



UNIVERSIDADE DE SÃO PAULO

INSTITUTO DE GEOCIÊNCIAS

DEPARTAMENTO DE GEOLOGIA SEDIMENTAR E AMBIENTAL

GSA0463 Geologia do Petróleo

Métodos Geoquímicos I – Introdução à Avaliação de Rochas Geradoras

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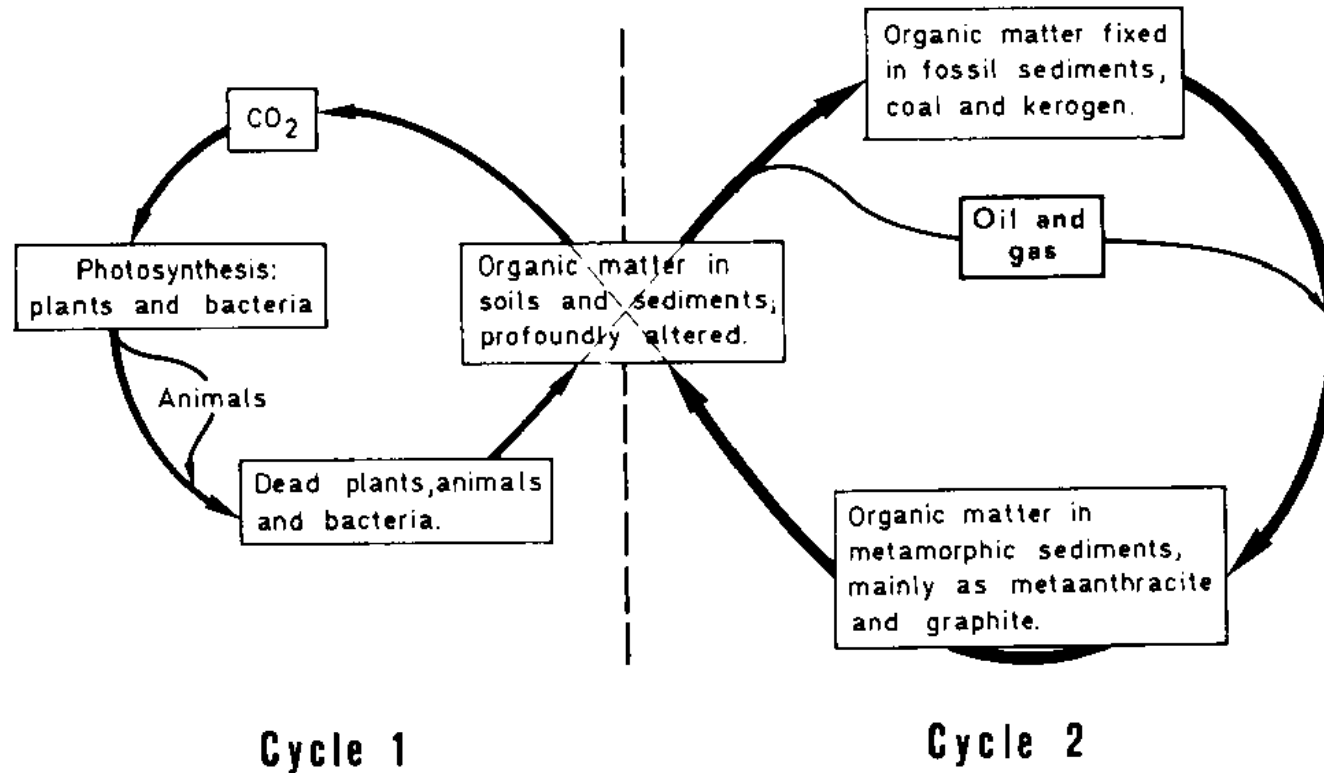
Sumário da Aula

1. Aplicação e Importância
2. Matéria orgânica: origem, tipos, maturação e reflectância de vitrinita
3. Carbono Orgânico Total (COT)
4. Pirólise Rock-Eval™
5. Interpretação de dados de COT e pirólise
6. Resumo
7. Referências

1. Aplicação e Importância

- Métodos tradicionais de **investigação do conteúdo orgânico de rochas siliciclásticas e carbonáticas** finas.
- Essenciais para **definição de intervalos geradores**;
- Parâmetros são **diretamente aplicáveis no fluxograma de novas descobertas** exploratórios em sistemas petrolíferos diversos;
- **Podem ser utilizados** no desenvolvimento de projetos exploratórios **não-convencionais**;
- Podem ser **utilizados para entendimento da história térmica de uma bacia sedimentar**;

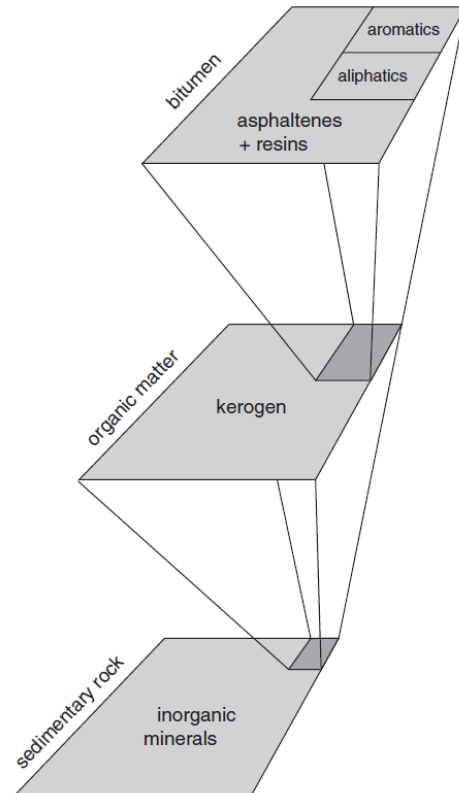
2. Querogênio – Origem & Tipos



Tissot & Welte, 1984

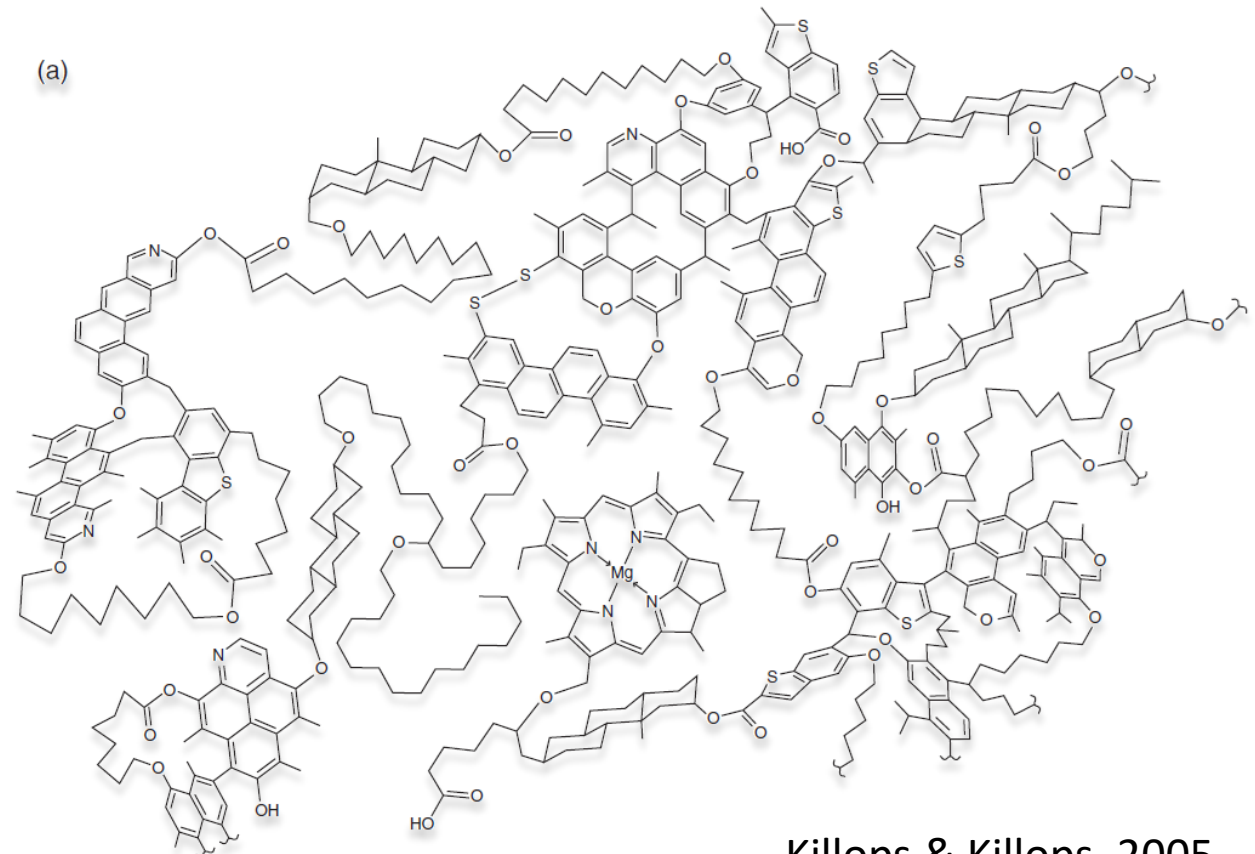
Origem & Tipos Primários

Matéria Orgânica nas Rochas Sedimentares



Killops & Killops, 2005

Estrutura do querogênio tipo II

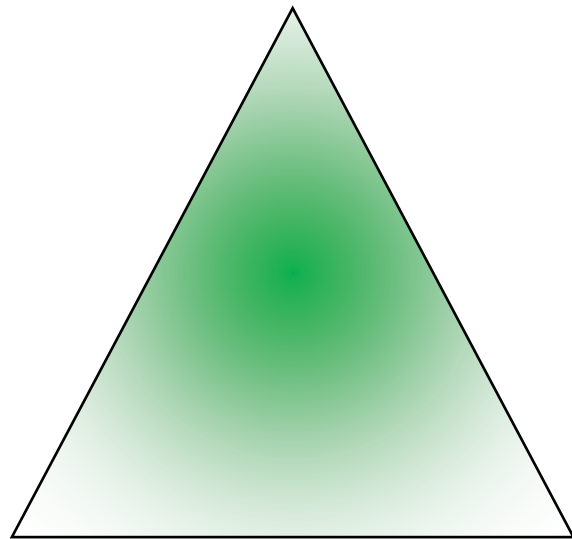


Killops & Killops, 2005

Origem & Tipos

Constituintes do Kerogêneo

Matéria Orgânica Amorfa



Fitoclastos

Palinomorfos

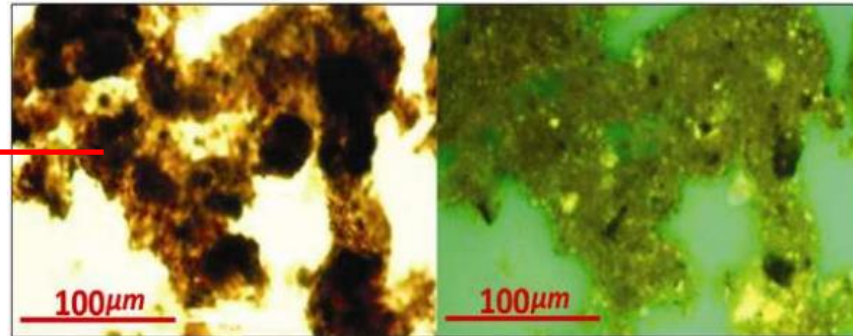
Baseado em Tyson, 1995

CONSITUENT		MACERAL GROUP	PURE KEROGEN TYPE		
			a	b	c
P A L Y N O M O R P H S	Prasinophyte phycmata	Exinite or Liptinite	I _A	1c	1pn
	Chroococcale cyanobacteria			1?	?
	Chlorococcales: Botryococcales Hydrodictyales			1a	1p
	Dinocysts Acritarchs Rhodophyte spores		II _A	IIa	2/3pp
			?	?	?
	Miospores: microspores pollen Megaspores		II _S	IIc?	2/3pp
P H Y T O C L A S T S	Cuticle	Vitrinite or Huminite	II _C	IIc?	?
	Cortex		III _w	III	3ap
	Secondary xylem (wood)				
	Bacterially modified wood		II _w	IIc?	3pp?
	Charcoal		IV _w	IVb	4
	Biochemically oxidized wood			IVa, c	
Fungal hyphae	?	?			
A M O R P H O U S	Resins	Exinite or Liptinite	I _R	IIc	1n
	Organic aggregates		II _A ?	IIa?	2pn
	Faecal pellets			IIb?	?
	Cyanobacteria/thiobacteria				
	Humic cell-filling ppt.s Humic extracellular ppt.s		Vitrinite or Huminite	III _w	III

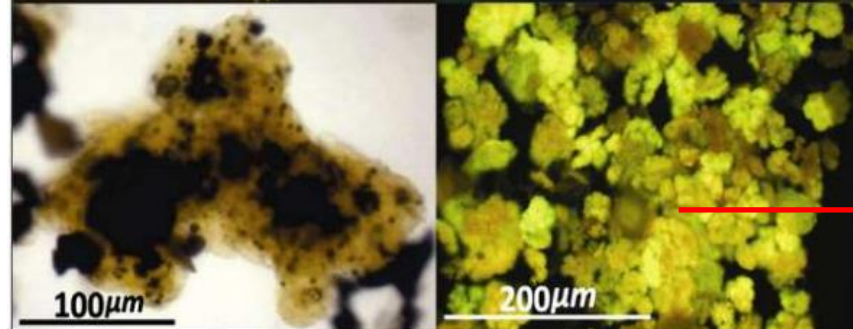
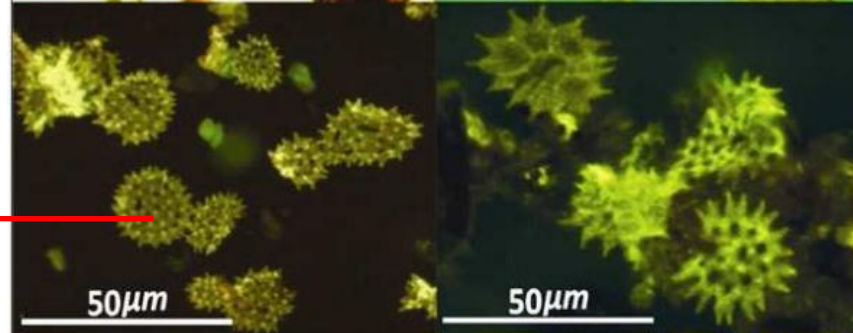
Figure 21.7 Correlation of modified kerogen types and their typical organic matter sources (for pure end-members). Column a after Horsfield (1984), b after Cooper and Barnard (1984), c after Larter (1985).

Origem & Tipos Primários Querogênio Tipo I

Matéria
orgânica
Amorfa (MOA)



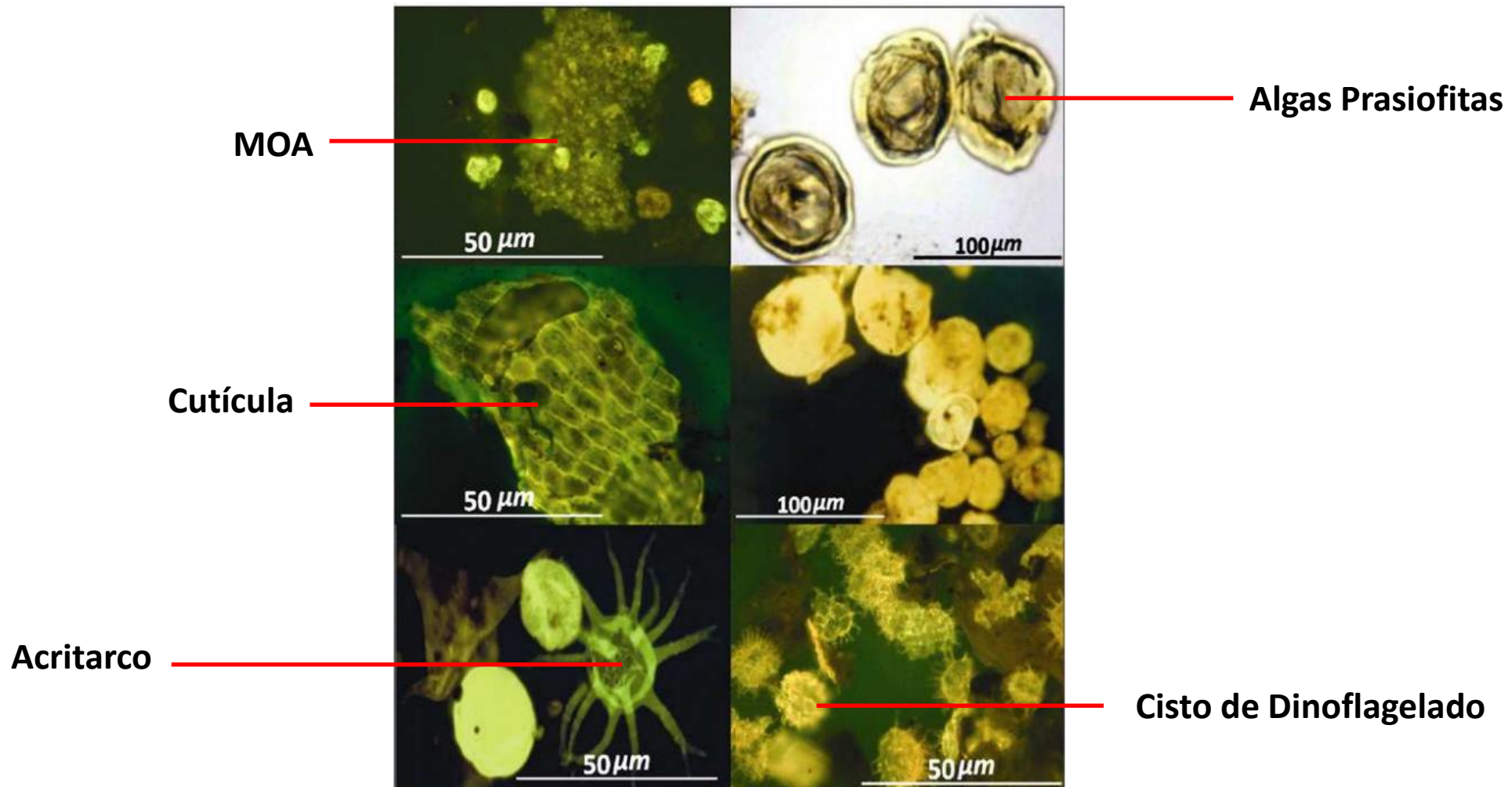
Algas Pediastrum



Algas Botriococcus

Origem & Tipos Primários

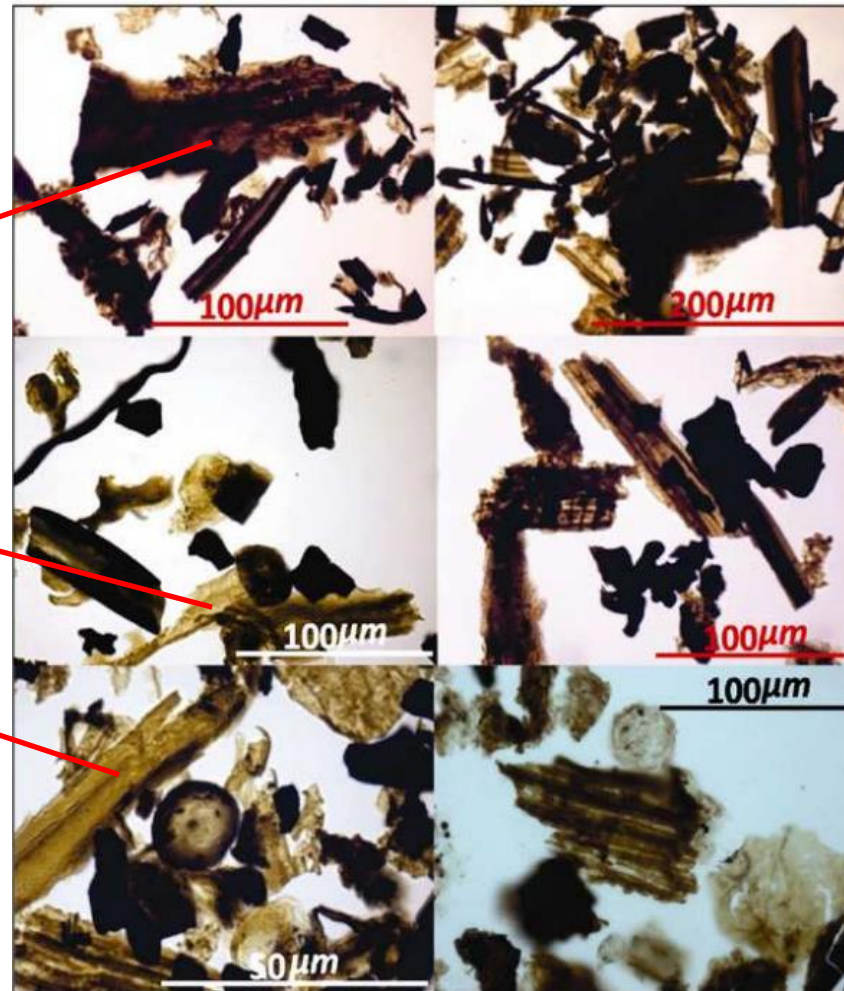
Querogênio Tipo II



Origem & Tipos Primários

Querogênio Tipo III

Fitoclastos
Não-Opacos
(podem ser vitrinitas)



Origem & Tipos – Equivalência de Nomenclaturas

Equivalent kerogen nomenclatures					
Hydrocarbon potential	Coal petrography	Palynology	Chemistry	Rock eval	Comments
Oil-prone (cracking to condensate and gas)	Liptinite	Algal/ Amorphous	Sapropel	Type I (Type IS)	Pure algal Includes bacterial biomass Cuticle gives waxy oil, Type II can be a mix of Types I, II and IV Amorphous vitrinite and oil-impregnated fluorescent vitrinite exist
Light oil, condensate-prone	Exinite	Herbaceous		Type II (Type IIS)	
Gas-prone	Vitrinite	"Woody"	Humic	Type III	Minor gas potential from semi-fusinite
Dead carbon	Inertinite	"Coaly"	(not recognised)	Type IV (or IIIB)	

Origem & Tipos – O Diagrama de Van Krevelen

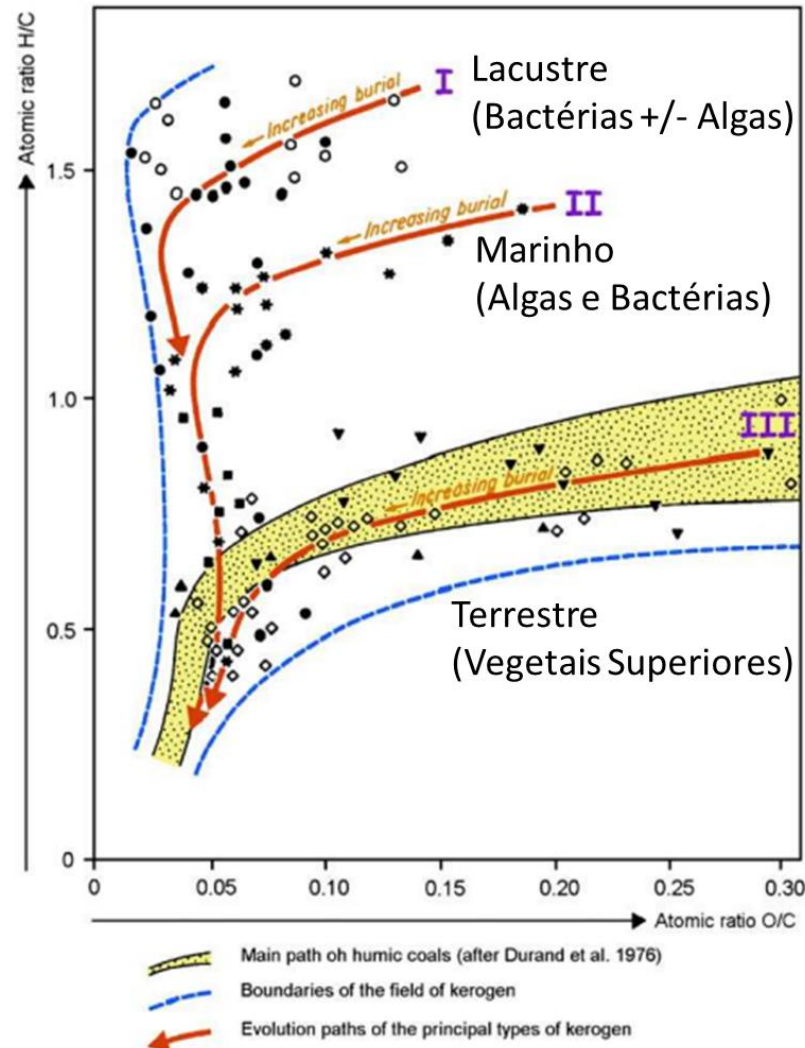
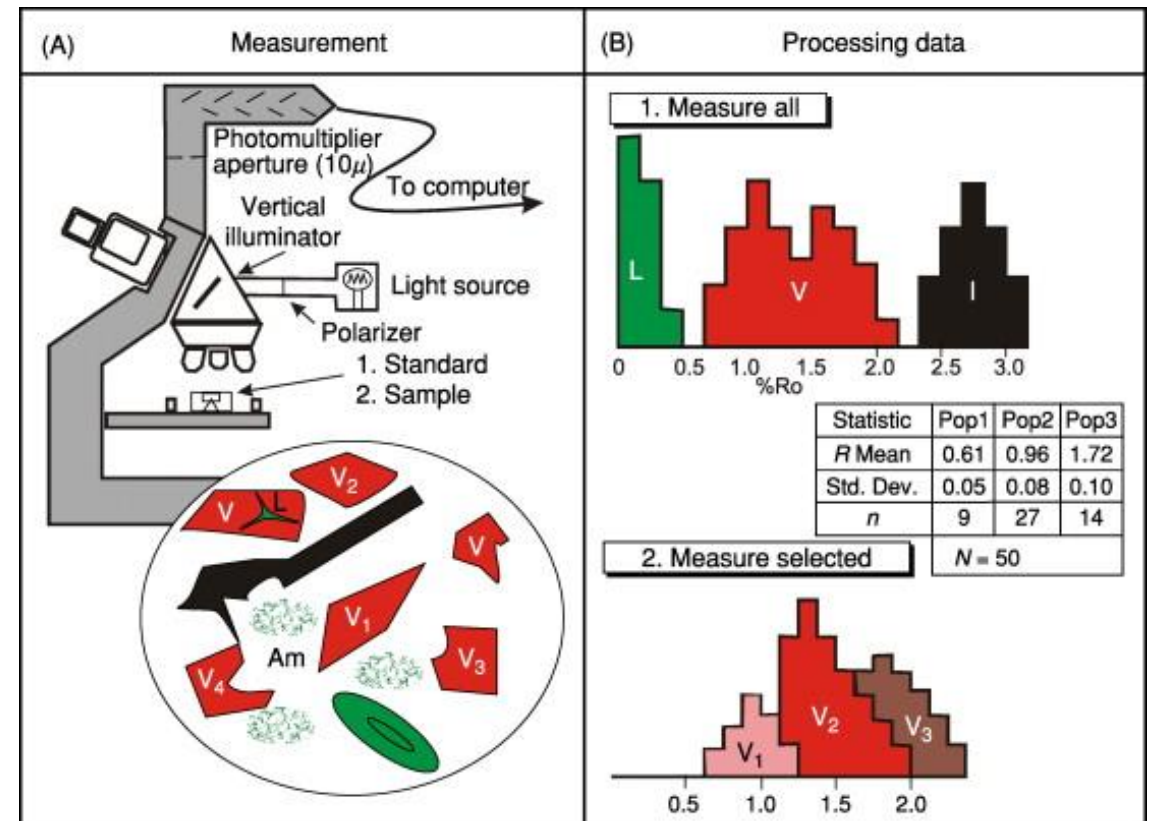


Diagrama de Van Krevelen - Suárez-Ruiz *et al.*, 2012

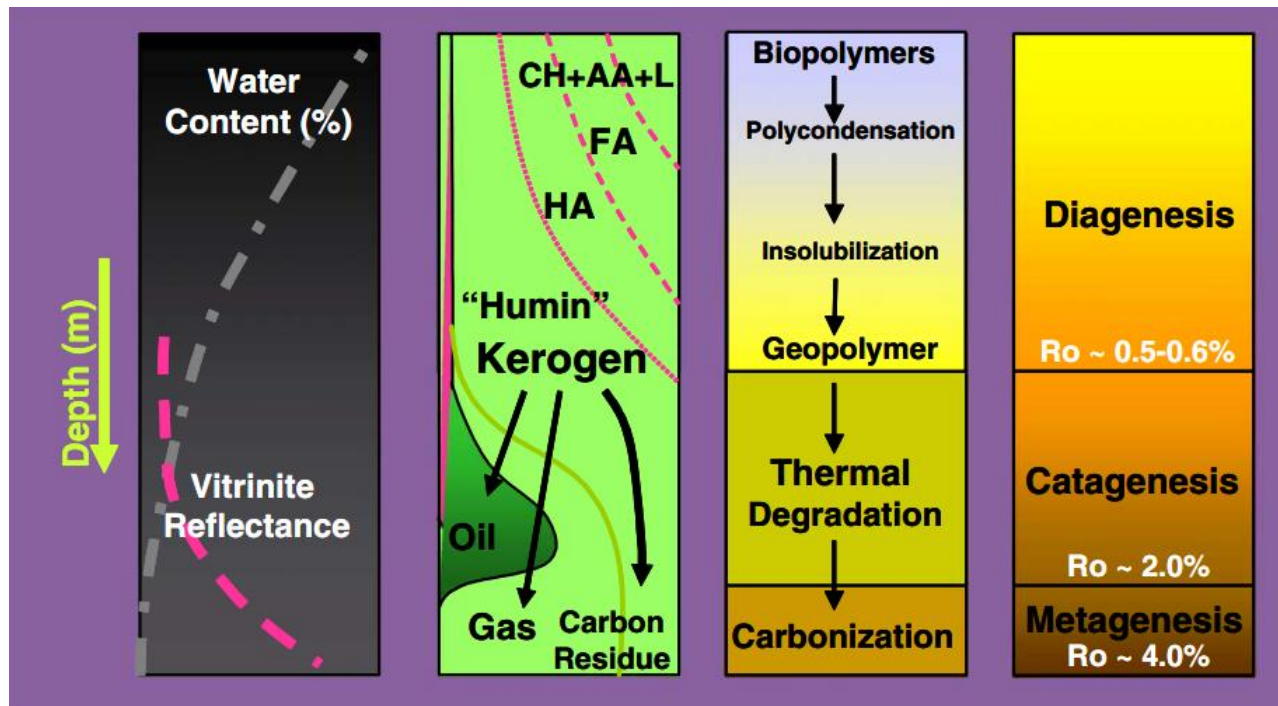
2. Reflectância de Vitrinita

$$\text{Reflectância de vitrinita (\%)} = \frac{\text{Reposta do Fotomultiplicado para Vitrinita}}{\text{eposta do Fotomultiplicado do Padrão}} \times \text{Reflectância do Padrão}$$

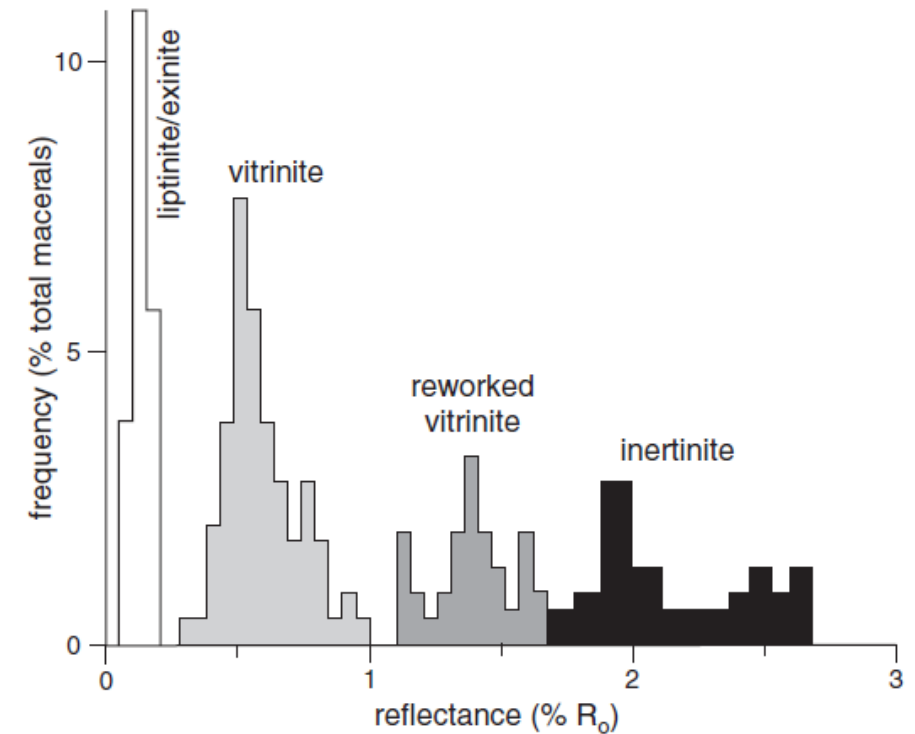
R_o = Reflectância de vitrinita imersa em óleo
 Am – Amorfa
 L – Liptinitas
 V – Vitrinitas
 I – Inertinitas



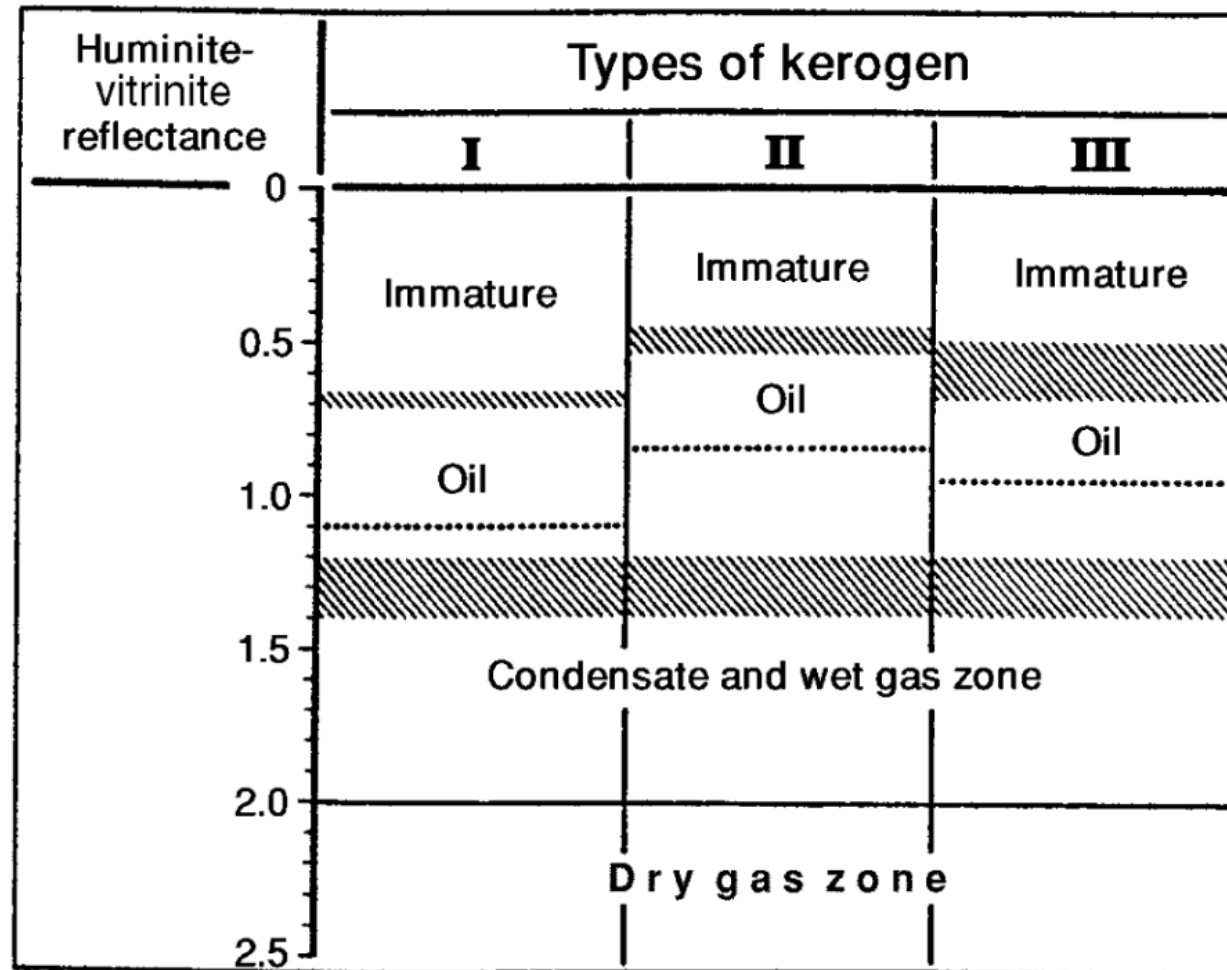
Evolução Térmica e Produtos Secundários



Suárez-Ruiz *et al.*, 2012

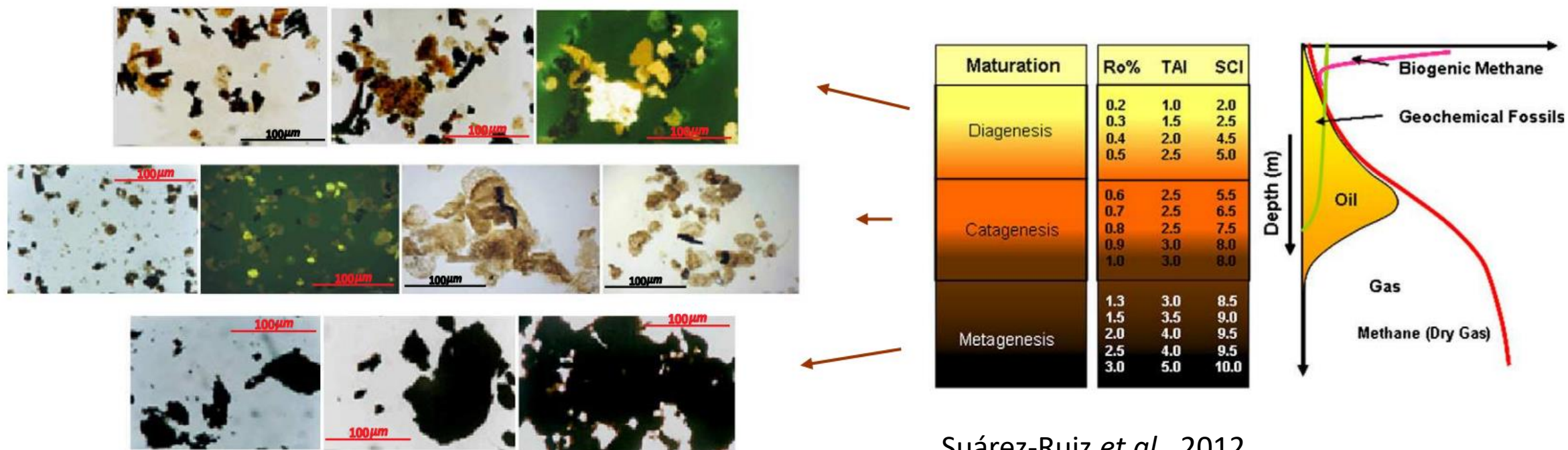


Evolução Térmica e Produtos Secundários



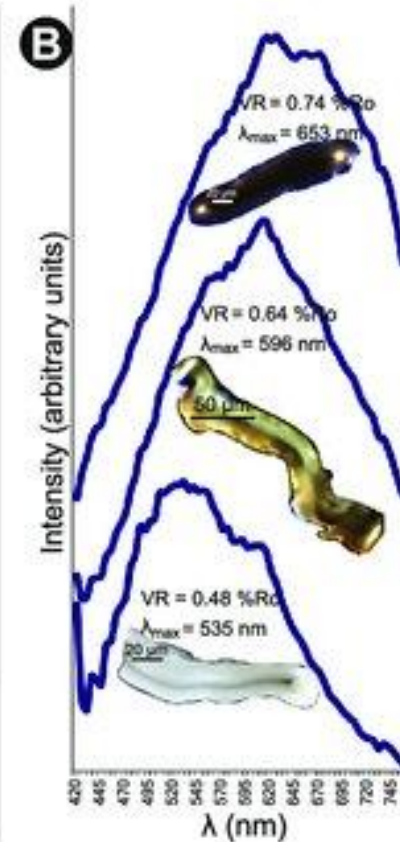
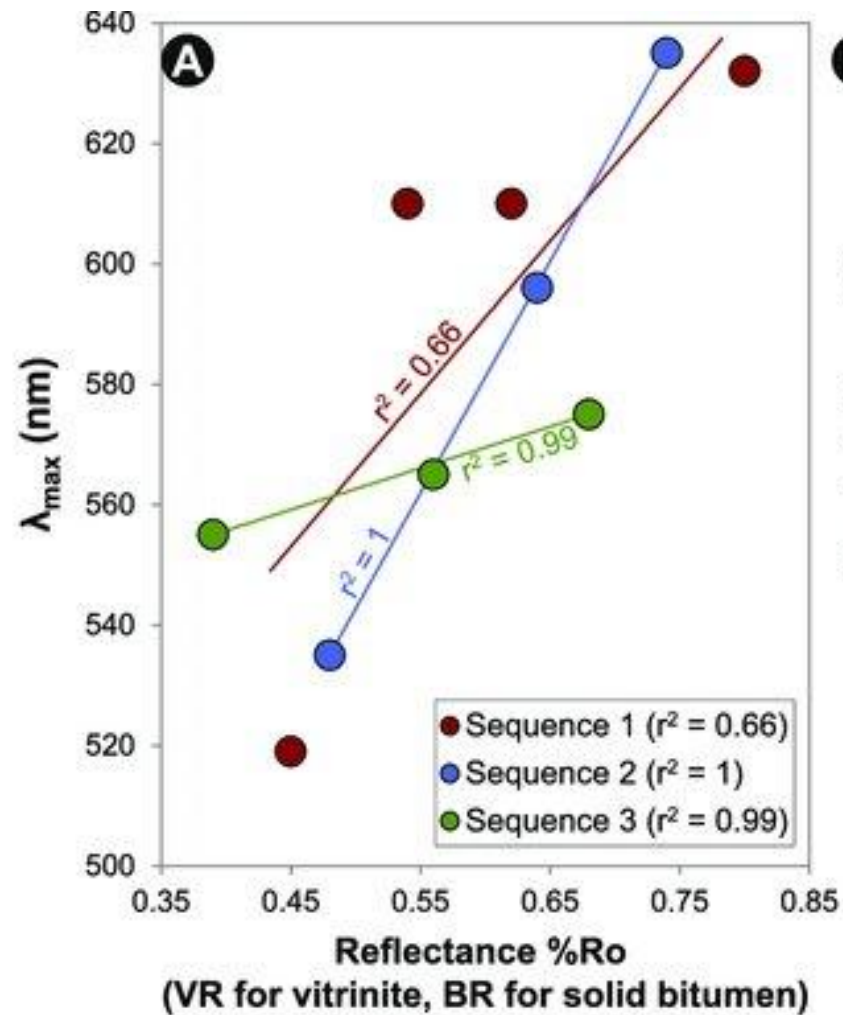
Tissot & Welte, 1984

Evolução Térmica e Produtos Secundários



Suárez-Ruiz *et al.*, 2012

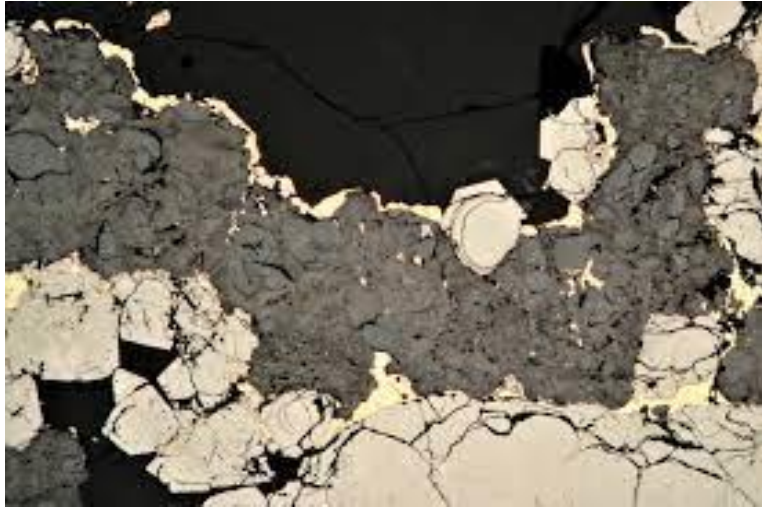
Ro x Fluorescência - Evolução Térmica e Produtos Secundários



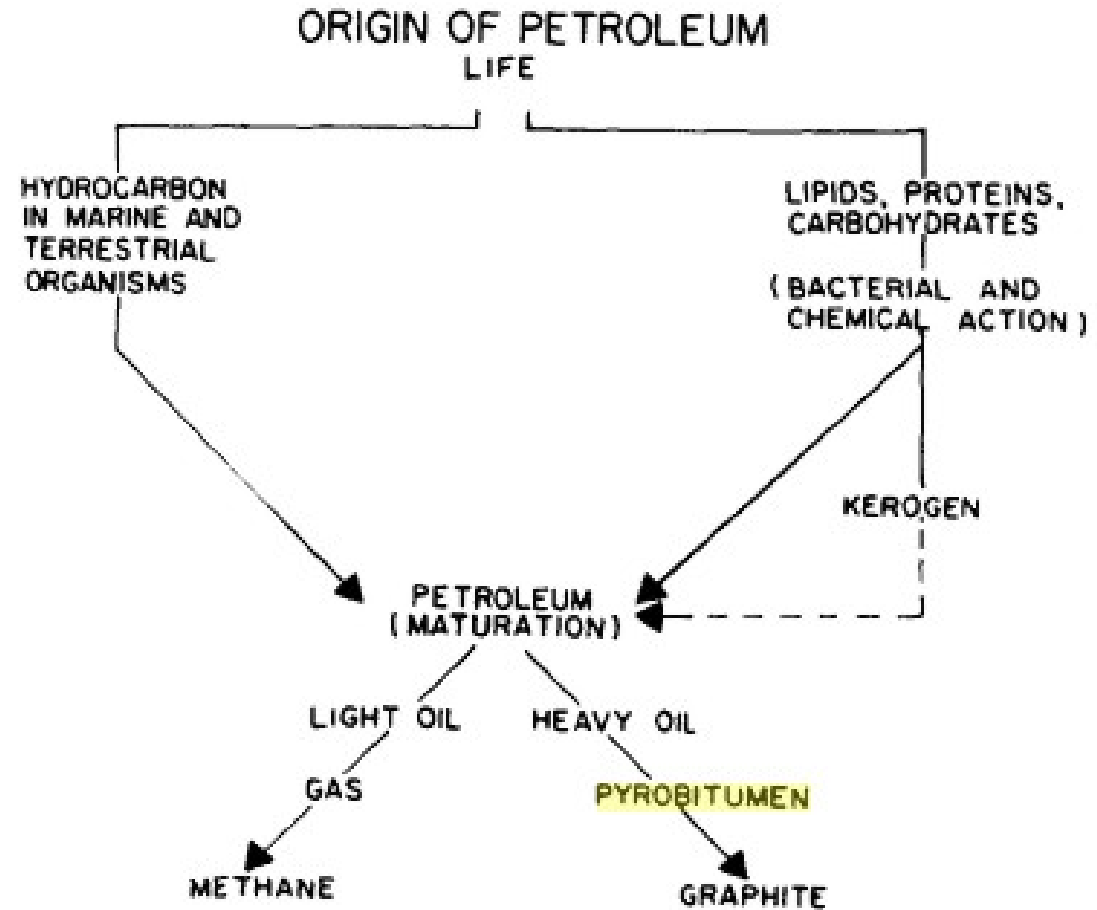
Hackley *et al.*, 2017

Maturação e Produtos Secundários

Piobetume (Ro eq. > 1 %)

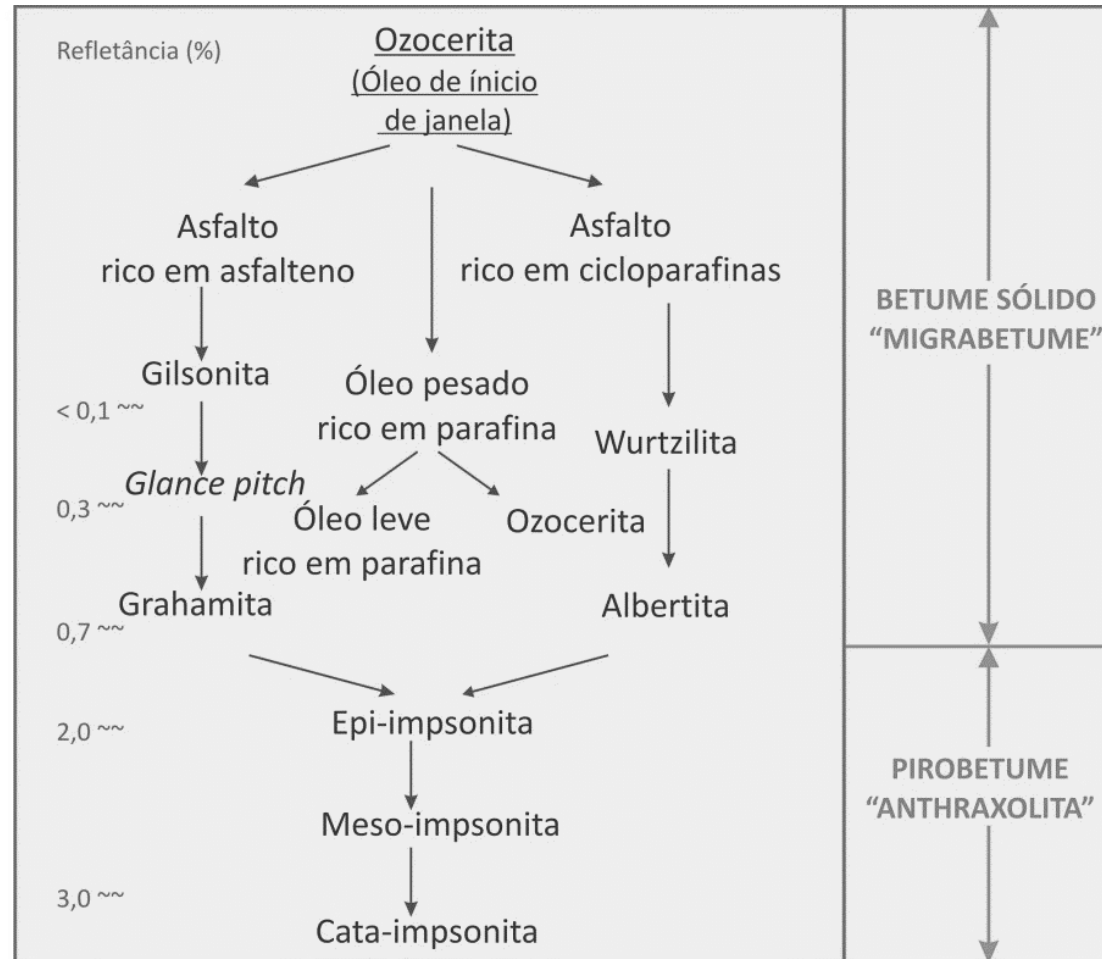


Graphite



Crain's Petrographic Handbook

Maturação e Produtos Secundários

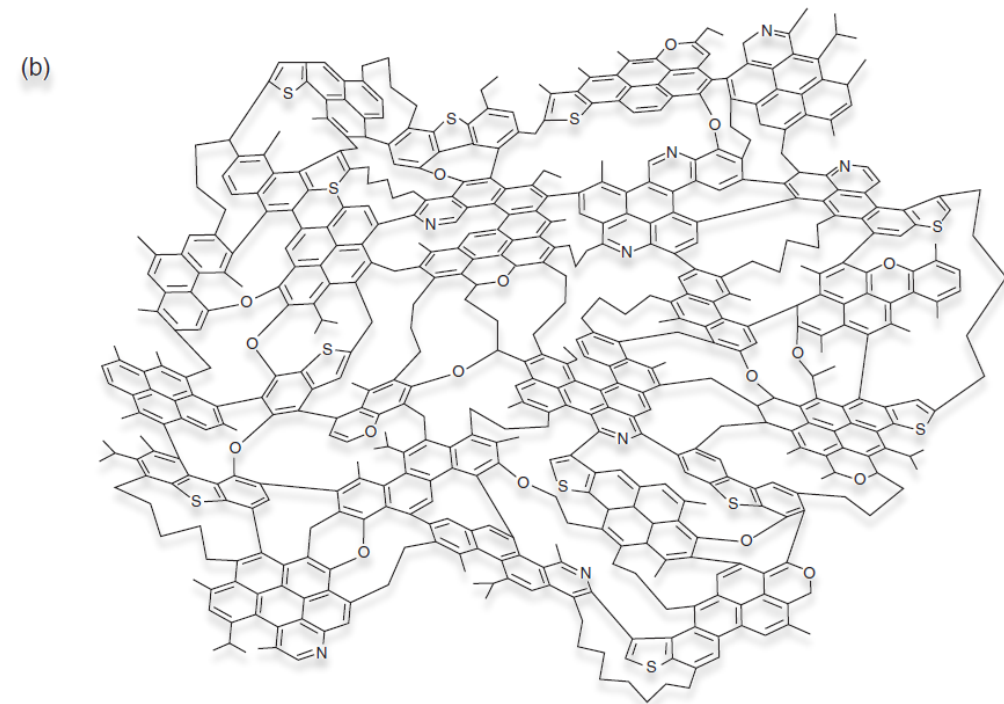
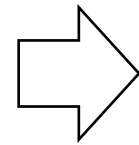
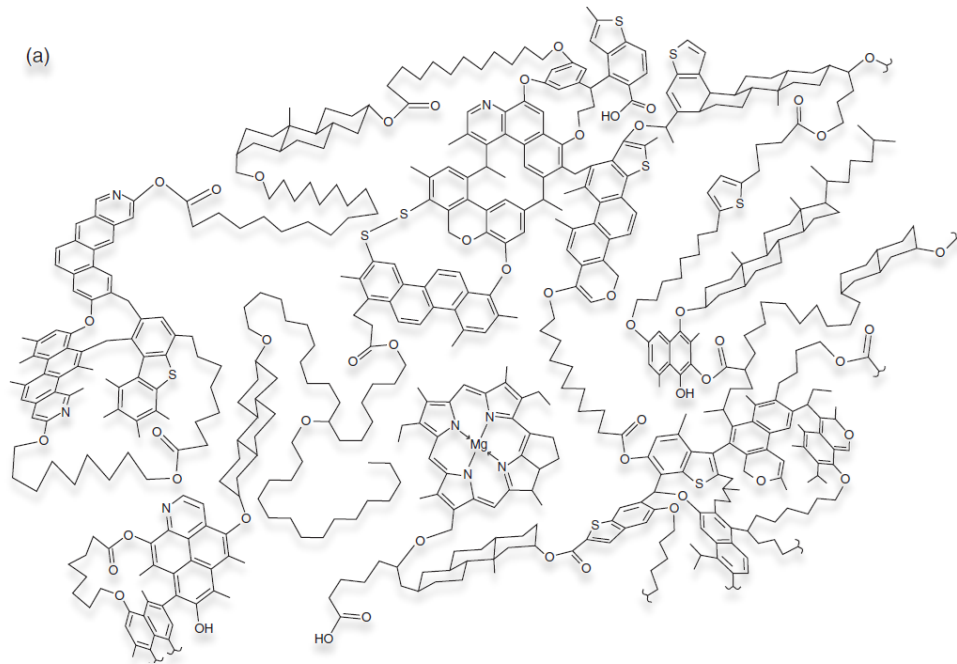


Maturação e Produtos Secundários

Estrutura do Kerogênio tipo II

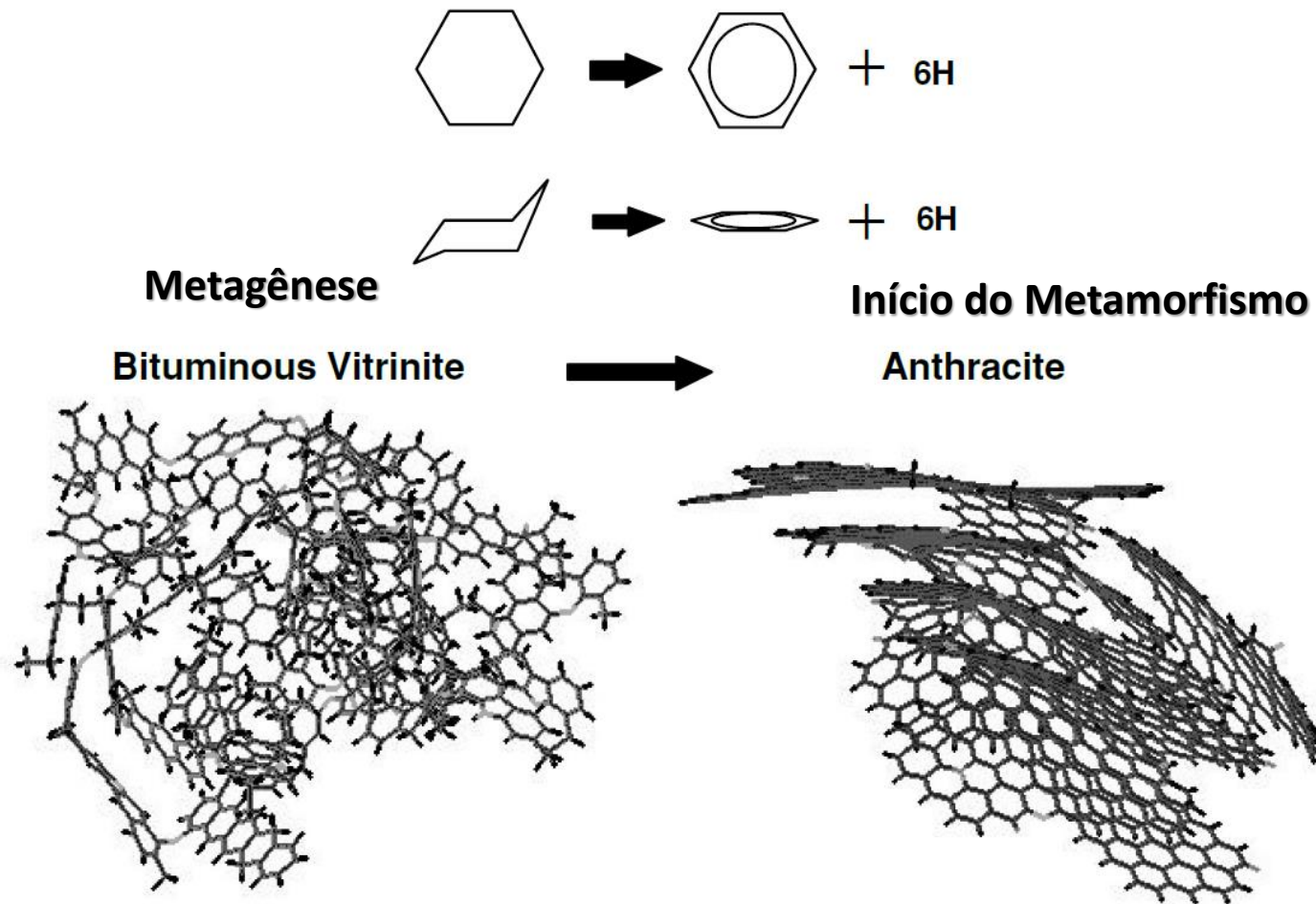
Início da Catagênese

Final da Catagênese

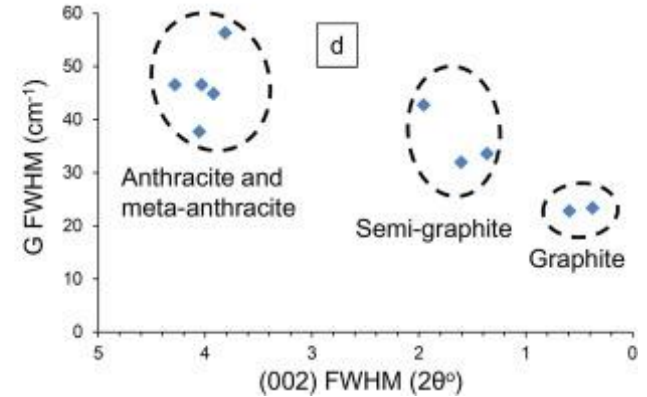
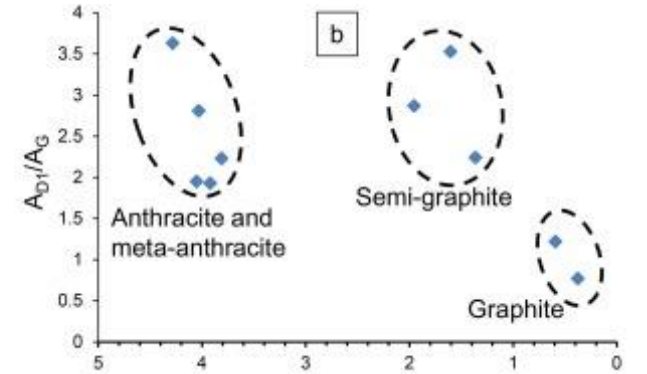
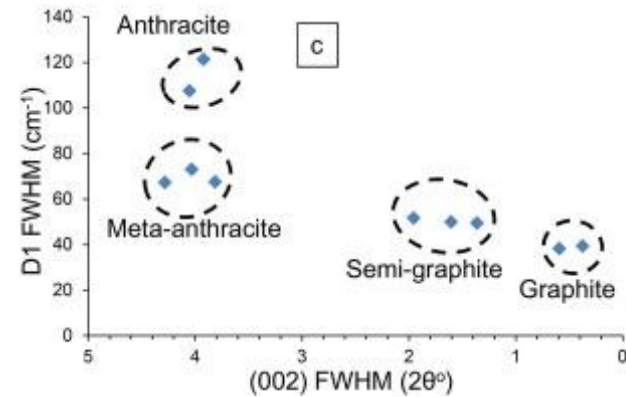
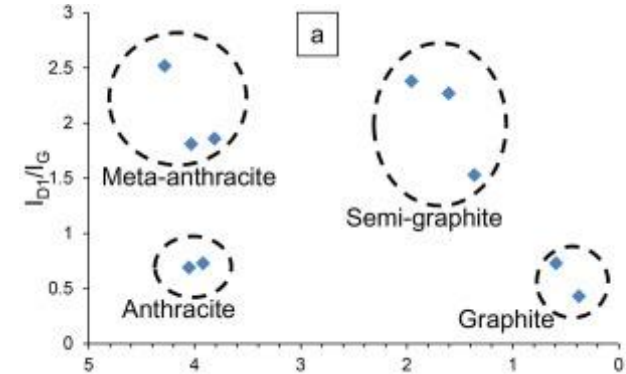
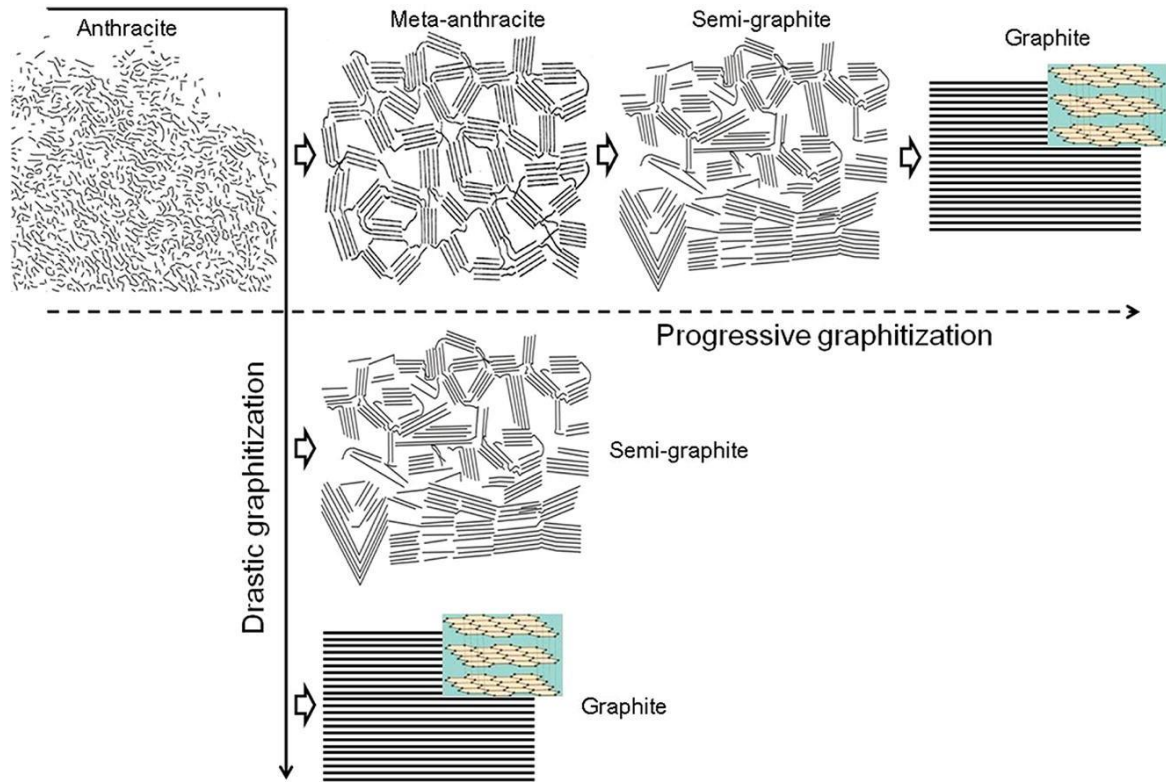


Killops & Killops, 2005

Maturação e Produtos Secundários



Maturação e Produtos Secundários



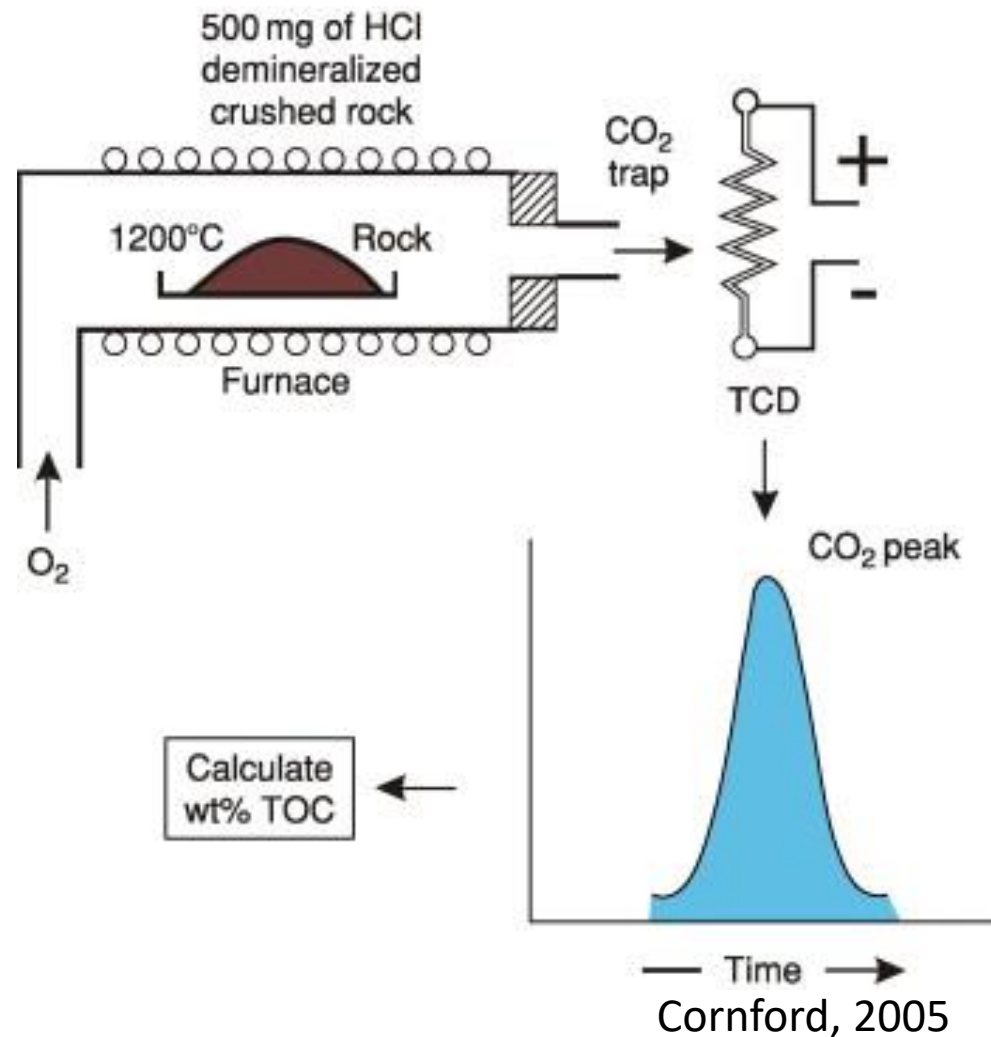
Li et al., 2017

3. Carbono Orgânico Total (COT)

- **Total Organic Carbon (TOC)** no inglês
- **Método destrutivo;**
- Determinação do **teor de matéria orgânica** em % em massa;
- **Não permite estimar a qualidade** da matéria orgânica!

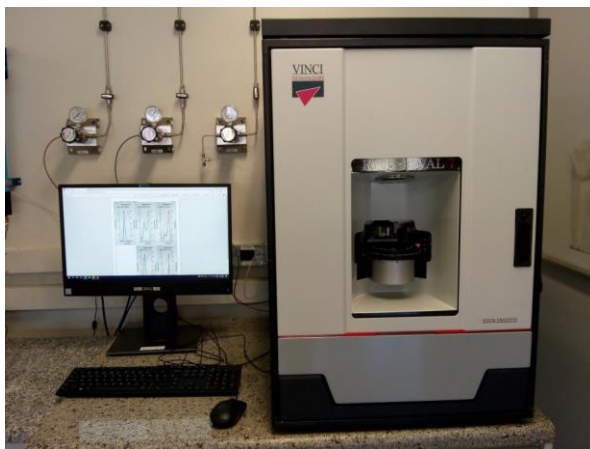


Fonte Imagem: LECO – [LINK](#) (acessado 02/06/2023)

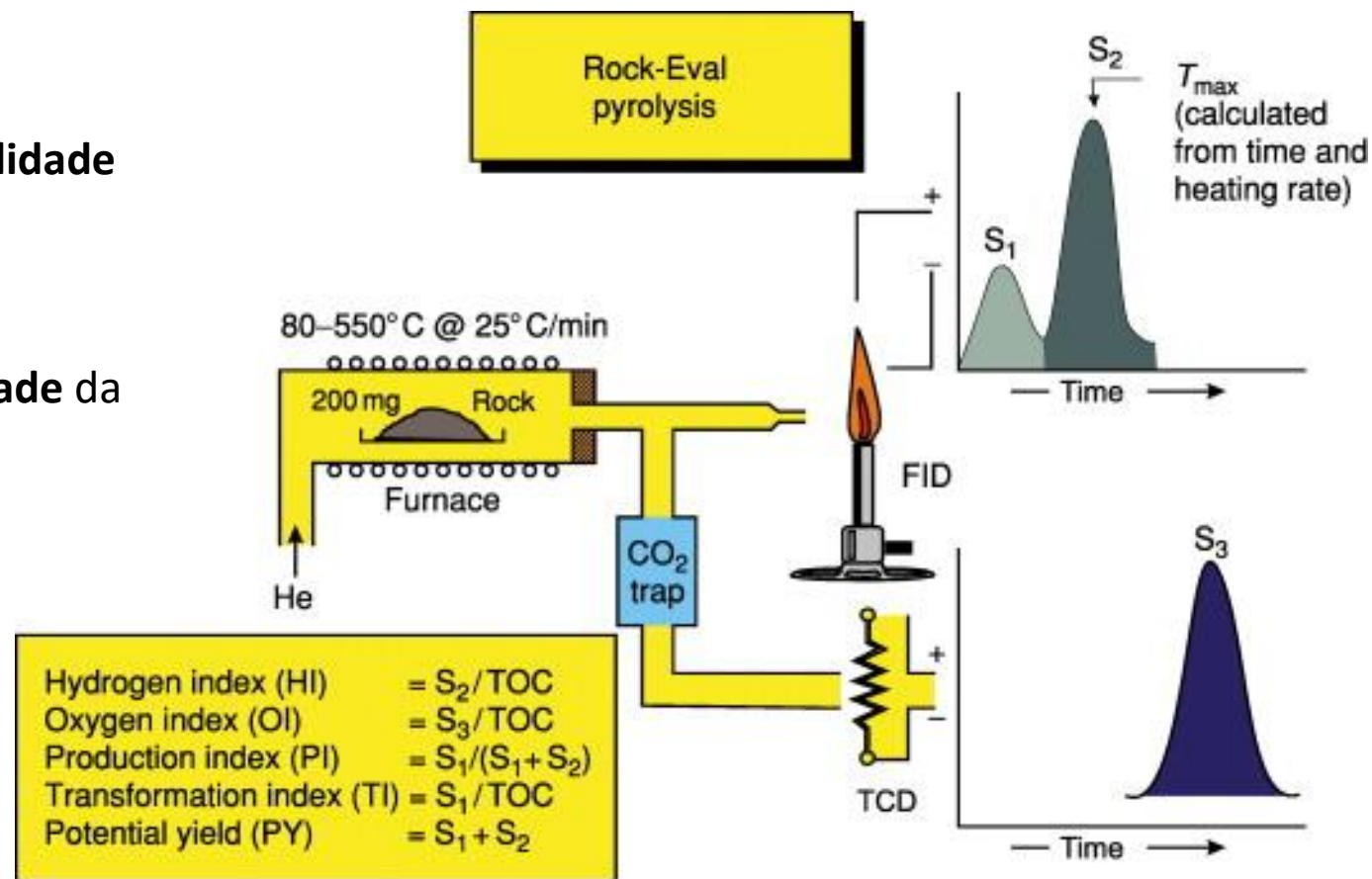


4. Pirólise Rock-Eval™

- Método destrutivo;
- Determinação de potencial gerador e qualidade matéria orgânica;
- Permite estimar indiretamente a maturidade da rocha geradora.



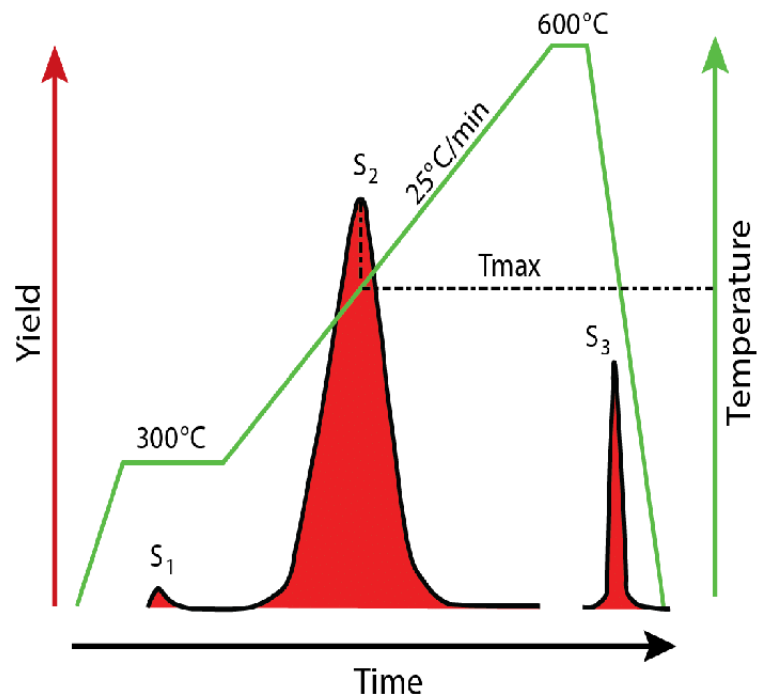
Fonte Imagem: LECO – [LINK](#) (acessado 02/06/2023)



FID = Flame ionization detector; TCD = Thermal conductivity detector

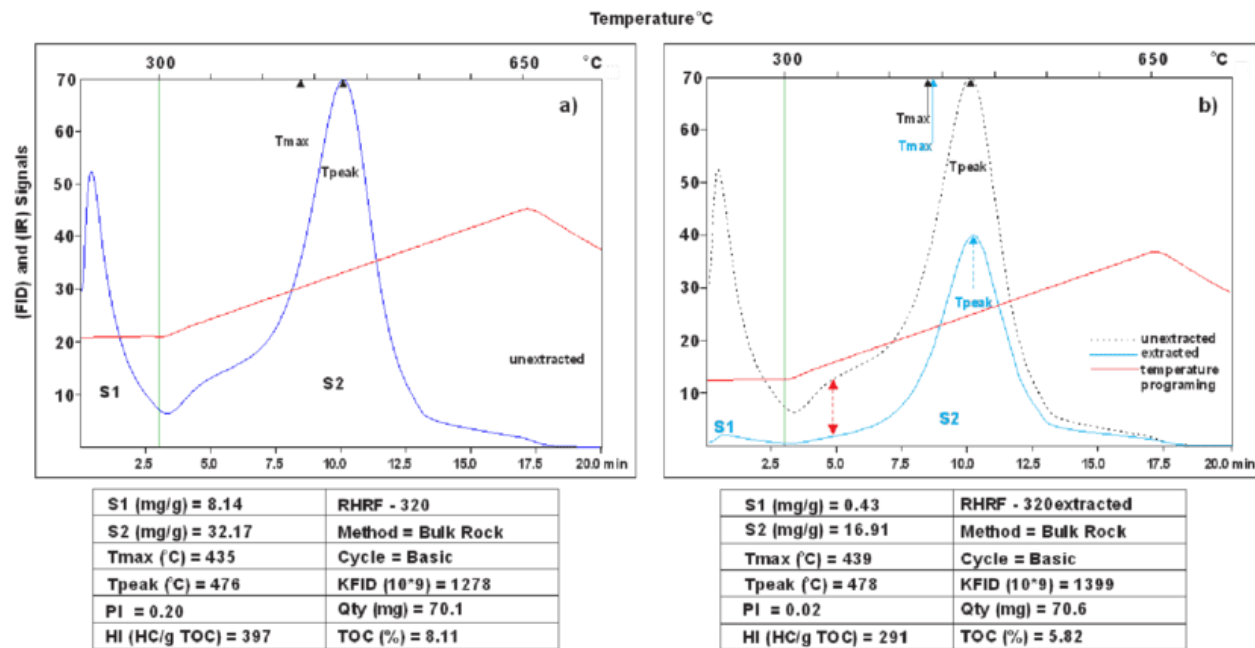
4. Pirólise Rock-Eval™ - O Pirograma

Pirograma e rampas de aquecimento



Jarret *et al.*, 2018

Pirograma real

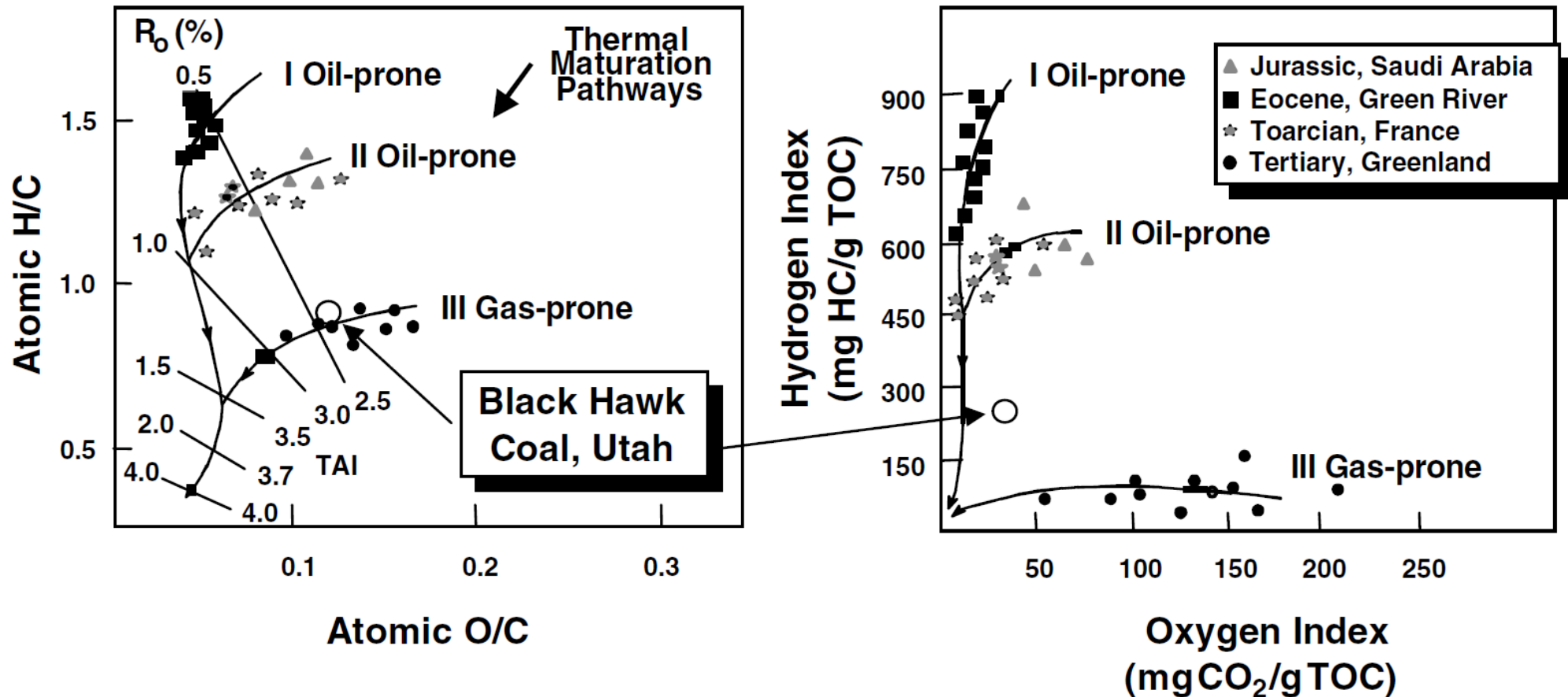


Reyes *et al.*, 2016

4. Pirólise Rock-Eval - Parâmetros

- S_1 – Quantidade de hidrocarbonetos presentes na **amostra antes da análise** (betume) >> mg de HC/g de rocha
- S_2 – Volume de **hidrocarboneto gerado no experimento** >> mg de HC/g de rocha
- S_3 – **CO₂ eliminado na quebra do querogênio** >> mg de CO₂/g de rocha
- T_{max} – Temperatura do **pico de expulsão de S_2**
- PI – Índice de produção (*transformation index*) >> $S_1 / (S_1 + S_2)$ >> **rochas mais maduras apresentam valores mais elevados de PI**
- TI – Índice de transformação (*transformation index*) >> S_1 / COT >> **Utilizado como parâmetro de controle** >> amostras contaminadas com HC externo apresentam TI anômalo
- PY – Potencial gerador (*potential yield*) >> $S_1 + S_2$ >> **total de hidrocarbonetos expelidos na pirólise**
- IH – Índice de Hidrogênio (*hydrogen index – HI*) >> S_2 / COT
- IO – Índice de Oxigênio (*oxygen index – OI*) >> S_3 / COT

5. Interpretando COT e Pirólise Rock-Eval – Interpretação: Qualidade da Rocha Geradora

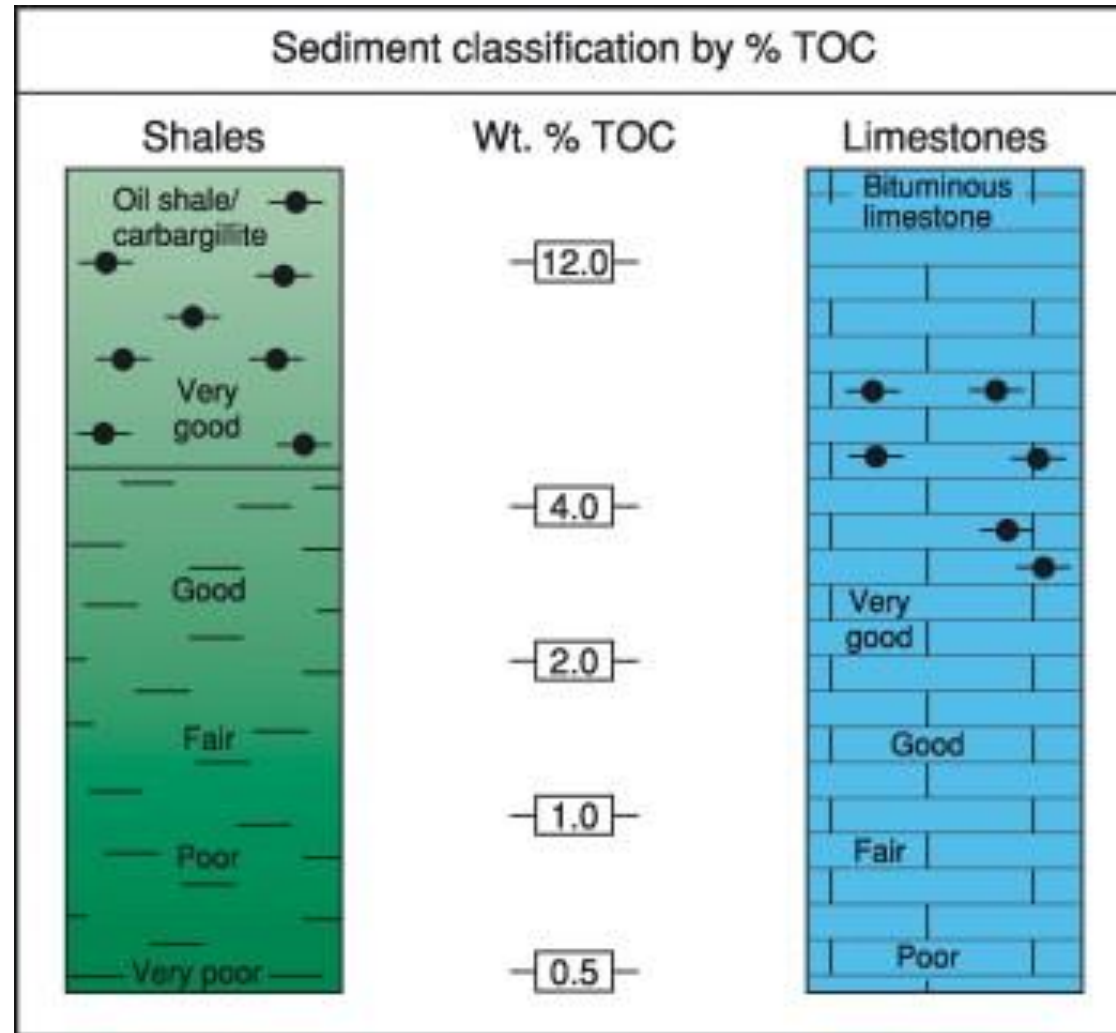


5. Interpretando COT e Pirólise Rock-Eval – Qualidade da Rocha Geradora

Potential (quantity)	TOC (wt.%)	Rock-Eval (mg/g rock)		Bitumen (ppm)	Hydrocarbons (ppm)
		S1	S2		
Poor	<0.5	<0.5	<2.5	<500	<300
Fair	0.5–1	0.5–1	2.5–5	500–1000	300–600
Good	1–2	1–2	5–10	1000–2000	600–1200
Very good	2–4	2–4	10–20	2000–4000	1200–2400
Excellent	>4	>4	>20	>4000	>2400

Kerogen (quality)	Hydrogen index (mg hydrocarbon/g TOC)	Rock-Eval		Atomic H/C	Main product at peak maturity
		S2/S3	S2		
I	>600	>15	>2.5	>1.5	Oil
II	300–600	10–15	2.5–5	1.2–1.5	Oil
II/III	200–300	5–10	5–10	1.0–1.2	Oil/gas
III	50–200	1–5	10–20	0.7–1.0	Gas
IV	<50	<1	>20	<0.7	None

5. Interpretando Qualidade da Rocha Geradora – Diferença entre carbonatos e siliciclásticas

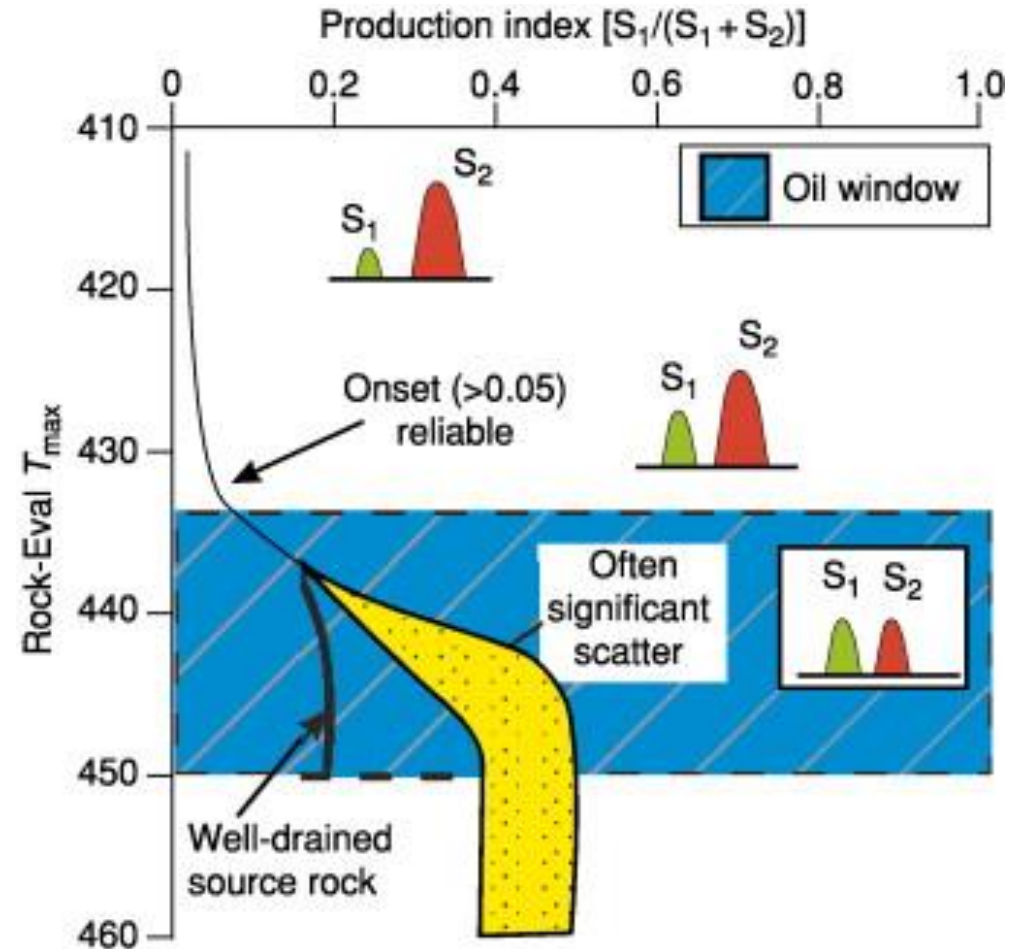
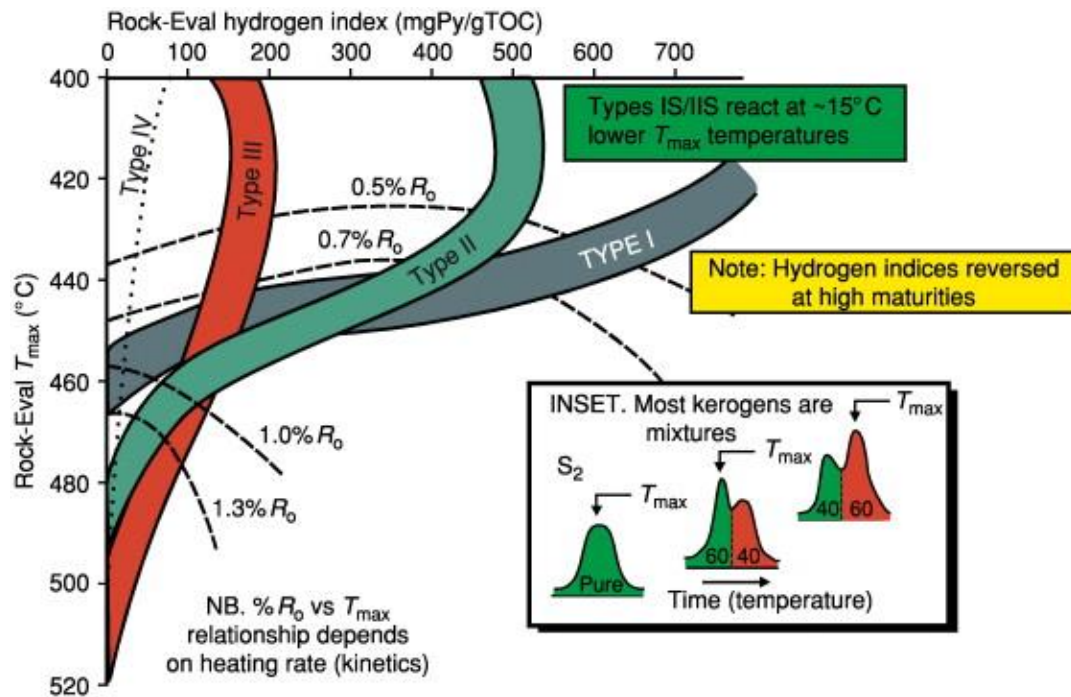


5. Interpretando COT e Pirólise Rock-Eval – Maturação

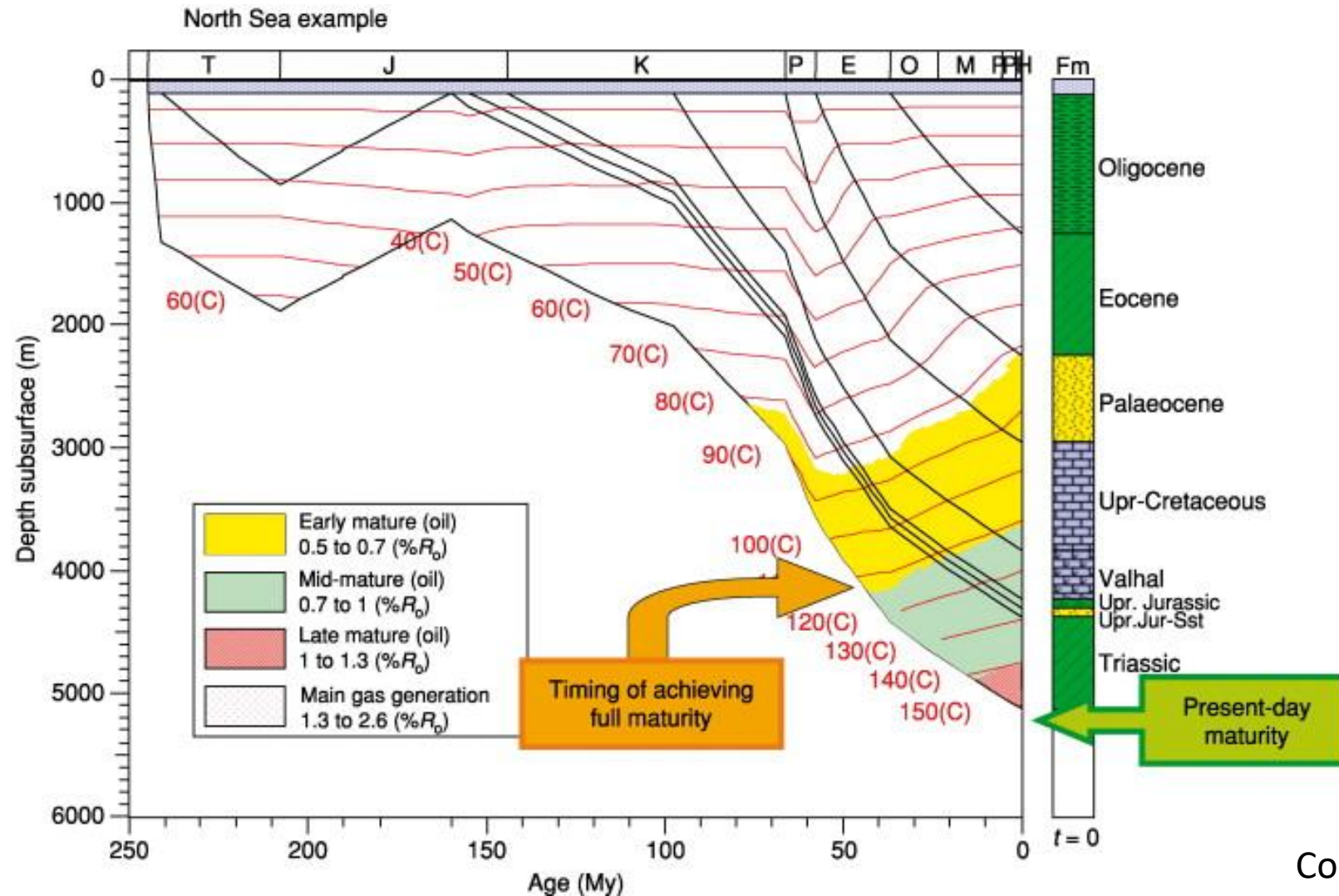
Maturity	Maturation			Generation		
	R _o (%)	T _{max} (°C)	TAI	Bitumen/TOC*	Bitumen (mg/g rock)	Production index (S1/(S1+S2))
Immature	0.20–0.60	<435	1.5–2.6	<0.05	<50	<0.10
Mature						
Early	0.60–0.65	435–445	2.6–2.7	0.05–0.10	50–100	0.10–0.15
Peak	0.65–0.90	445–450	2.6–2.7	0.15–0.25	150–250	0.25–0.40
Late	0.90–1.35	450–470	2.9–3.3	–	–	>0.40
Postmature	>1.35	>470	>3.3	–	–	–

(c)

5. Interpretando COT e Pirólise Rock-Eval – Maturação



5. Maturação na história evolutiva de uma bacia sedimentar



6. Resumo da Aula

- Nessa aula foram abordados:

1. Contextualização e objetivo do método;
2. Revisamos a definição de **constituintes orgânicos das rochas, tipos de querogênio e os produtos do processo de maturação;**
3. O método de **reflectância de vitrinita** e sua aplicação como principal geotermômetro vinculado ao sistema petrolífero;
4. Os métodos de determinação de **medição do carbono orgânico total e pirólise Rock-Eval™;**
5. Parâmetros geoquímicos de caracterização de **qualidade da rocha geradora, potencial gerador e estimativa da maturação via Tmax;**

7. Referências

- Crain's Petrographical Handbook from anthracite to natural coaly graphite by XRD, Raman spectroscopy, and HRTEM. *Spectrochimica Acta Part A*.
(<https://www.spec2000.net/index.htm>) Acessado: Janeiro/2023
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