



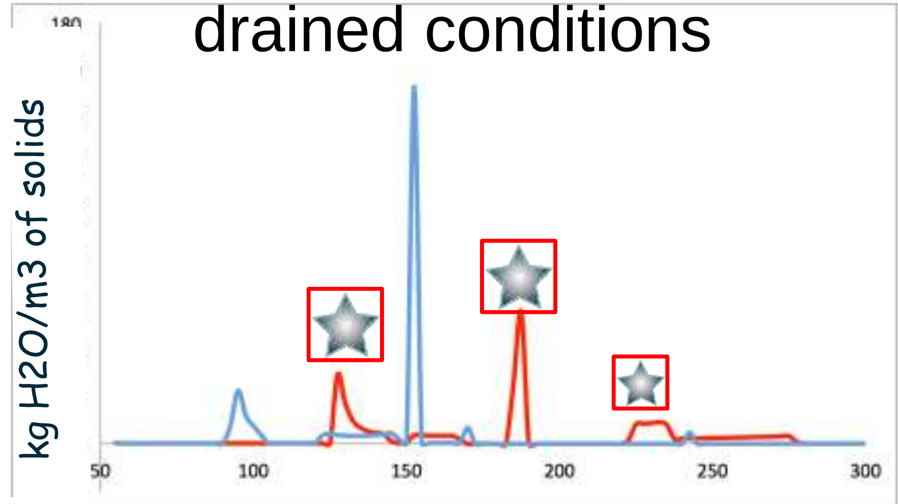


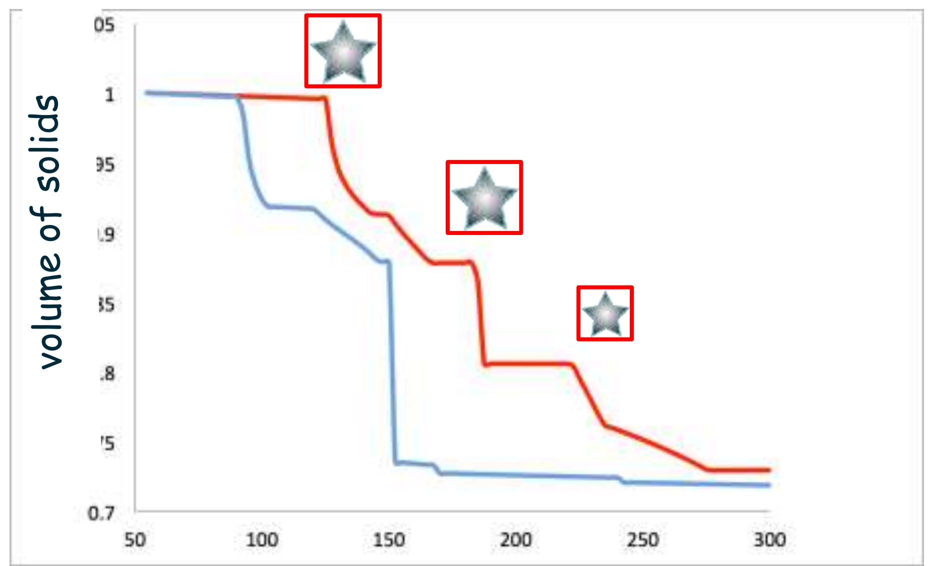
Three years ago, there was no macroscopic thermodynamic model able to account the multi-step dehydration of smectite, or to model the effect of pressure on the phase relations of clays.

Mineral reaction, water budget and rock volume change during burial diagenesis to incipient metamorphism (energy minimizing)



Average pelite composition

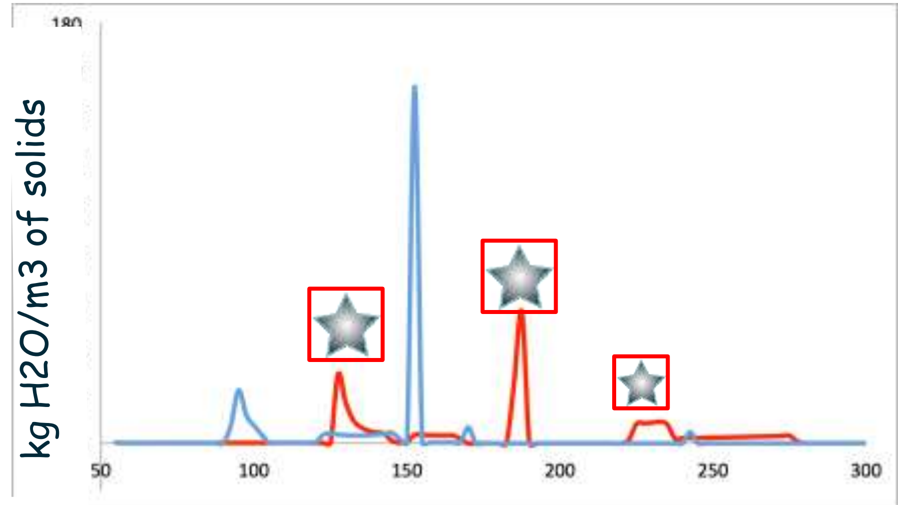


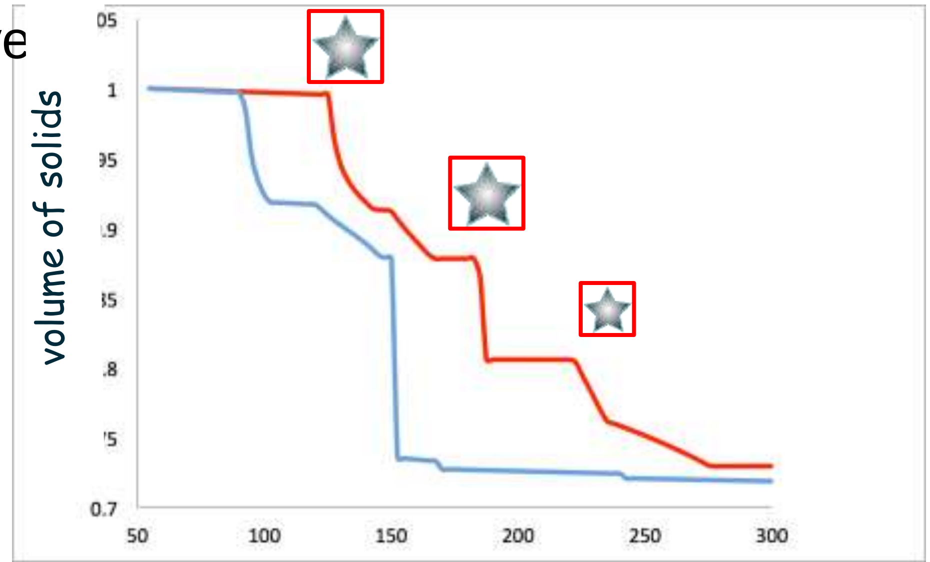


•Massive dehydration and volume change over a narrow range of T

•Variation of porosity – permeability

•Increase of P_{fluid} and reduction of effective stress ? Hydraulic fracturing ? Drained vs undrained conditions





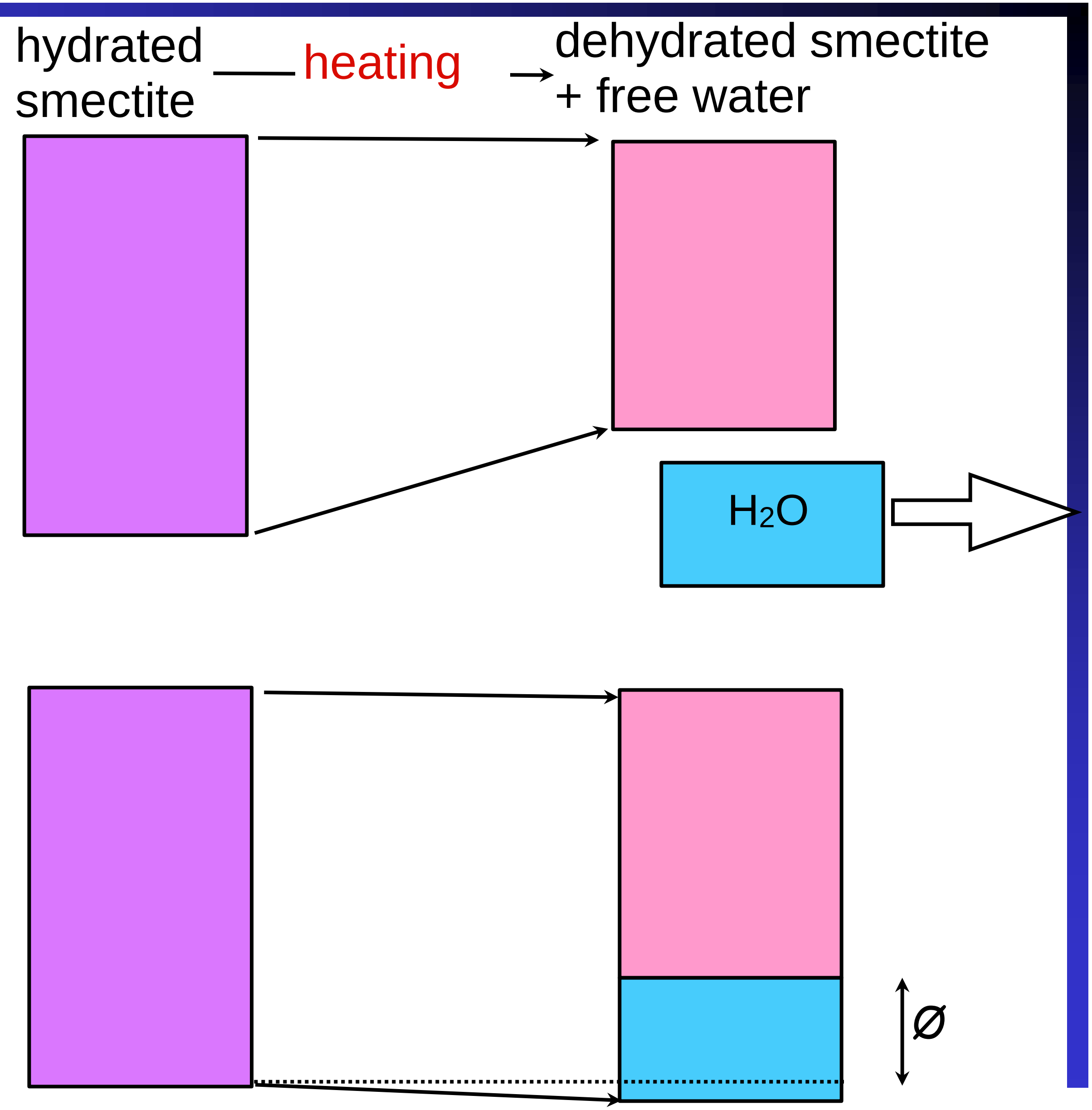
Drained conditions

Decrease of Vsolid and Vtotal

Compaction

No overpressure (Pf/PT <0.5)

$aH_2O < 1$



Closed system

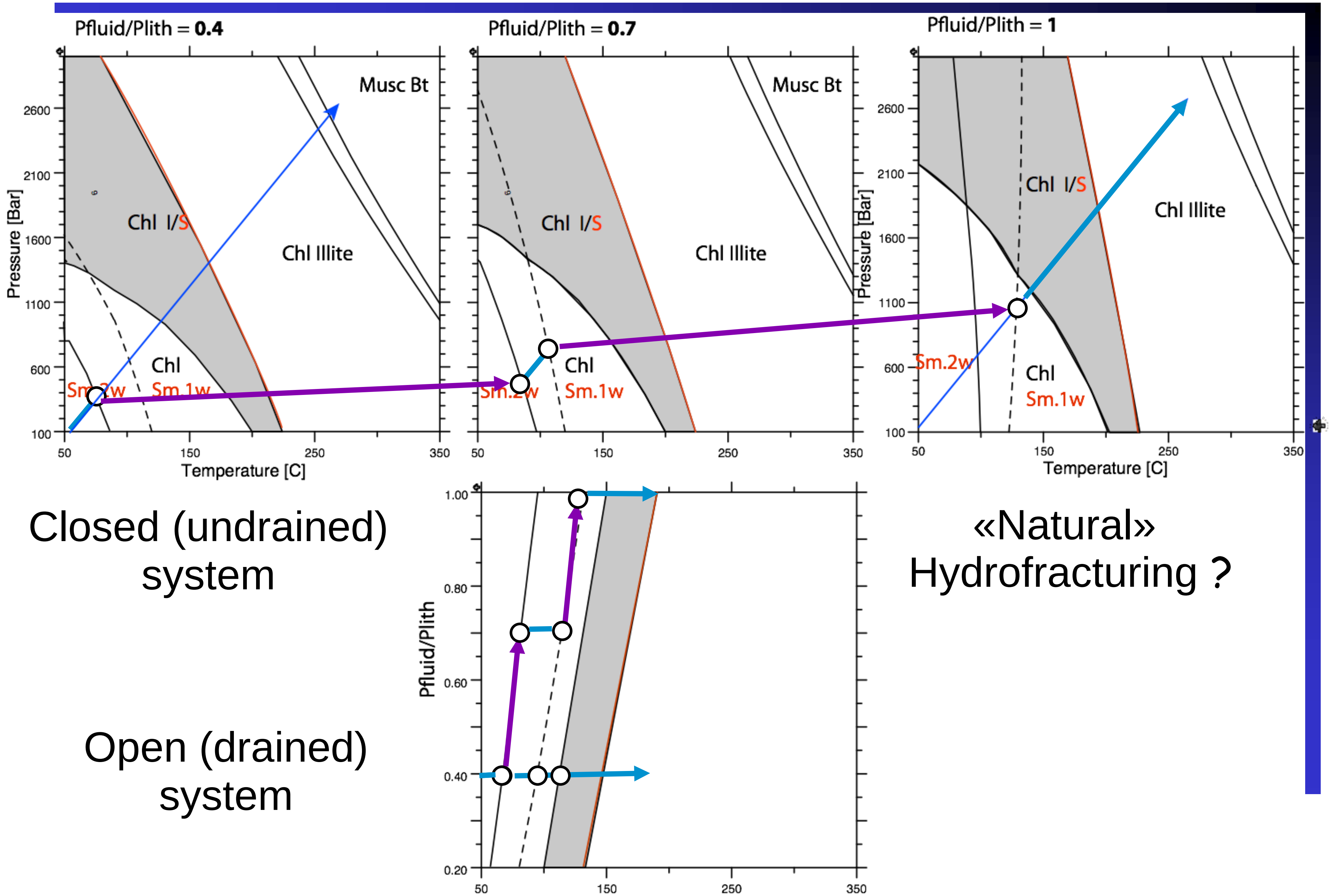
«Increase» of Vtotal

High porosity

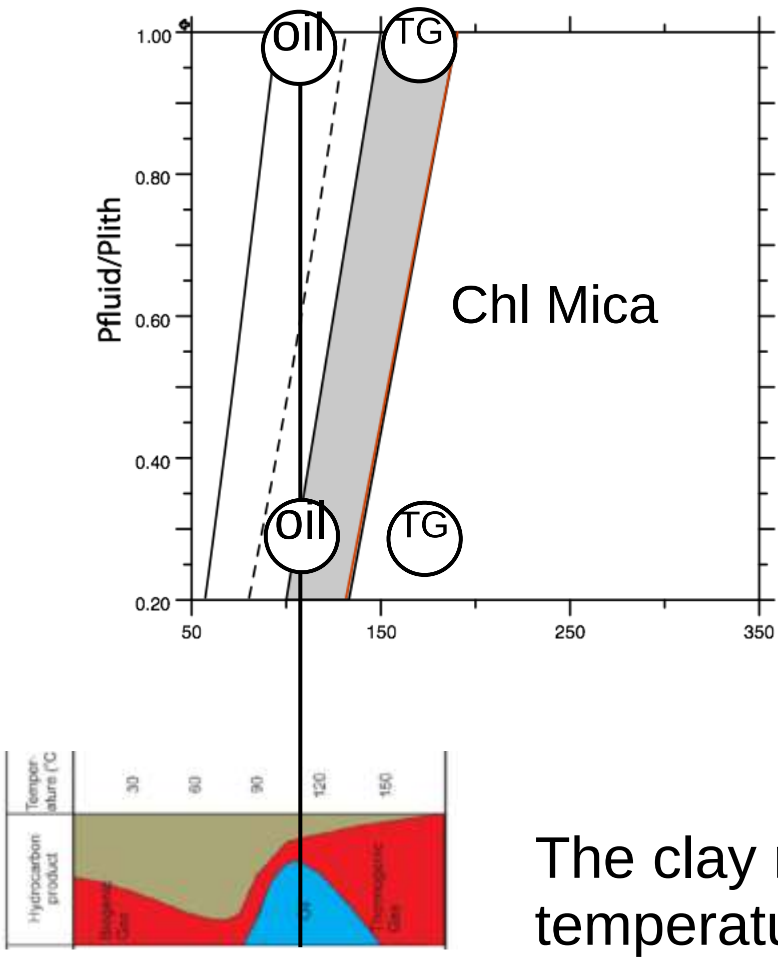
No compaction

Overpressure (Pf/PT > 0.4) until «fracturing»… gas and oil expulsion

$aH_2O = 1$

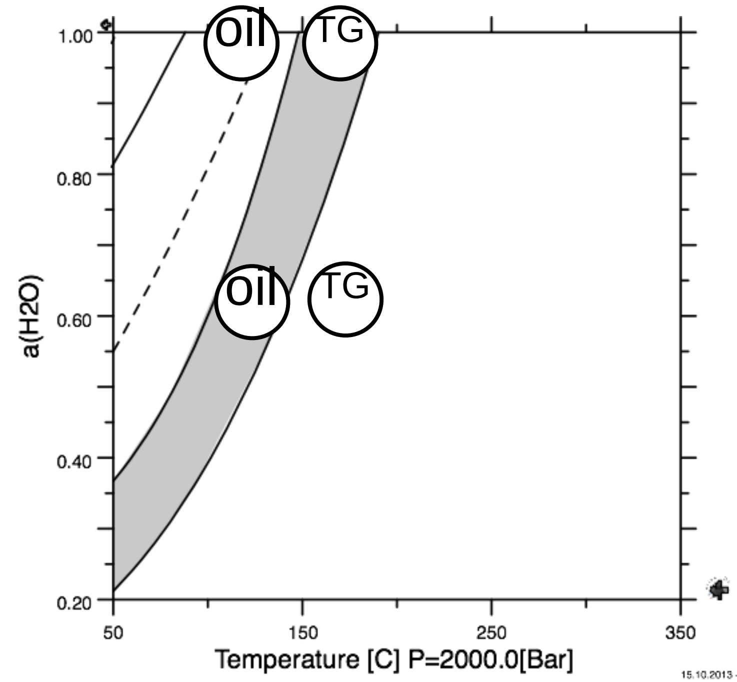


Pfluid/Plith = 0.4
Pfluid/Plith = 0.7
Pfluid/Plith = 1
Musc Bt
Musc Bt
Chl I/S
Chl Illite
Chl
Sm.2w
Sm.1w
Chl I/S
Chl Illite
Chl
Sm.2w
Sm.1w
Chl I/S
Chl Illite
Sm.2w
Chl
Sm.1w
Pressure [Bar]
Temperature [C]
Pfluid/Plith
Closed (undrained) system
Open (drained) system
«Natural» Hydrofracturing ?



smectite

transition smectite to I/S



The clay mineralogy is not sensitive to the temperature conditions only. The pressure conditions, aH_2O and Pf/Plith ratio are important parameters that should be included in the modeling of clay evolution.

Detailed modeling of clay phase relations provide information on the P, T, Pf/PL evolution, but it requires complex models... which just begin to be available

More work is necessary

- New in-situ and under pressure experimental constrains (various Pf/PL conditions, various and controlled redox conditions, etc)

- Atomistic approaches designed to derive macroscopic properties

- Natural case studies with the most recent analytical tools at the micro to kilometer scale. Combination with high-resolution geophysics

- Modeling approaches coupling thermodynamic, kinetics, transport, rock properties, mechanics

Application to a very wide range of natural conditions (Earth and extraterrestrial) and industrial processes, including the extraction of schists gas and oil