Innovative Approaches of Carbonate Diagenesis Characterization to Predict Thermochemical Sulphate Reduction (TSR) Occurrence in Sedimentary Basins*

Marta Gasparrini[1], Xavier Mangenot[1], Alexy Elias Banhan[1], Isabelle Kowalewski[1], Xavier Guichet[1], Tristan Euzen[2], and Nicolas Maurand[1]

Search and Discovery Article #42370 (2019)**
Posted April 29, 2019

*Adapted from oral presentation given at AAPG Middle East Region GTW, Regional Variations in Charge Systems and their Impact on Petroleum Fluid Properties in Exploration, Dubai, UAE, February 11-13, 2019
 DOI:10.1306/42370Gasparrini2019

[1]Geosciences Division, IFP Energies nouvelles, Rueil-Malmaison, France (nicolas.maurand@ifpen.fr)
[2]FP Technologies (Canada), Calgary, Canada

Abstract

The reconstruction of paleo-fluid circulations in sedimentary basins is often under-constrained. This results from both the analytical challenge of performing the required analyses on the diagenetic mineral phases available in small quantities and the lack of tracers for some of the key diagenetic parameters (temperature, timing, fluid composition). Modern thermal reconstructions rely on various thermochronology methods such as fission-track, (U-Th)/He or K-Ar systems on U- or K-rich minerals, generally limited to siliciclastic lithologies. Carbonate rocks do not contain such mineral phases, limiting the possibilities to evaluate their thermal history. Given the widespread occurrence of carbonate lithologies, and their ubiquity in a variety of crustal and sedimentary settings, the development of a carbonate thermo-chronometer would open a new realm of applications in basin analysis. By coupling carbonate clumped isotope Δ47 thermometry, laser ablation U-Pb dating and fluid inclusion studies, new perspectives are opened for determining the temperatures of carbonate diagenetic phases together with the origin and composition of their parent fluids.

To validate these approaches on a well constrained case history, analyses were performed on carbonate specimens from 2000 m deep cores in a Middle Jurassic reservoir formation of the Paris Basin (France). Laser ablation U-Pb dating was achieved on low U-bearing carbonates with an absolute uncertainty between 2.2 Ma and 16 Ma across a time span from 154 to 37 Myrs. These ages revealed successive phases of carbonates precipitated from early to late diagenetic conditions. The integration of these U-Pb data with Δ47 paleo-temperatures allowed defining time-temperature couples for each carbonate phase investigated that directly reveal the thermal history of the reservoir unit. This time-temperature path well agrees with the thermal scenario modelled on underlying shale layers and calibrated against organic matter maturity. This emerging carbonate Δ47/(U-Pb) thermo-chronometer has thus the ability to accurately and self consistently reconstruct thermal and fluid-flow histories of carbonate-bearing rocks within the oil window maturity zone (0-120°C). Then, this methodology was applied to constrain the occurrence of the Thermochemical Sulphate Reduction (TSR) reaction during the burial history of carbonate reservoirs from the Western Canada Sedimentary

Basin. The study focused on the Devonian reefal carbonate reservoirs of the Nisku and Leduc formations, where some hydrocarbon fields have experienced TSR and contain up to 30% of H_2S. Seven cores were chosen from areas of the basin having experienced different thermal histories and characterized by contrasting H_2S production. The thermal information obtained from calcite fluid inclusions was combined with the burial-thermal history modelled for Devonian rocks of each of the investigated cores. This allowed to infer possible timing and fluid geochemistry for the occurrence of TSR reaction at basin scale.

Reference Cited

Machel, H.G., and B.E. Buschkuehle, 2008, Diagenesis of the Devonian Southesk-Cairn Carbonate Complex, Alberta, Canada: Marine cementation, burial dolomitization, thermochemical sulfate reduction, anhydritization, and squeegee fluid flow: Journal of Sedimentary Research, v. 78/5, p. 366-389.

INNOVATIVE APPROACHES OF CARBONATE DIAGENESIS CHARACTERIZATION TO PREDICT TSR OCCURRENCE IN SEDIMENTARY BASINS

CONTRIBUTION FROM CLUMPED ISOTOPES (Δ47) THERMOMETRY, LASER ABLATION U-PB CHRONOMETRY AND FLUID INCLUSION STUDIES

M.GASPARRINI[1], X. MANGENOT[1], A. BANHAN[1], I. KOWALEWSKI[1], X. GUICHET[1], T. EUZEN[2], N. MAURAND[1]

1 - IFP ENERGIES NOUVELLES (PARIS) – GEOSCIENCES DIVISION

2 - IFP CANADA (CALGARI)

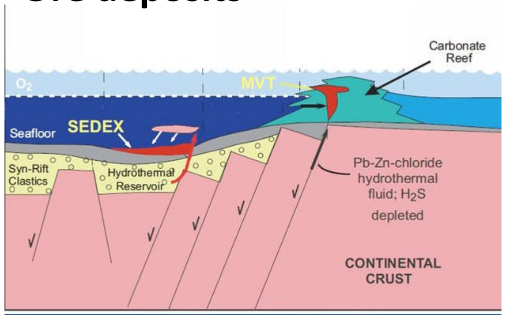
OVERVIEW

RESPONSIBLE
OIL AND GAS

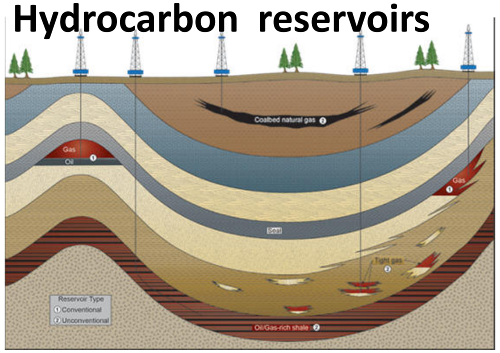
- Carbonate Diagenesis, what for?
- Conventional / advanced Thermometry - Chronometry
- Application on basin scale
  - Paris basin for temperature calibration
  - Western Canadian Basin for TSR occurence

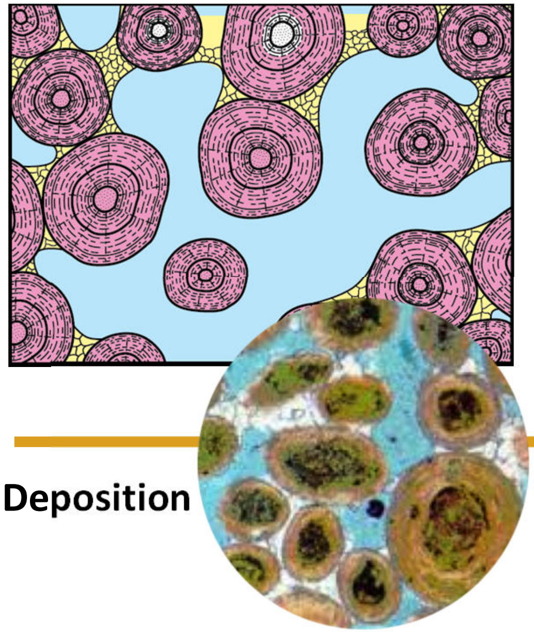
CARBONATE DIAGENESIS: WHY WE CARE?

Ore deposits

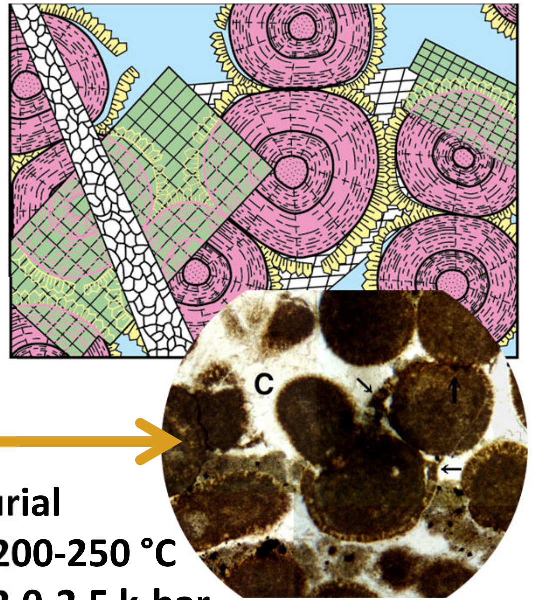


Hydrocarbon reservoirs





Deposition



Burial
< 200-250 °C
< 2,0-2,5 k-bar

Processes

- **Recrystallization**
- **Dolomitization**
- **Cementation**
- **Thermo-Chemical Reduction (TSR)**

↓

Kind of fluid? When was that? Which conditions?

→ **Temperature (T)**

→ **Pressure (P)**

→ **Timing (t)**

→ **$\delta^{18}O_{fluid}$**

→ **Salinity**

The most hunted parameters governing diagenesis !

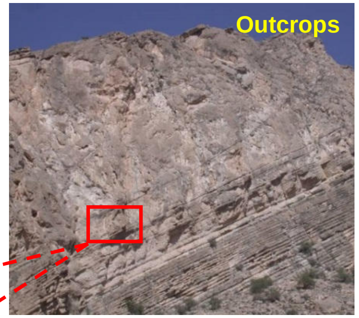
TOOLS FOR INTEGRATED STUDIES

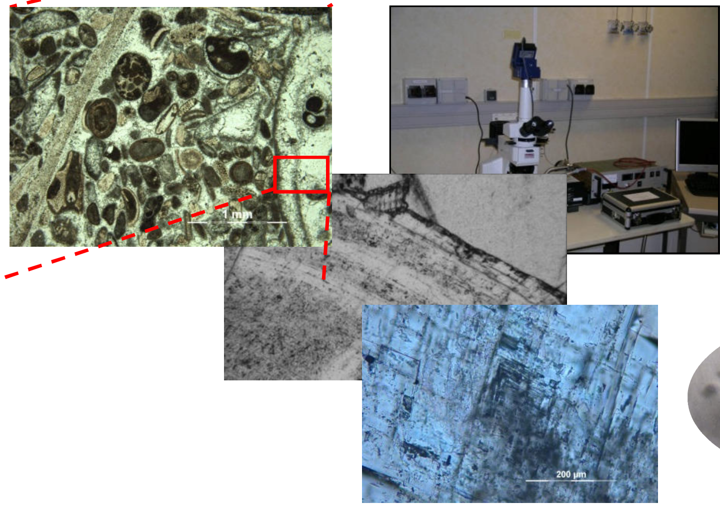
– *Field / cores observation (macro-, mesoscopic study)*

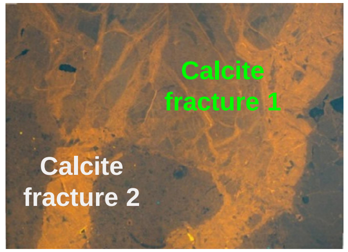
– *Petrographic tools (microscopic study)*

– *Fluid inclusions (micron-scale study)*

– *Geochemistry s.l. (atomic-scale study)*







Fluorescence

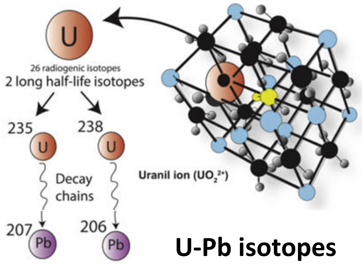
Cathodoluminescence

SEM

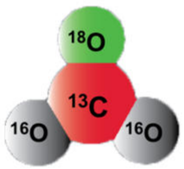
Microthermometry

Raman

FT-IR



U-Pb isotopes



Clumped isotopes (Δ_{47})

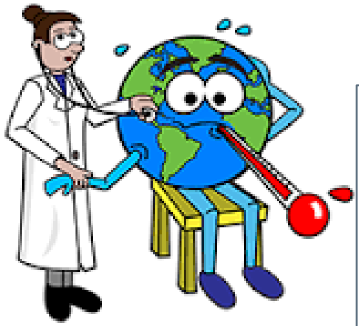
New developments promise to overcome limitations of conventional approaches

Potential to unravel carbonate diagenesis key parameters: T, P, t, $\delta^{18}O_{fluid}$

OVERVIEW

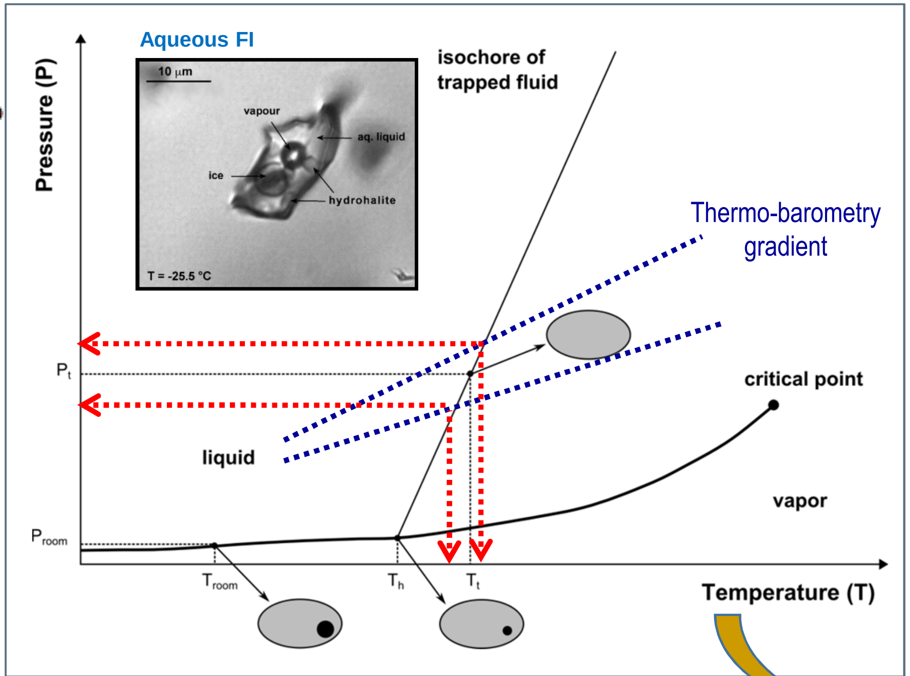
- Carbonate Diagenesis, what for?
- Conventional / advanced Thermometry - Chronometry
- Application on basin scale
  - Paris basin for temperature calibration
  - Western Canadian Basin for TSR occurence

CONVENTIONAL THERMOMETERS & FLUID TRACERS IN CARBONATE DIAGENESIS



1) Fluid Inclusions (FI) microthermometry

- Temperature - Salinity - Pressure



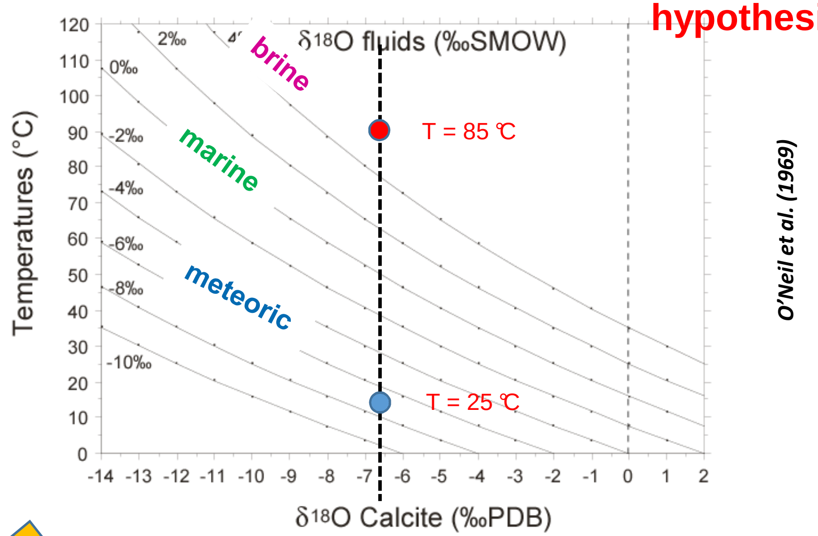
Common practice

Limitations of FIs in carbonates: small, metastable, reequilibrated…

2) Carbonate-fluid O isotope equilibrium

$$\delta^{18}O_{fluid} = f\,(T, \delta^{18}O_{carb})$$

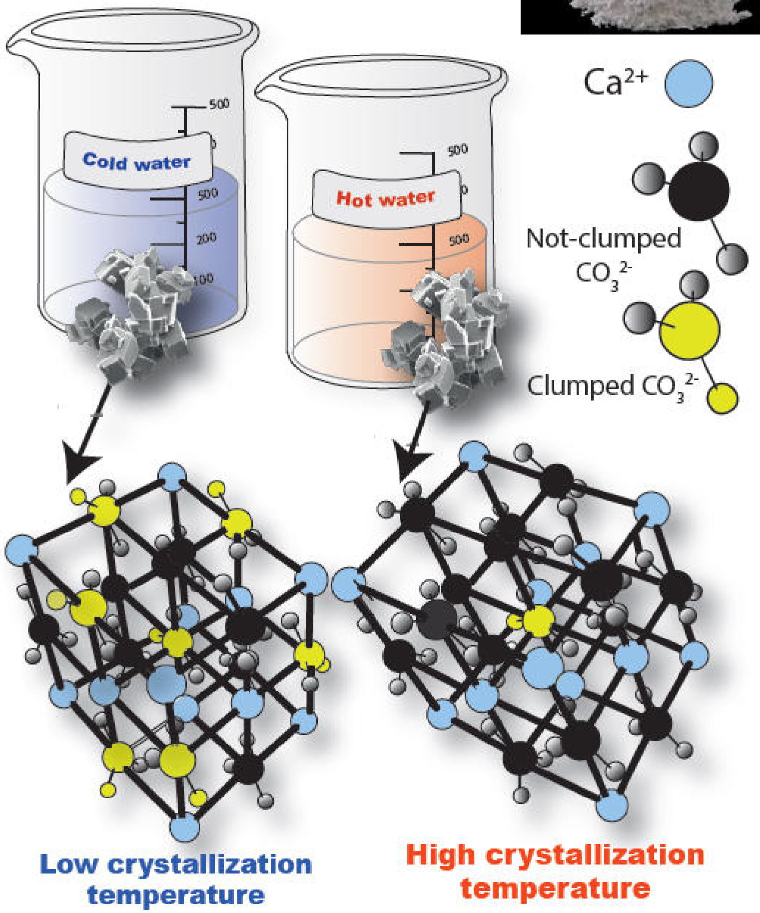
Need of hypothesis



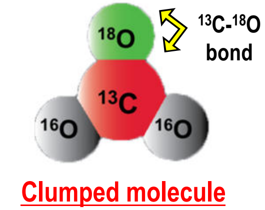
Measured = known

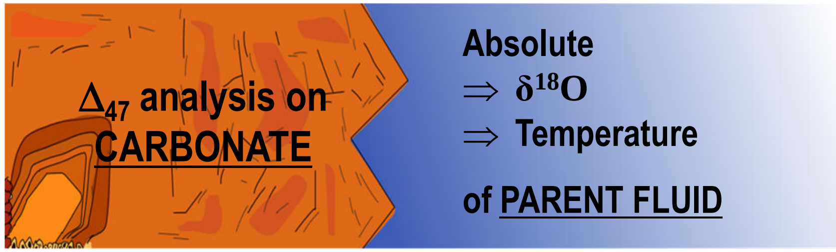
$\delta^{18}O_{fluid}$ may vary through time, difficult to predict for burial diagenetic carbonates

« NEW » THERMOMETER & FLUID TRACER : CLUMPED ISOTOPES (Δ_{47})



- Abundance of ^{13}C-^{18}O in carbonate molecules ➔ function of crystallisation T
- Applicable to ≠ mineralogy (calcite, dolomite…) in the 0 to 200 ° C ➔ diagenesis realm
- Allows to reconstruct independently the $\delta^{18}O_{fluid}$ composition ➔ marine, meteoric, brine...





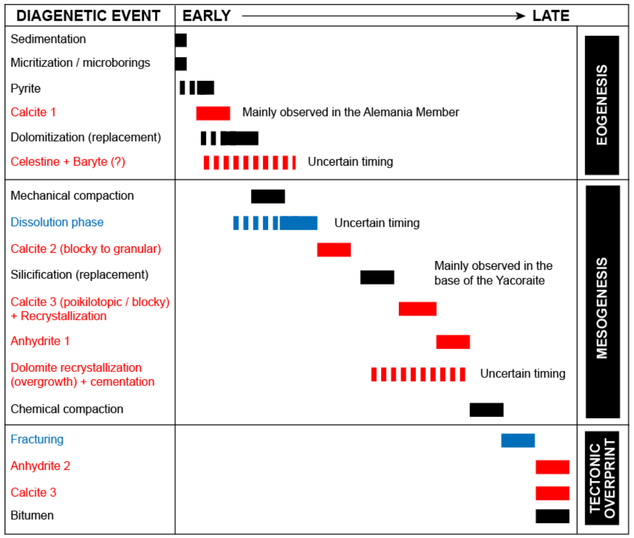
Overcomes many limits of fluid inclusion microthermometry (optical, thermal reequilibration, metastability…)

BUT: very few study on natural samples

CONVENTIONAL « CHRONOMETERS » IN CARBONATE DIAGENESIS

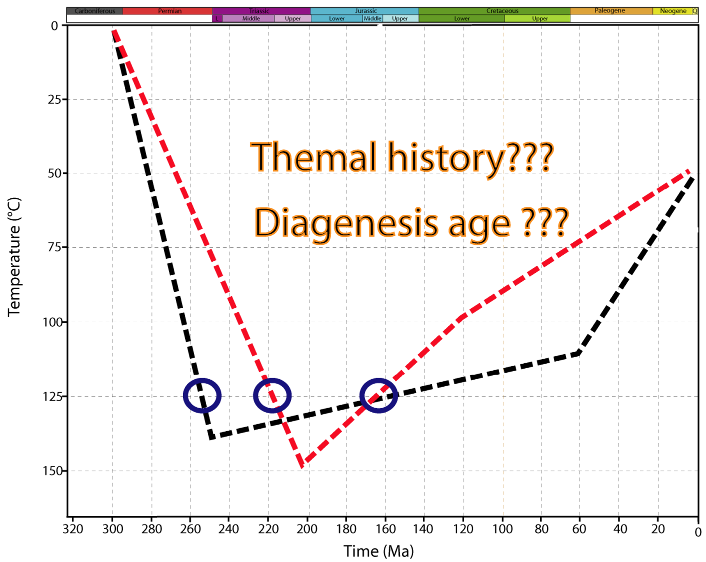
Strongly « user » dependent

<u>Relative</u>: Paragenesis



Based on cross-cutting relationships between carbonate phases

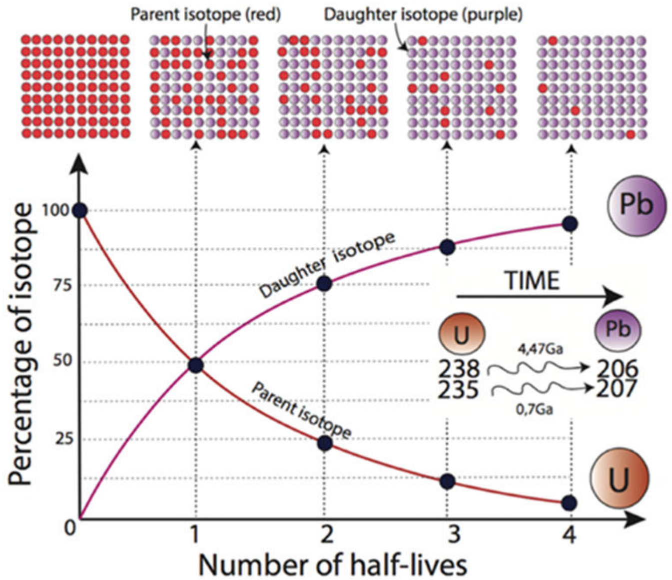
<u>Indirect</u>: FIs + thermal modeling



In basins with well-known burial-thermal histories: fitting FI microthermometry data with modeled thermal curves.

- **Uncertainties in thermal model and FI data**
- **Thermal equilibrium hypothesis**
- **Different age solutions for a given T**

<u>Absolute</u>: U-Pb decay series



Used since the '80s via **ID-TIMS**. Strong limits: high U contents needed, large volumes required, bulk analysis, time consuming

Absolute constraint on diagenesis timing, though so far seldom applied…

« NEW CHRONOMETER » : U AND PB DATING

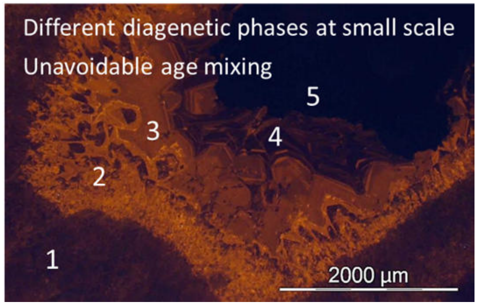
U-Pb absolute dating of carbonate minerals

by Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS)

- In situ ablation on thin section or slab
- **Spot size: 213µm (or less)**
- **U detection limit: 0.1 – 0.04 <u>ppb</u>**
- Very light sample preparation
- **Pre-screening to detect good spots for dating**

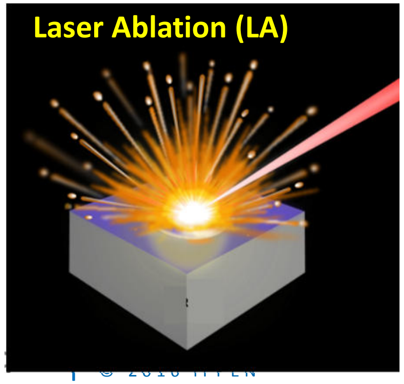
No sample destruction
No phase mixing

Suitable for low U minerals
No time consuming

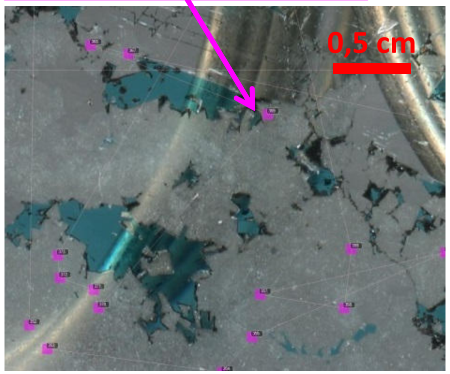


Best if

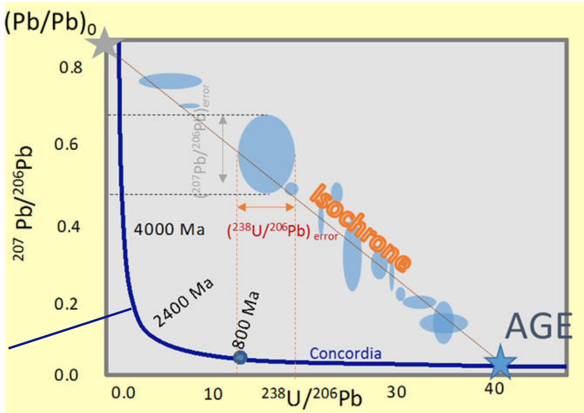
- High heterogeinity in the U/Pb and Pb/Pb ratios
- U/Pb is high
- No mixing among phases (ex. partial dolomitization)



Laser Ablation spots (~200µm) on thin section



Concordia CURVE: locus of point giving concordant ages with the two U decays series (^{238}U-^{206}Pb and ^{235}U-^{207}Pb)



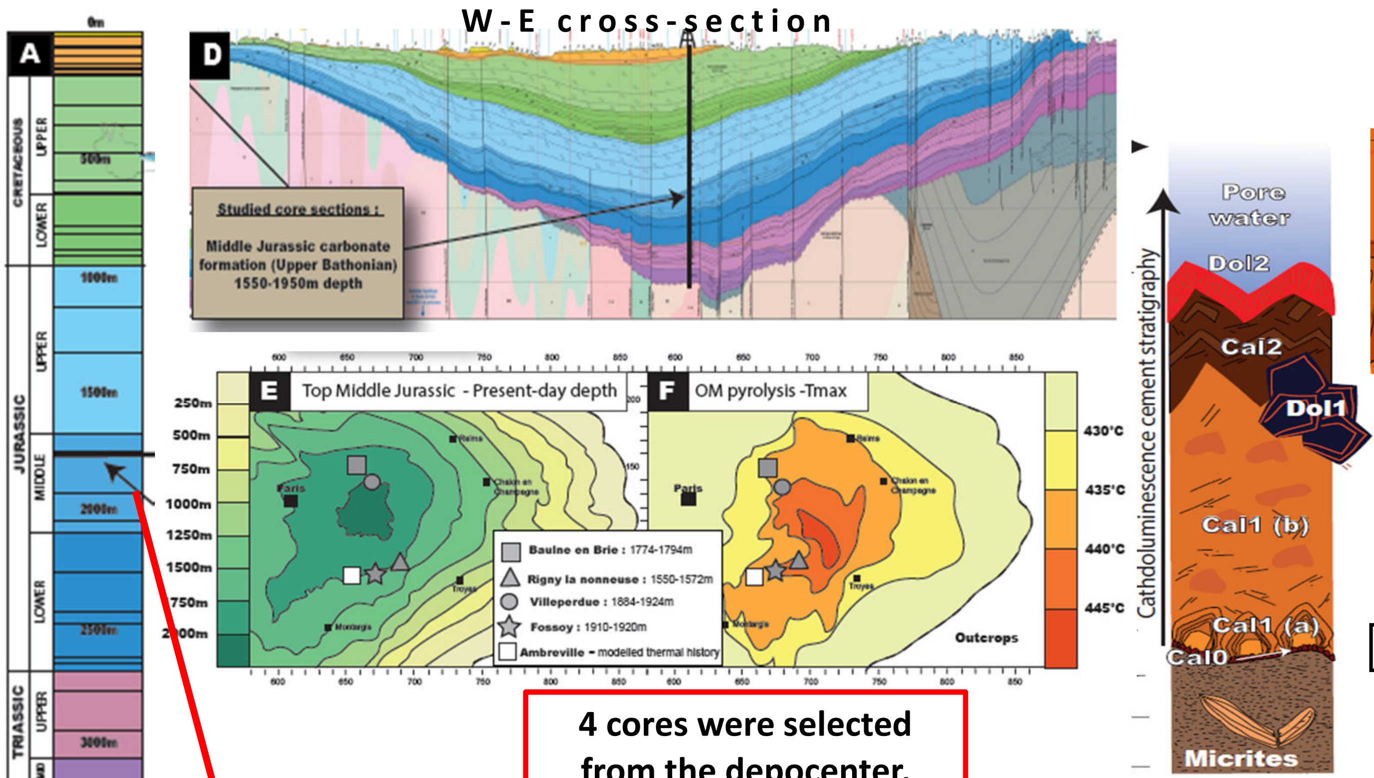
TERA-WASSERBURG DIAGRAM

OVERVIEW

- Carbonate Diagenesis, what for?
- Conventional / advanced Thermometry - Chronometry
- Application on basin scale
  - Paris basin for temperature calibration
  - Western Canadian Basin for TSR occurence

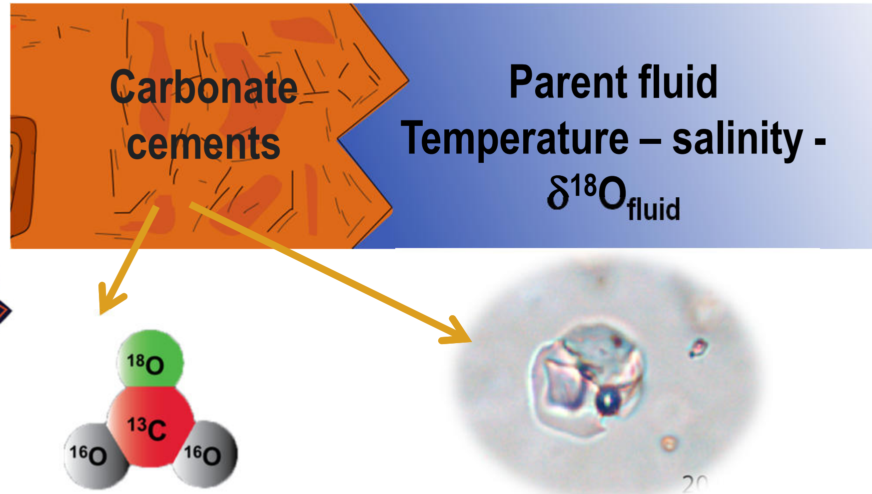
PARIS BASIN

THERMAL AND FLUID-FLOW HISTORY (MIDDLE JURASSIC, PARIS BASIN)



Present depth: 1,6-1,9 km
Max heating: 90-95 ° C

4 cores were selected from the depocenter, similar thermal history (T_{max} Toarcian 435-440 °C)



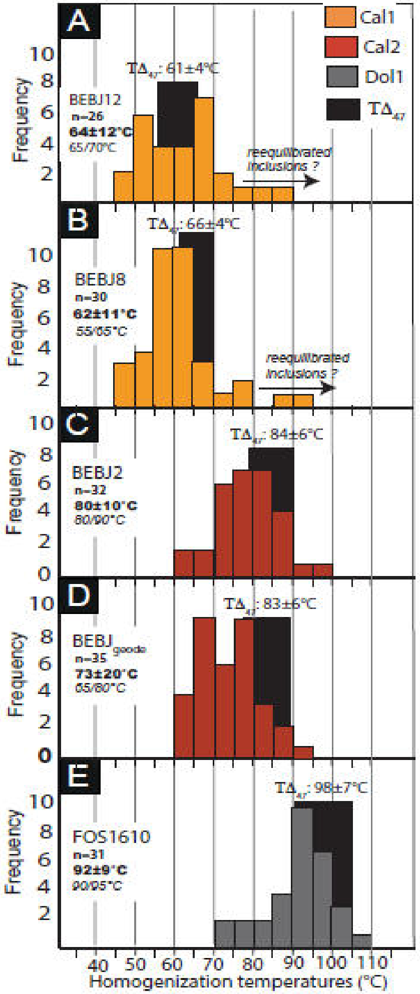
~15 mg of carbonate powder

Single FI analysis (few µm)

PARIS BASIN

Δ_{47} VALIDATION ON NATURAL BURIAL CALCITES AND DOLOMITES (60-100°C)

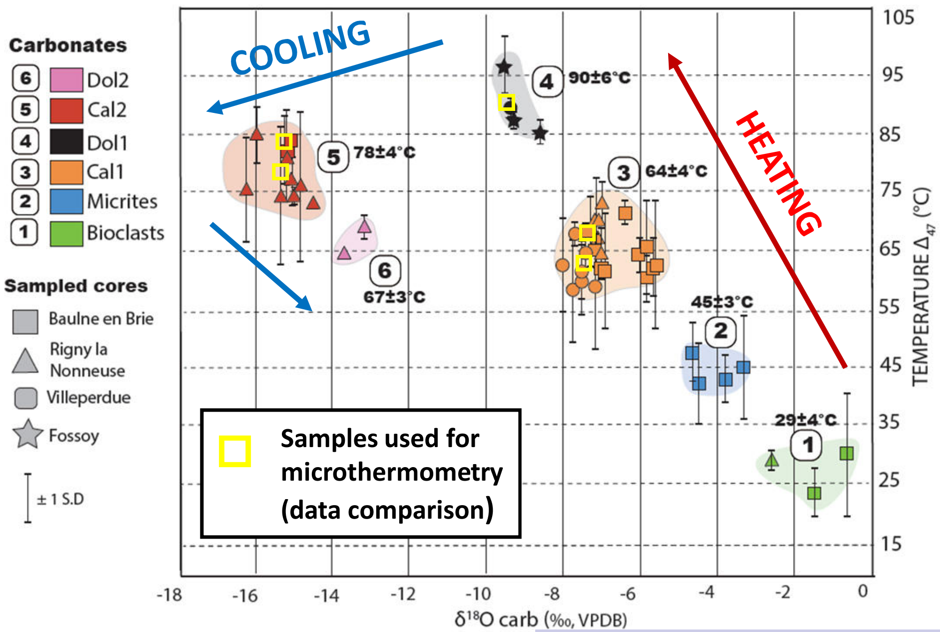
5 Cal-Dol cements with uniform CL, $\delta^{18}O$, $\delta^{13}C$, Primary FIs

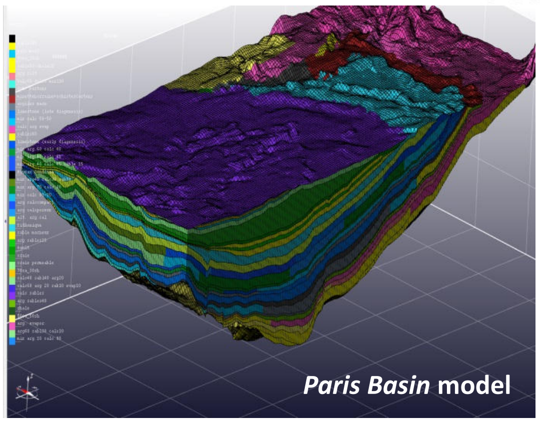


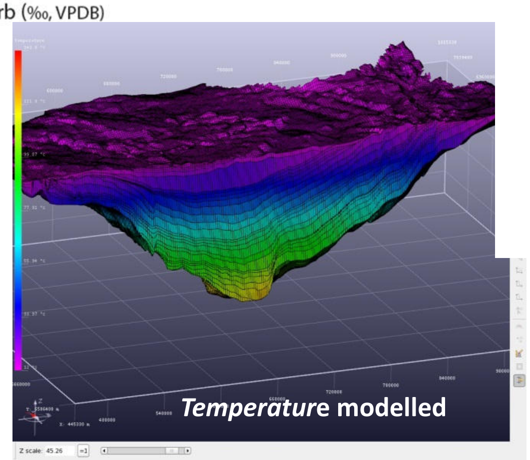
- Excellent match between the two thermometers for T between 60-100 °C.
- Overcome microthermometry limits due to metastability ➔ less time-consuming temperature measurements
- Variable salinity of the parent fluids does not affect the Δ47 signal.

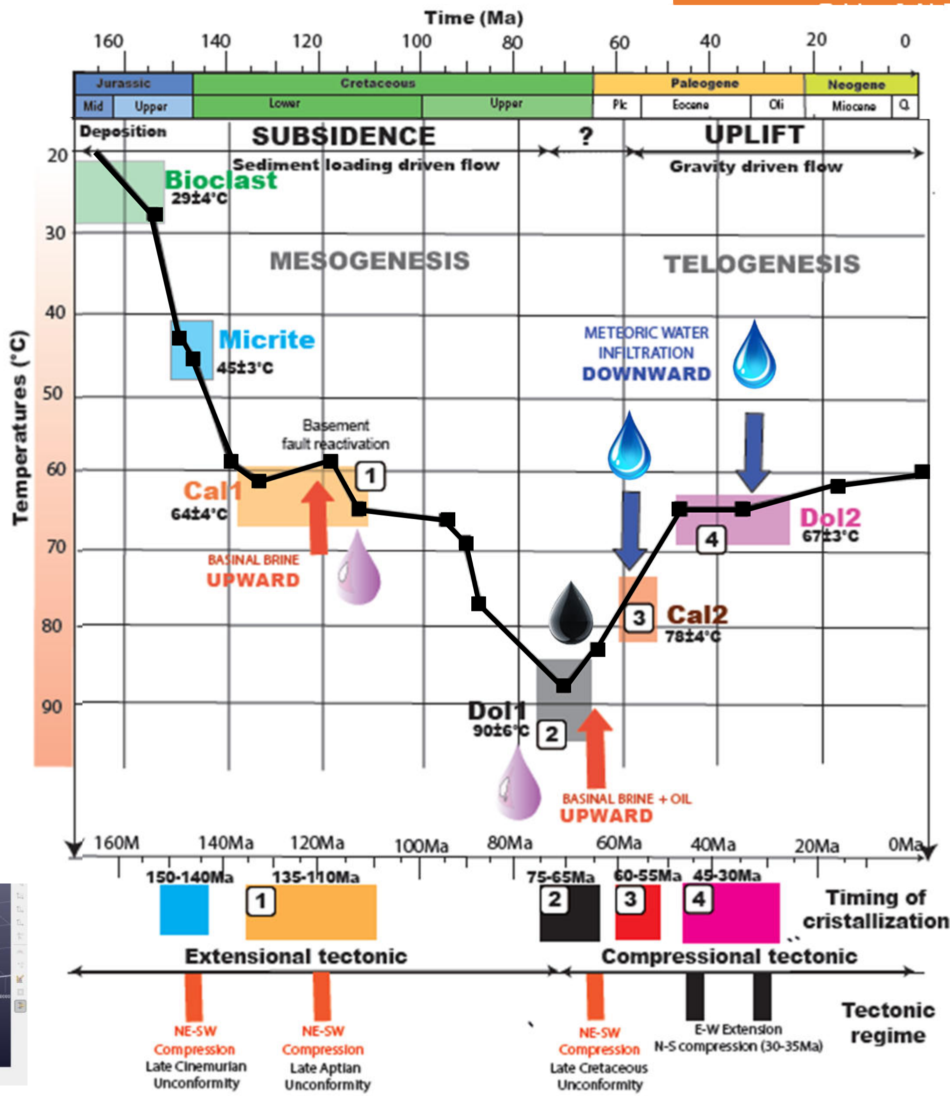
PARIS BASIN

THERMAL AND FLUID-FLOW HISTORY (MIDDLE JURASSIC, PARIS BASIN)



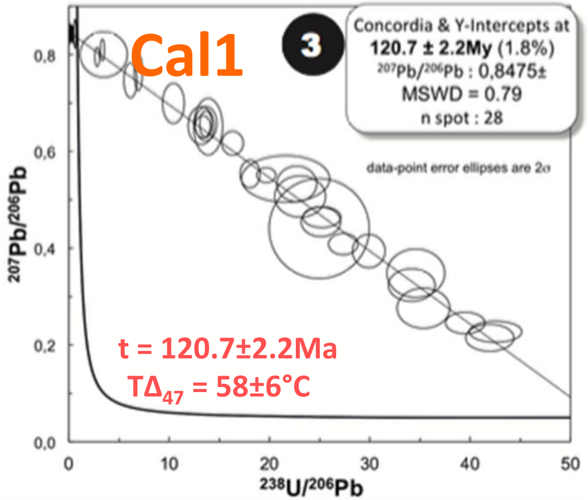


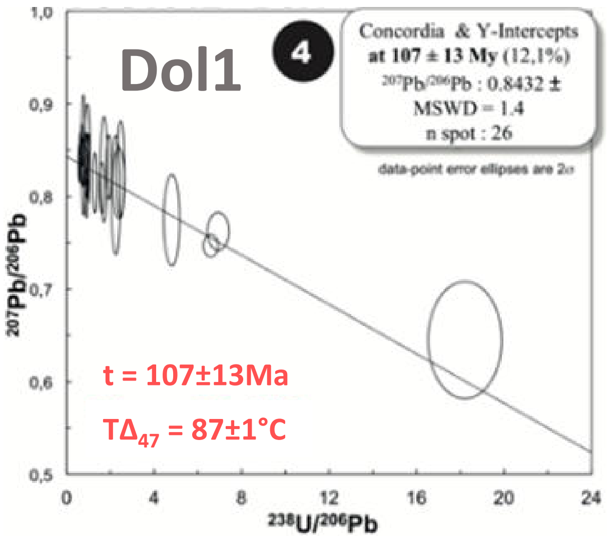


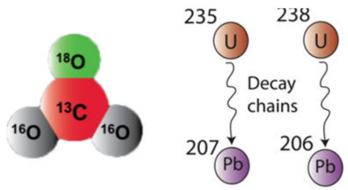


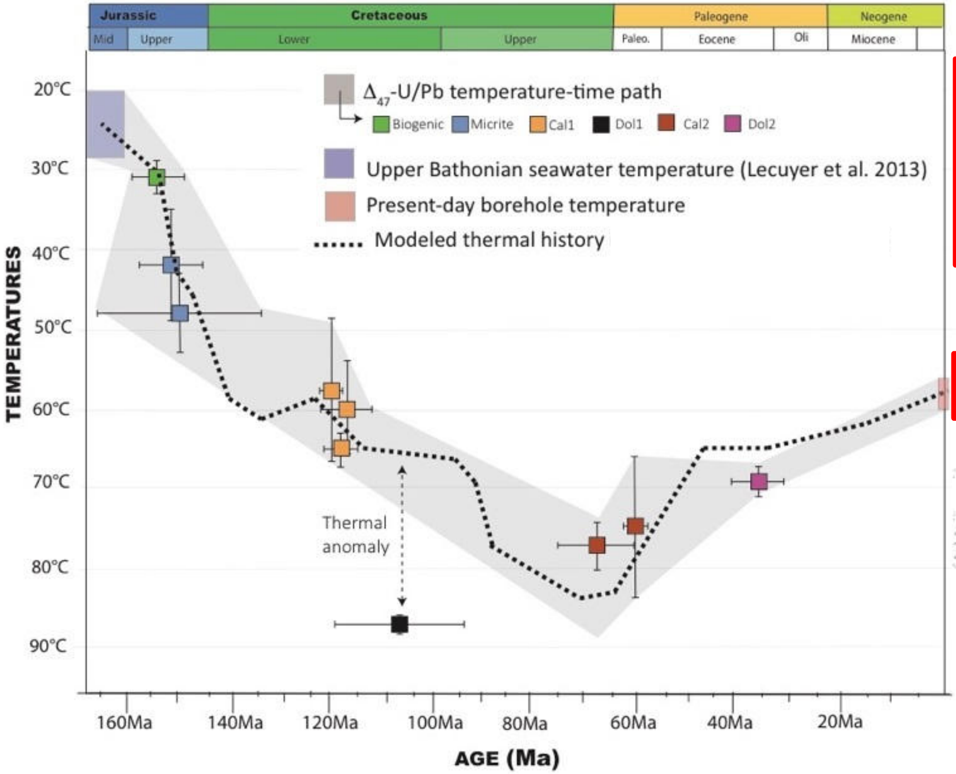
PARIS BASIN

DIRECT DATING AND FLUID-FLOW







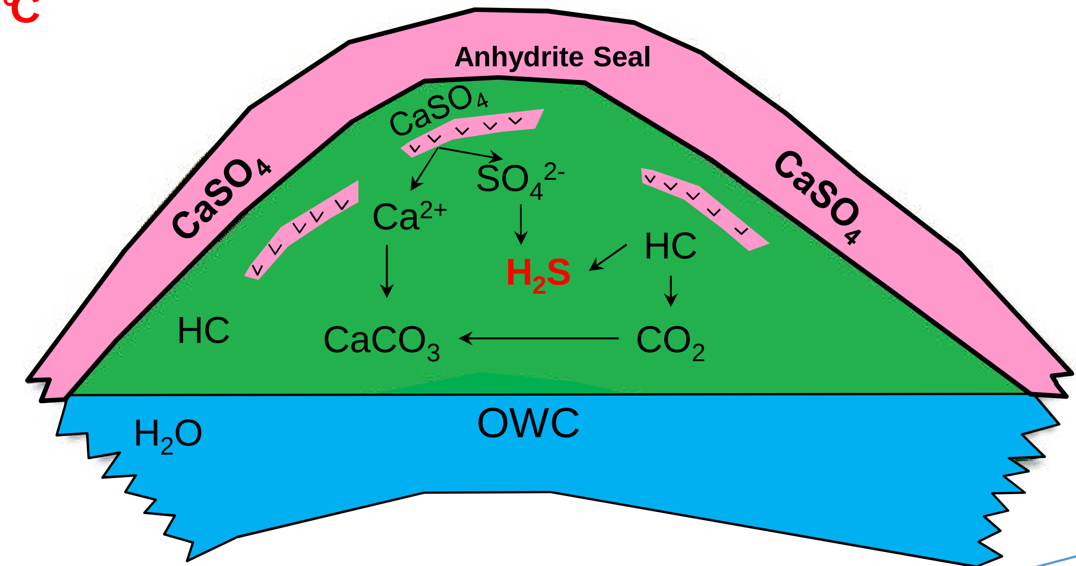


Δ_{47}/U-Pb: A new thermo-chronometer for carbonate bearing rocks to help to better calibrate numerical model

Hydrothermal origin for Dol1?

WESTERN CANADIAN BASIN
THERMOCHEMICAL SULFATE REDUCTION (TSR)

Temperature > 110℃



Complex series of redox reactions

Can we use diagenetic characterisation tools to contrain TSR modelling?

$CaMg(CO_3)_{2(s)}$

Within Carbonate (Dolomite) reservoir

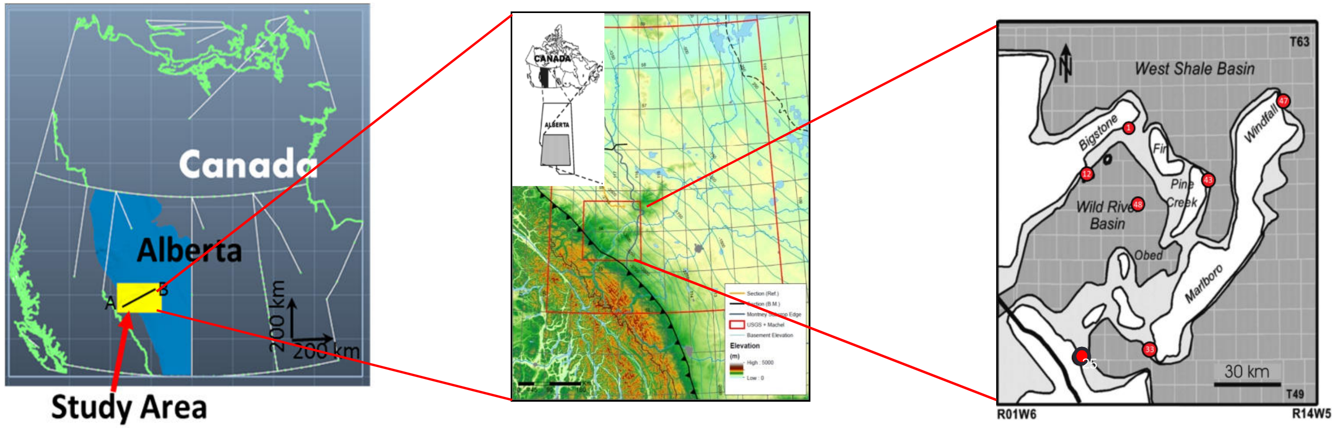
Sulfate (Anhydrite) + HC$^{(1)}$ + H_2O → Carbonate (Calcite) + H_2S + CO_2 + HC$^{(2)}$ + H_2O

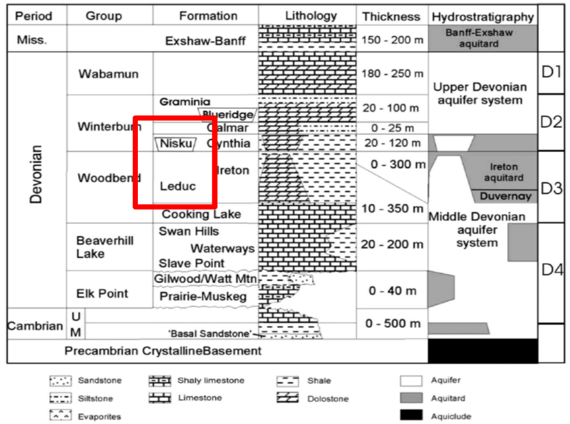
$CaSO_{4(s)}$ **(HC ± S)$^{(1)}$** **$CaCO_{3(s)}$** **(HC ± S)$^{(2)}$ + $S_{(s)}$ $OSC_{(l)}$ + $PB_{(s)}$**

Enriched in S

WESTERN CANADIAN BASIN
FLUID-MINERAL CHARACTERIZATION METHODS

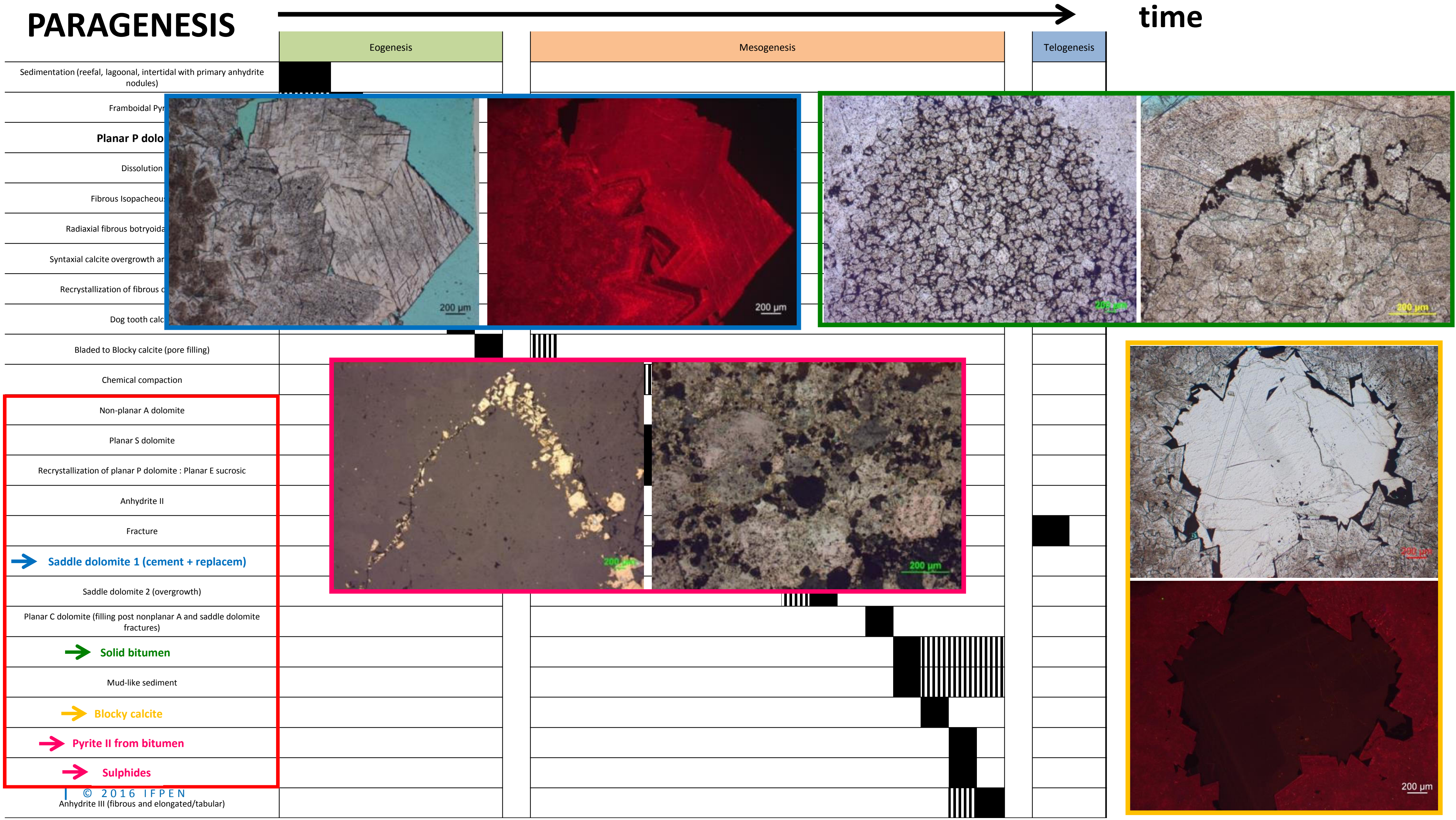
(modified from Machel & Buschkuehle, 2008)





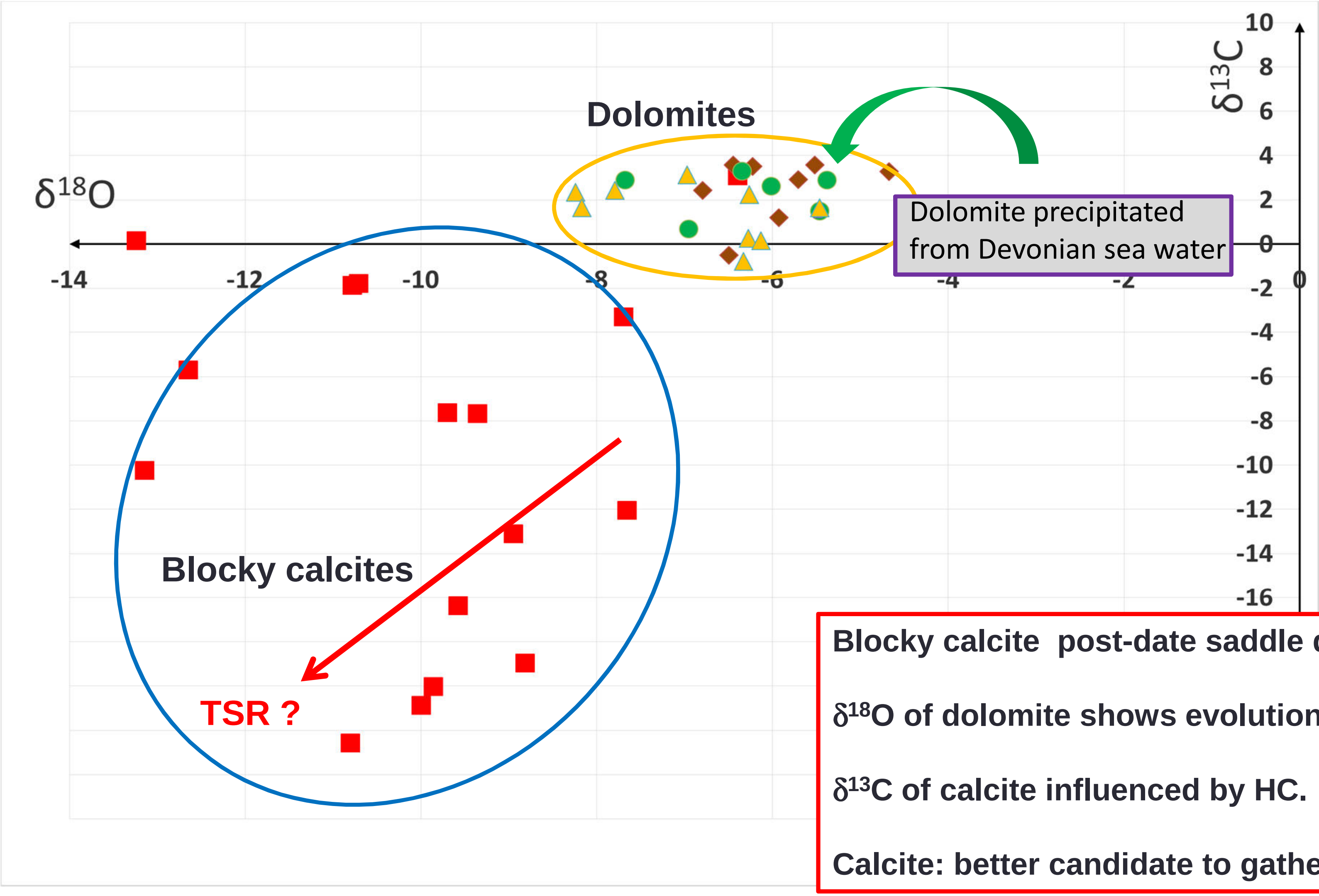
Frasnian-Fammenian:
375-365 Ma

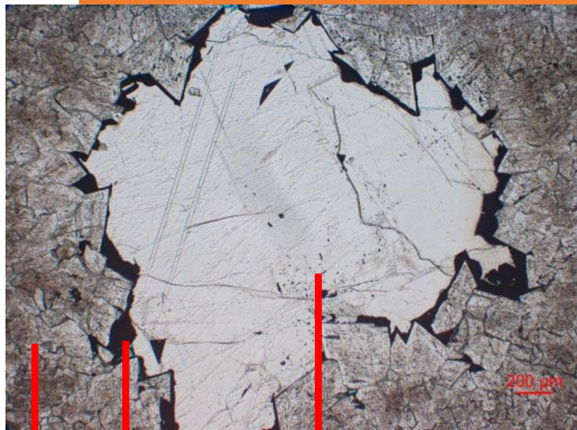
- Study area:
  - Southesk-Cairn Carbonate Complex - SCCC). 7 studied wells.
  - Platform sediments (white), reefs (light grey) and basin sediments (grey).
  - Fields in Devonian reef carbonates produce >> 30% H2S.
- Tools:
  - Optical, cathodoluminescence petrography
  - O-C isotope analysis
  - Fluid inclusion (FI) microthermometry
  - U-Pb carbonate chronometry by LA-ICP-MS


PARAGENESIS
time
Eogenesis
Mesogenesis
Telogenesis
Sedimentation (reefal, lagoonal, intertidal with primary anhydrite nodules)
Framboidal Pyr
Planar P dolo
Dissolution
Fibrous Isopacheou
Radiaxial fibrous botryoida
Syntaxial calcite overgrowth ar
Recrystallization of fibrous c
Dog tooth calc
Bladed to Blocky calcite (pore filling)
Chemical compaction
Non-planar A dolomite
Planar S dolomite
Recrystallization of planar P dolomite : Planar E sucrosic
Anhydrite II
Fracture
Saddle dolomite 1 (cement + replacem)
Saddle dolomite 2 (overgrowth)
Planar C dolomite (filling post nonplanar A and saddle dolomite fractures)
Solid bitumen
Mud-like sediment
Blocky calcite
Pyrite II from bitumen
Sulphides
© 2016 IFPEN
Anhydrite III (fibrous and elongated/tabular)
200 µm
200 µm
200 µm
200 µm
200 µm
200 µm
200 µm
200 µm

WESTERN CANADIAN BASIN

O-C ISOTOPES (‰, V-PDB)





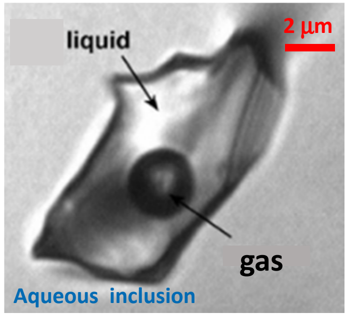
Blocky calcite post-date saddle dolomite and bitumen.

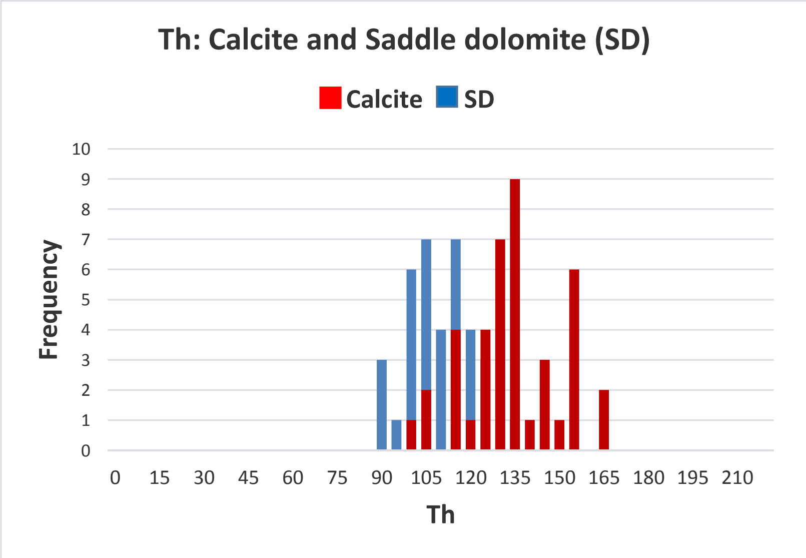
$\delta^{18}O$ of dolomite shows evolution of water content from deposit.

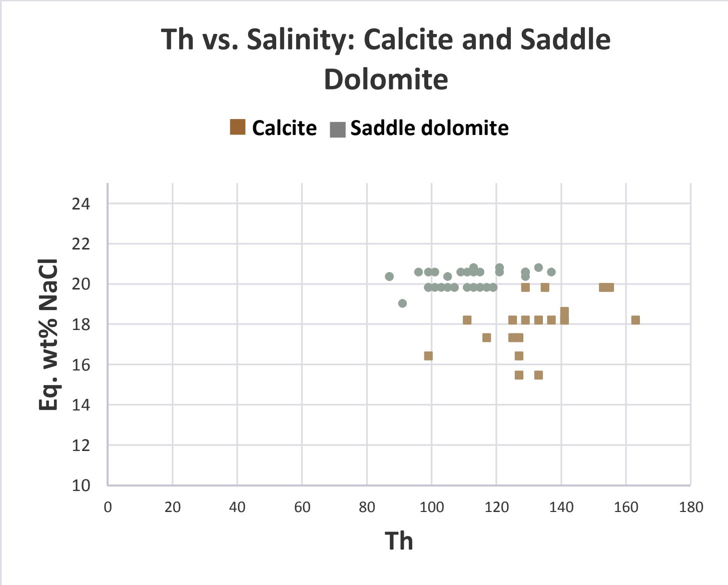
$\delta^{13}C$ of calcite influenced by HC.

Calcite: better candidate to gather constraints on TSR !!

WESTERN CANADIAN BASIN
FLUID INCLUSION MICROTHERMOMETRY







Dolomite: aqueous FI, NO GAS.

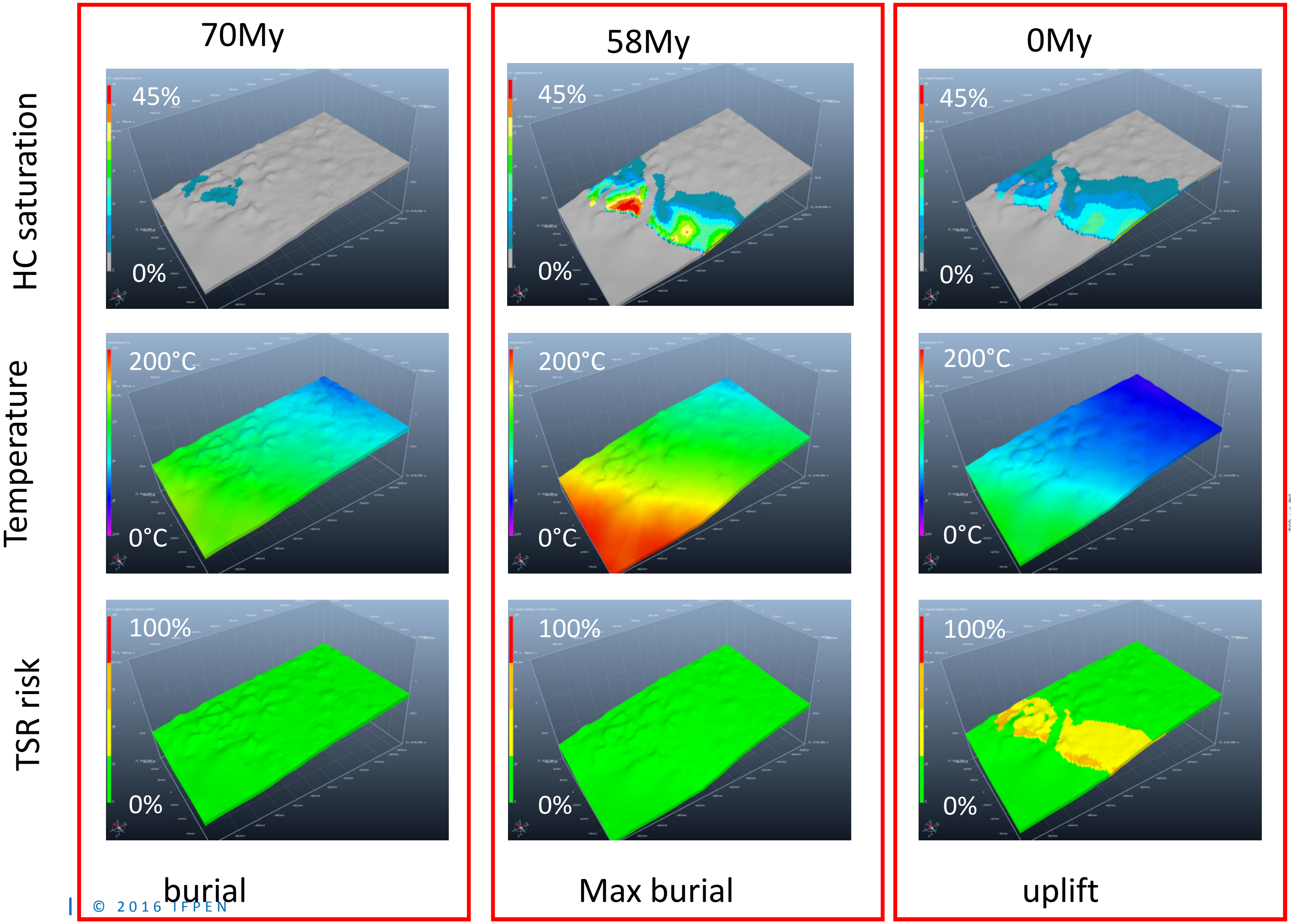
Calcite: acqueous FI, presence of CLATHRATES (water-GAS)

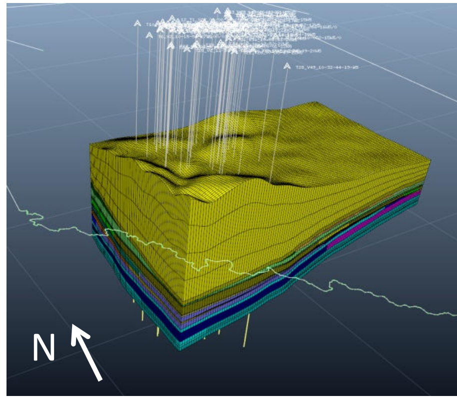
Homogenization temperature of Dolomite between 80-120°C

Homogenization temperature of Calcite > 100°C

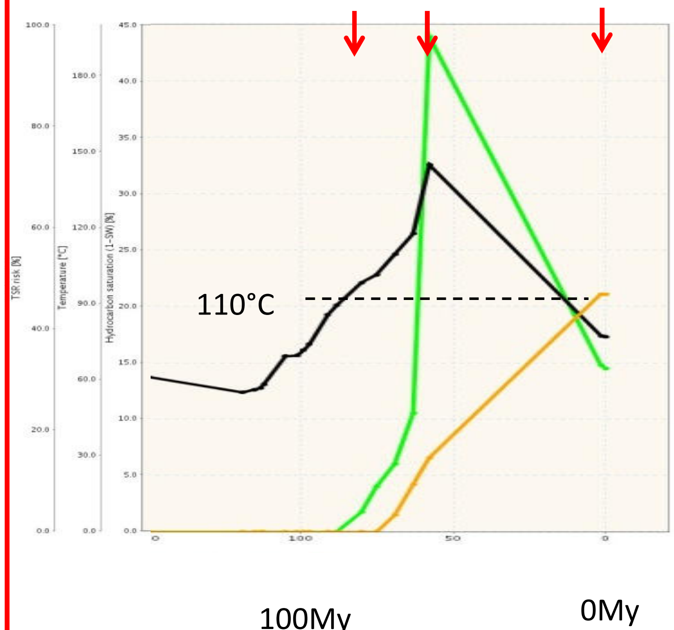
Water salinity of Calcite FI < Dolomite FI

WESTERN CANADIAN BASIN
BASIN MODELLING AT NISKU FM.



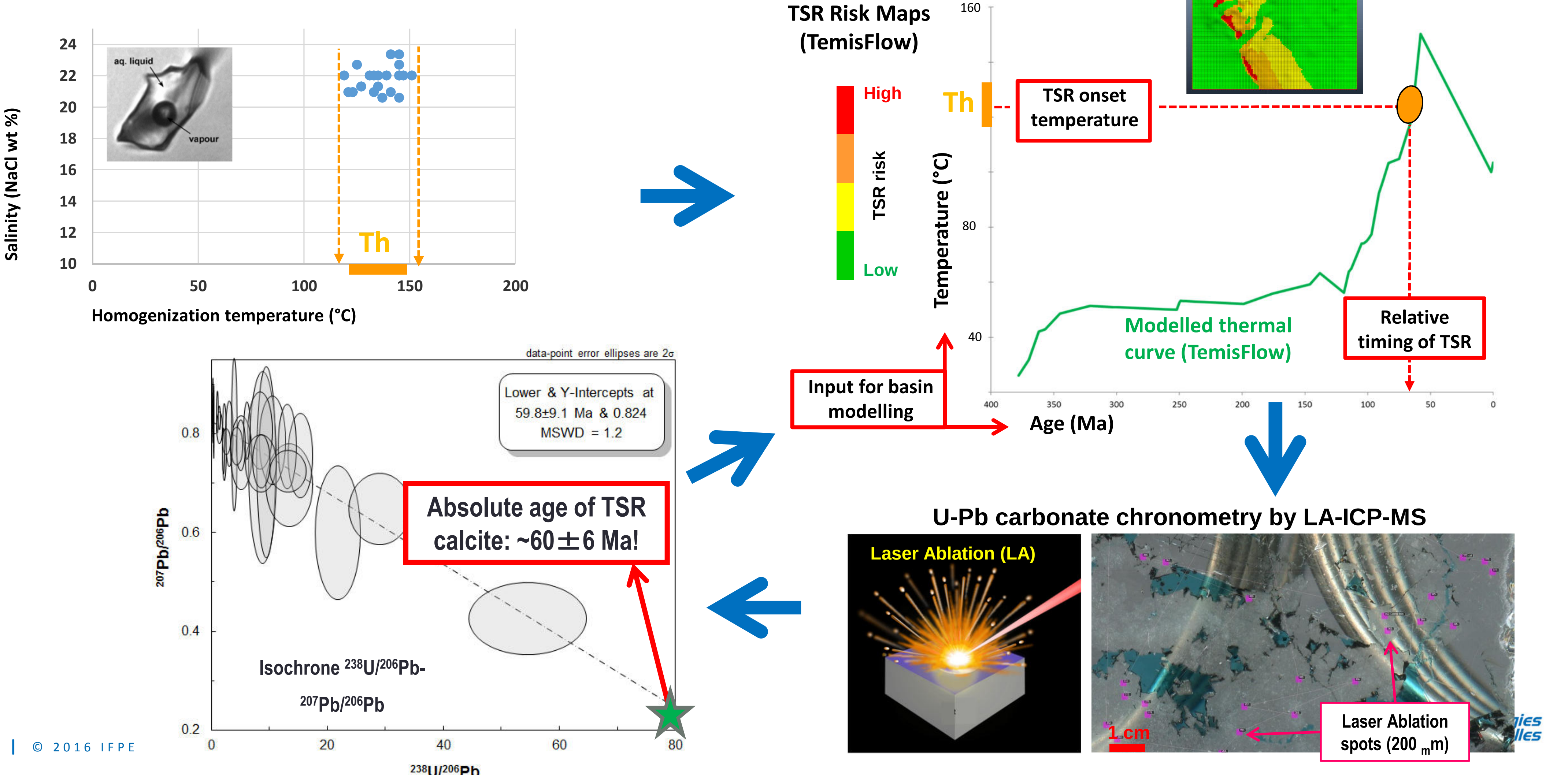


Cell history



WESTERN CANADIAN BASIN

FITTING CALCITE T DATA WITH THERMAL HISTORY

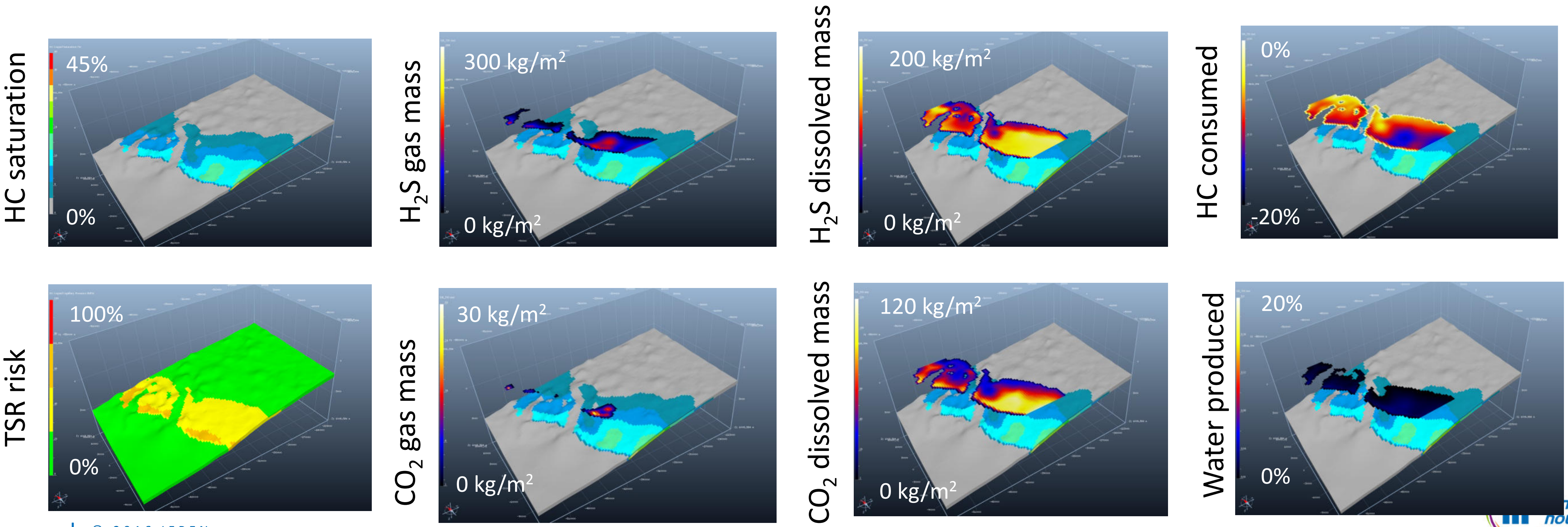


WESTERN CANADIAN BASIN

MODELLING TSR

- Chemical balance of TSR reaction proposed by Uteyev (2011)

$$8\ C_nH_m + (4n+m)\ CaSO_4 \rightarrow (4n+m)\ CaCO_3 + (4n+m)\ H_2S + (4n-m)\ CO_2 + (3m - 4n)\ H_2O$$



Guichet et al. AAPG Houston 2017

TAKE HOME MESSAGE

RESPONSIBLE
OIL AND GAS

Application of a characterization workflow based on diagenetic carbonate minerals allowed to:

- **Temperature (T)**
- **Timing (t)**
- **H_2S**
- **$\delta^{18}O_{fluid}$**
- **Salinity**

(a) Quantify Temperature and Timing of Carbonate formation

(b) Provide calibration points of numerical models in the past

(c) Identify TSR related carbonate phases

(d) Quantify the possible Temperature-Timing of TSR onset

(e) Help to validate the hypothesis of the TSR risk study (basin modeling)

IFP Energies nouvelles

Innovating for energy

Find us on:

www.ifpenergiesnouvelles.com

@IFPENinnovation