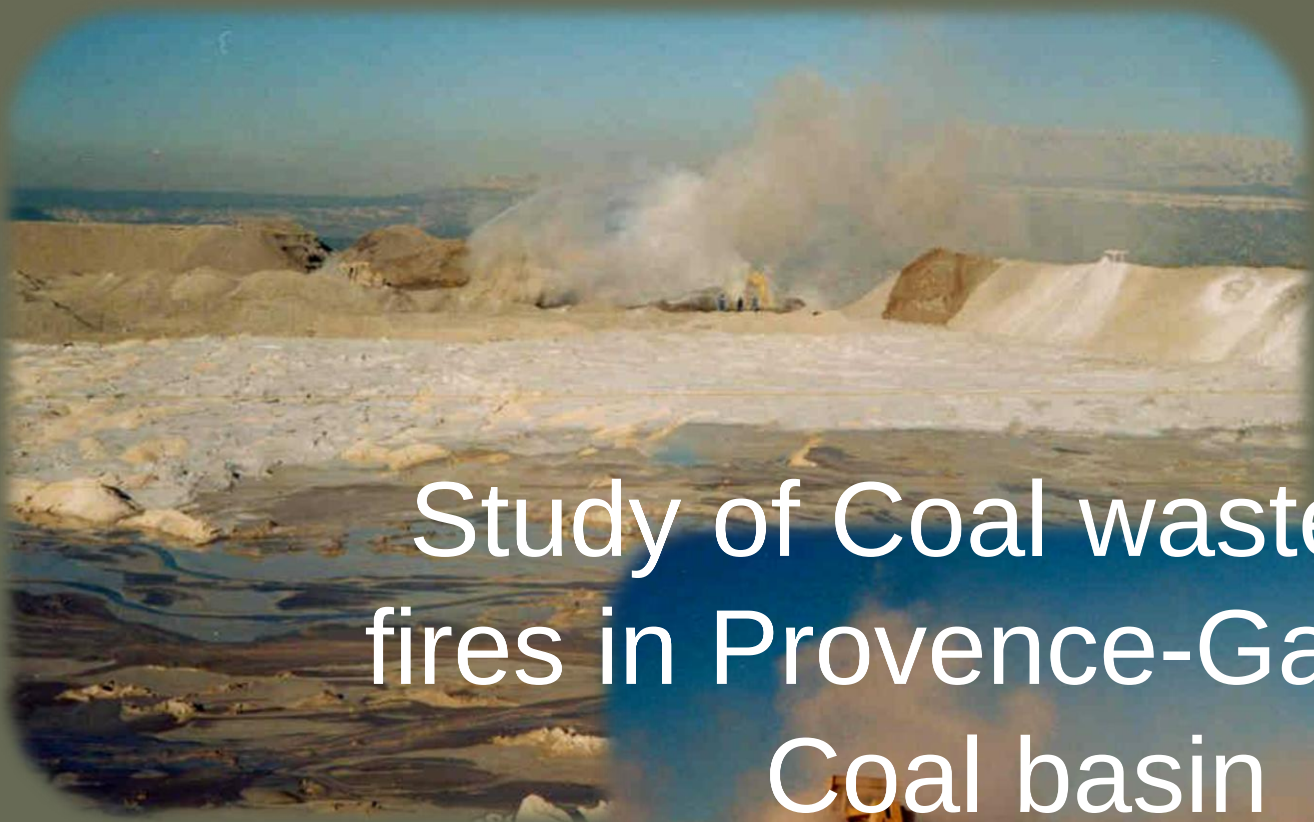


Study of Coal waste heap fires in Provence-Gardanne Coal basin

Photos : waste heap Bramefan, 1998

with collaboration of Mélanie Clouard

Naze - Nancy Masalehdani & Jean-Luc Potdevin
Naze-Nancy.Masalehdani@univ-lille1.fr

Bassin minier de Provence


Sauvaires (2001)
Emission of admixed gas
and water vapour around
gas vents
Défends (2001)

Lignite waste heaps: Molx

- Height: 65-85 m
- Slope: 33
- Granulometry: 20-400 mm

- Materials:
  - Unburnt rock debris
    - Limestone 60%
    - Sandstone 5-10%

  - Rejected lignite 15-20%
  - Burnt debris «Clinkers»
  - Fly ash

MAIN OBJECTIVES

- Determine the mineralogy & the chemical compositions
  - unburnt original rock debris
  - burnt rock debris «clinkers»
  - rejected lignite
- Investigate the spontaneous combustion
- Determine the secondary-by products

ANALYTICAL METHODS

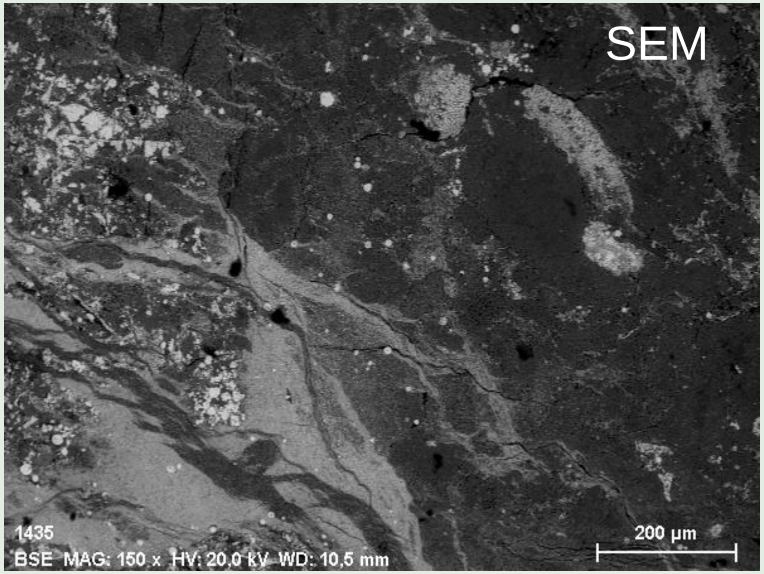
- X-Ray Diffraction (XRD)
- Optical microscope (OM)

- Scanning electron microscope - Energy-dispersive spectroscopy (SEM-EDS)
- Electron microprobe - wavelength dispersion spectrometry (EMP-WDS)

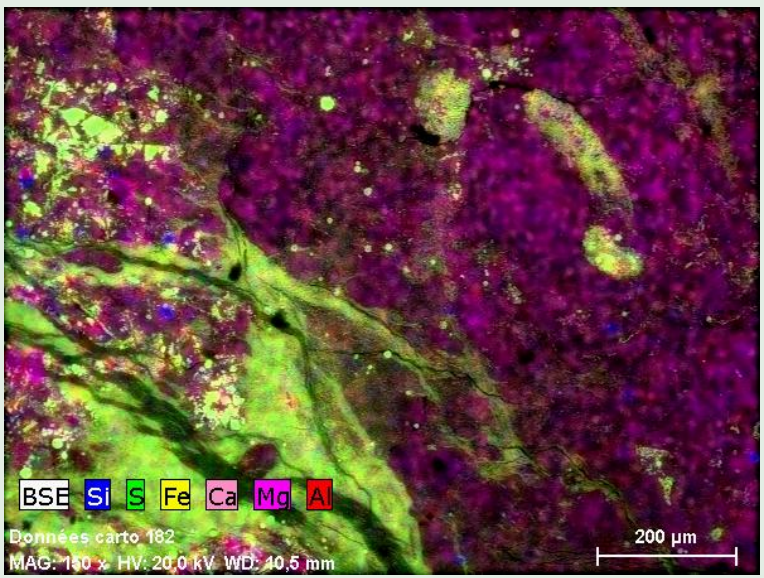
- Raman spectroscopy (RS)
- Chemical analyses (ICP-FIMS-INAA)

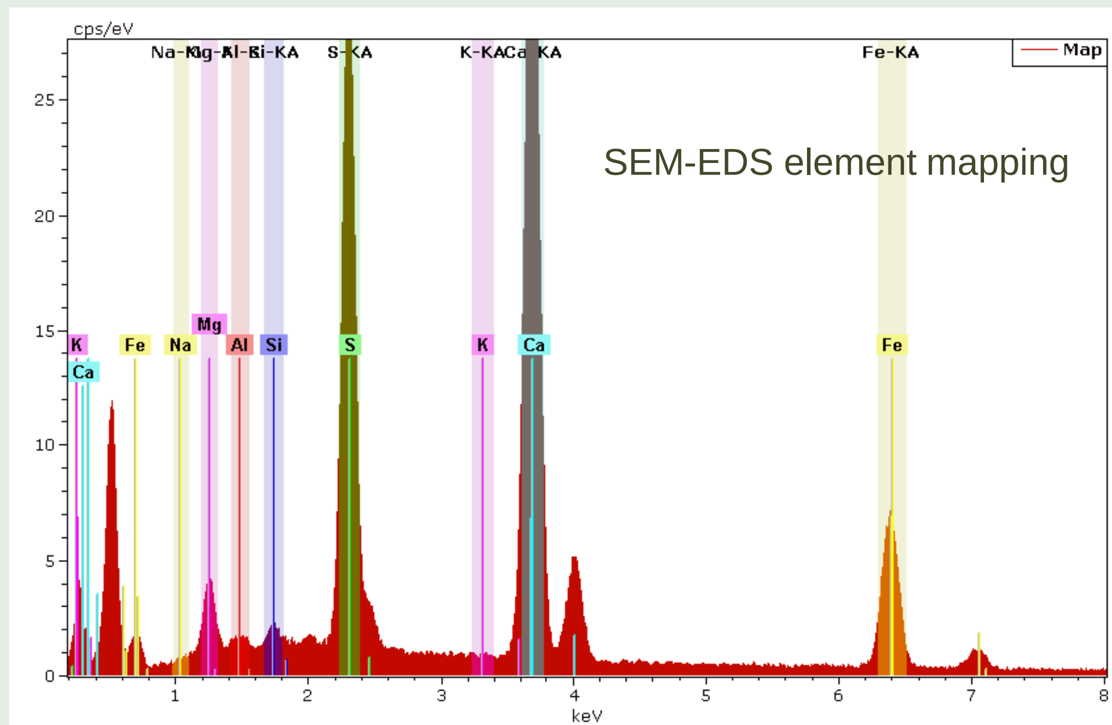
RESULTS

- Unburnt Limestone debris components
  - Minerals
    - Calcite $CaCO_3$
    - Dolomite $CaMg(CO_3)_2$
    - Pyrite FeS_2
    - Marcasite FeS_2
    - Quartz SiO_2
    - Kaolinite $Al_2Si_2O_5(OH)_4$
  - Fossils
    - Ostracods & Lamellibranches
  - Organic matter

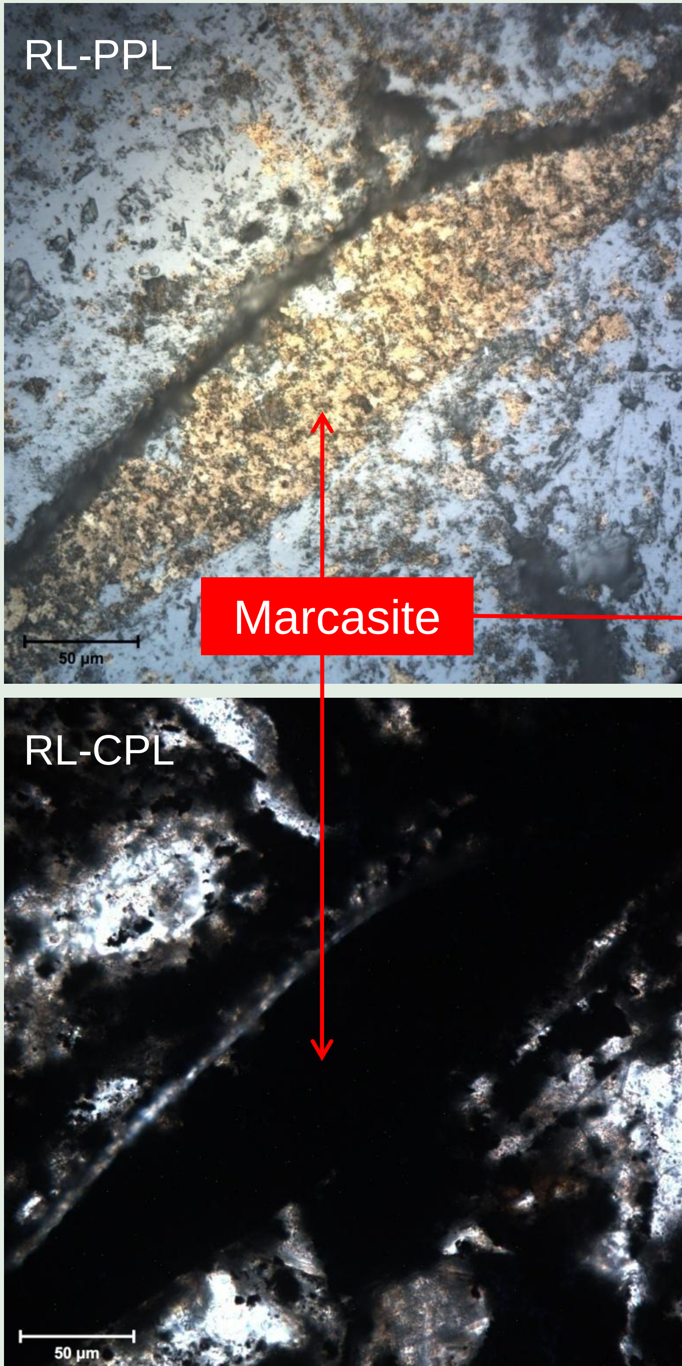


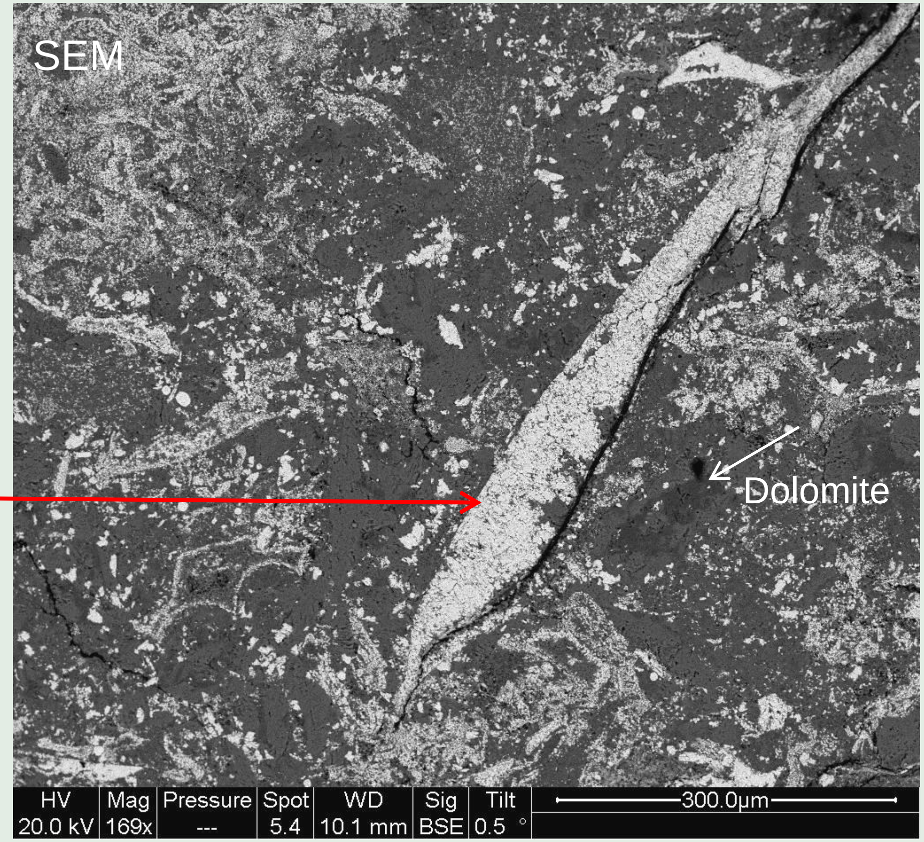
- Mineral assemblages
  - Calcite - Dolomite - Pyrite - Marcasite Quartz Kaolinite
  - Calcite - Pyrite Quartz Kaolinite

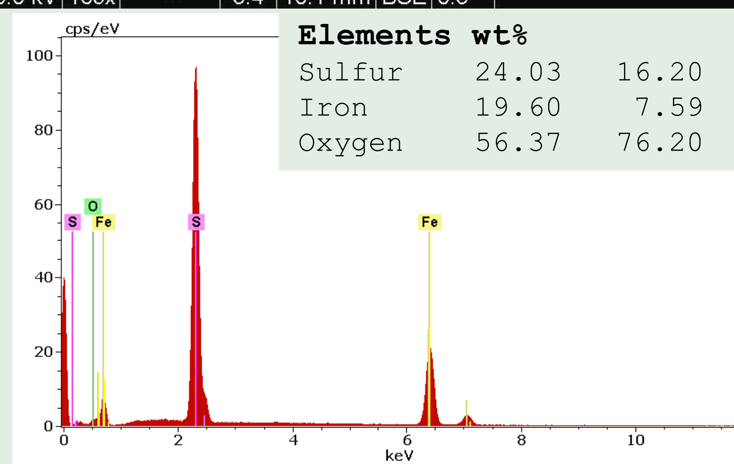




Marcasite (iron disulphide) FeS_2

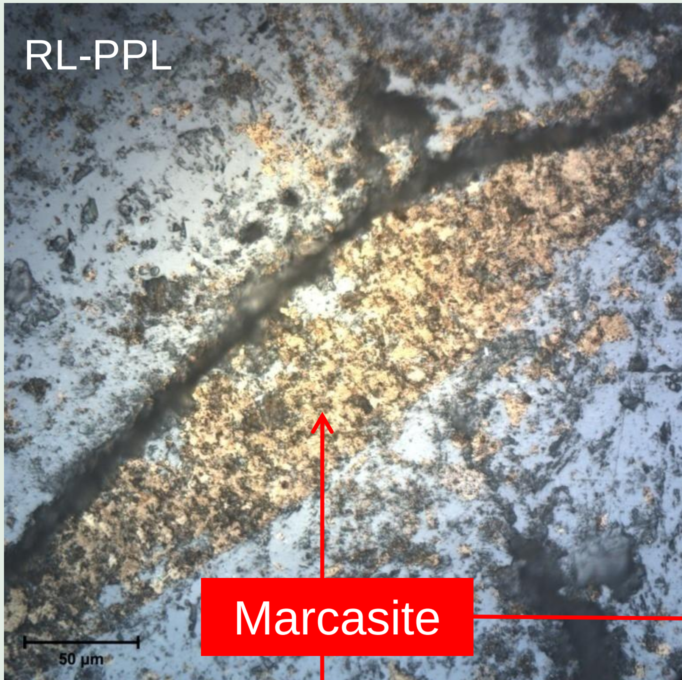


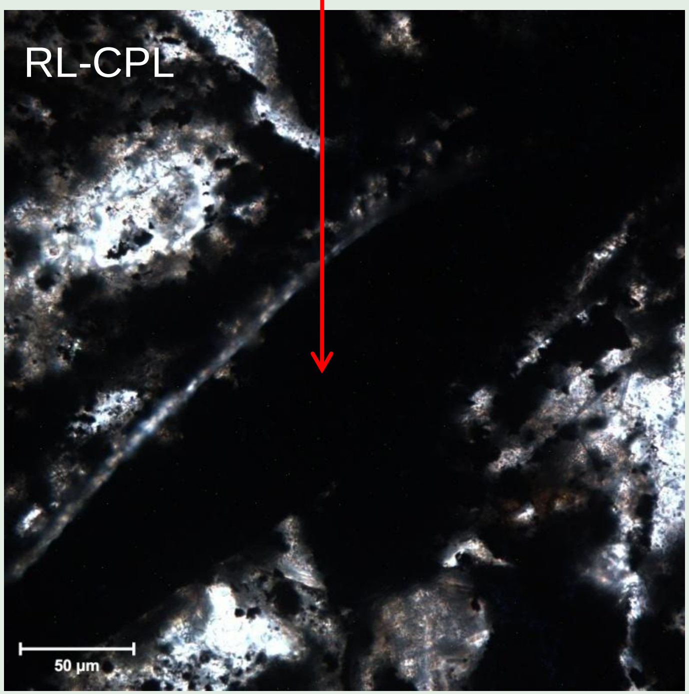


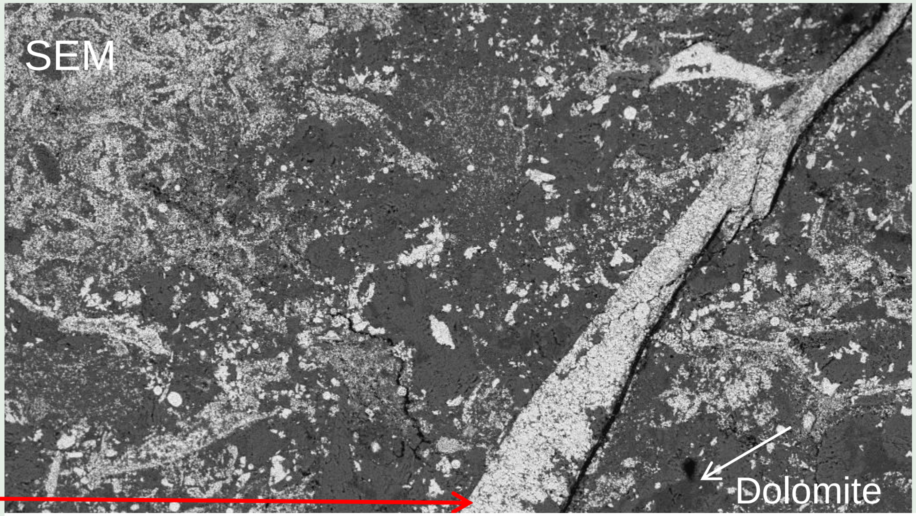


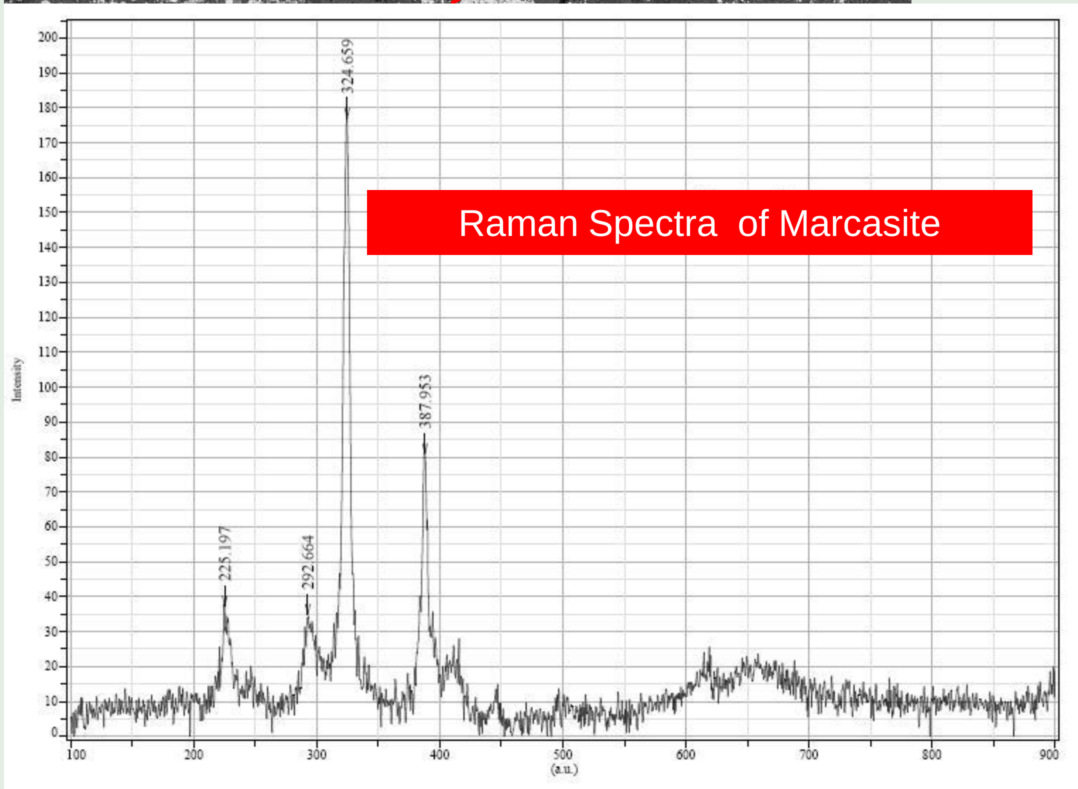
Elements	wt%			
Sulfur	24.03	16.20	SO_4	71.98
Iron	19.60	7.59	Fe_2O_3	28.02
Oxygen	56.37	76.20		0.00

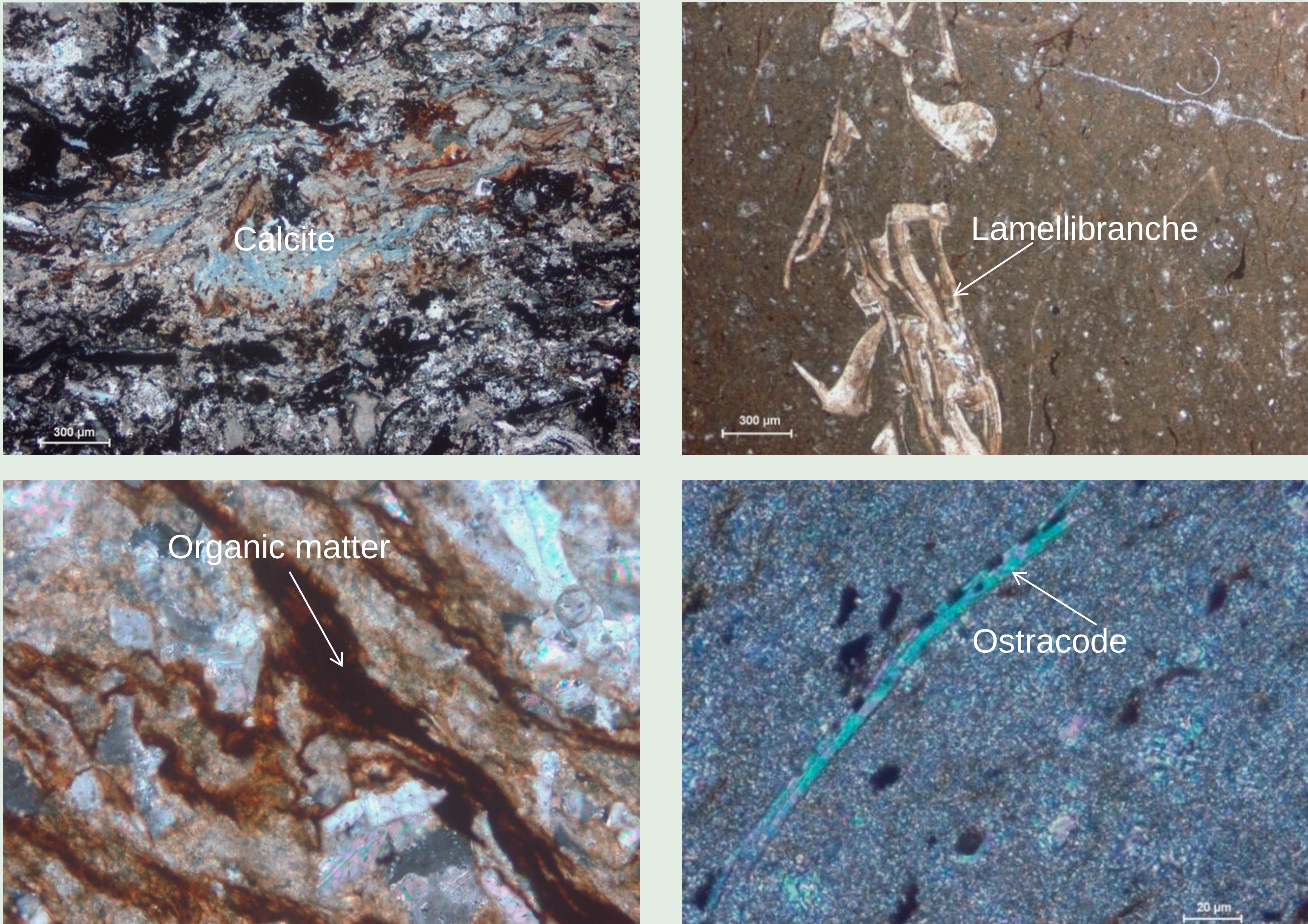
Marcasite (iron disulphide) FeS_2










Calcite
300 µm
Lamellibranche
300 µm
Organic matter
Ostracode
20 µm

▪ **ICPS-MS Analysis:** Variegated Limestone

Wt%	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	MgO	MnO	P_2O_5	TiO_2	H_2O	LOI	Total
AVE.	3.17	1.25	42.02	0.041	0.34	3.05	1.39	0.69	0.047	0.045	6.4	43.13	85.82

ppm	As	Ag	Au	Ba	Be	Bi	Br	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er
AVE.	44.1	0.5	0.00	71.2	0.1	0.01	10.5	0.5	6.43	1.1	14.5	0.85	9.30	0.41	0.22

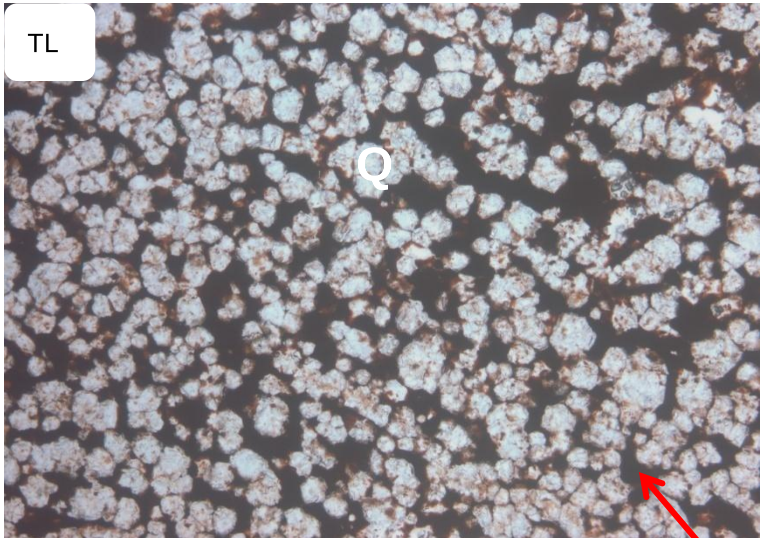
ppm	Eu	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Lu	Mo	Nb	Nd	Ni
AVE.	0.10	1.90	0.44	0.56	0.26	0.06	0.1	0.00	3.71	0.72	0.05	3.2	1.07	2.81	8.30

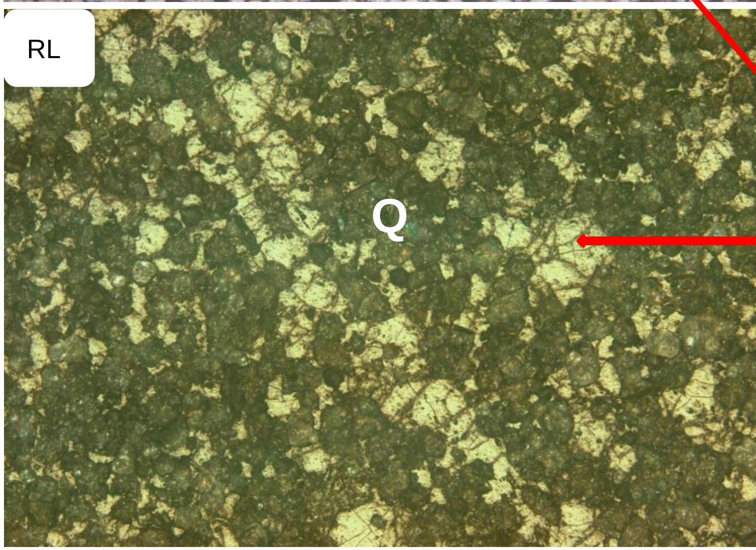
	Pb	Pr	Rb	Sb	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	Tl	Tm	U
AVE.	4.37	0.80	8.37	0.34	1.65	3	0.53	1	634	0.6	0.70	1	0.08	0.03	1.8

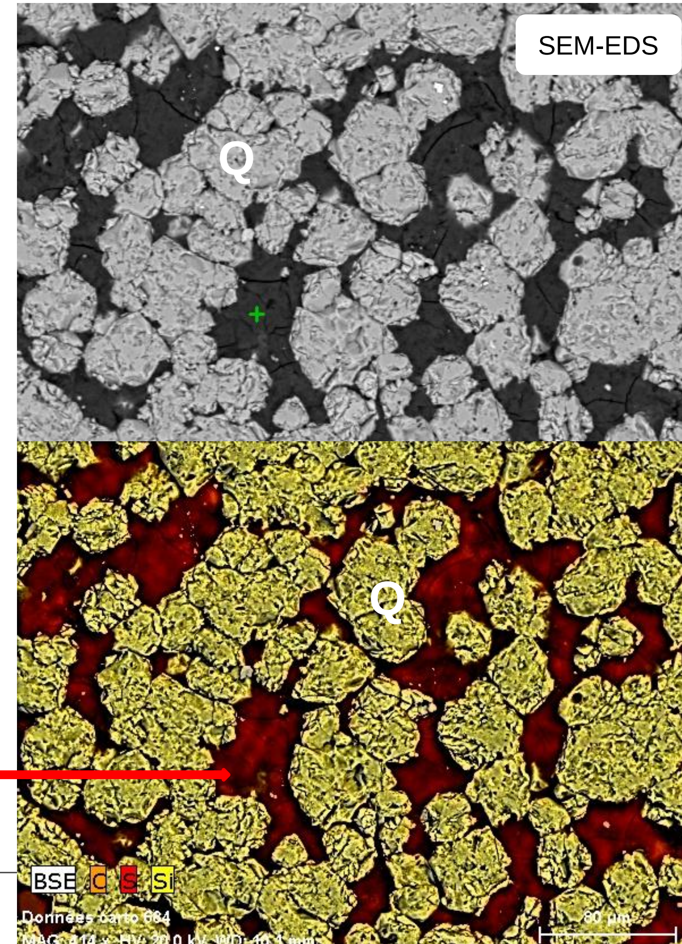
ppm	V	W	Y	Yb	Zn	Zr
AVE.	14	0.5	2.80	0.60	14.3	9.30

Wt%	C	S	N	H
AVE.	16.75	2.50	0.208	0.90

➢ Unburnt Sandstone

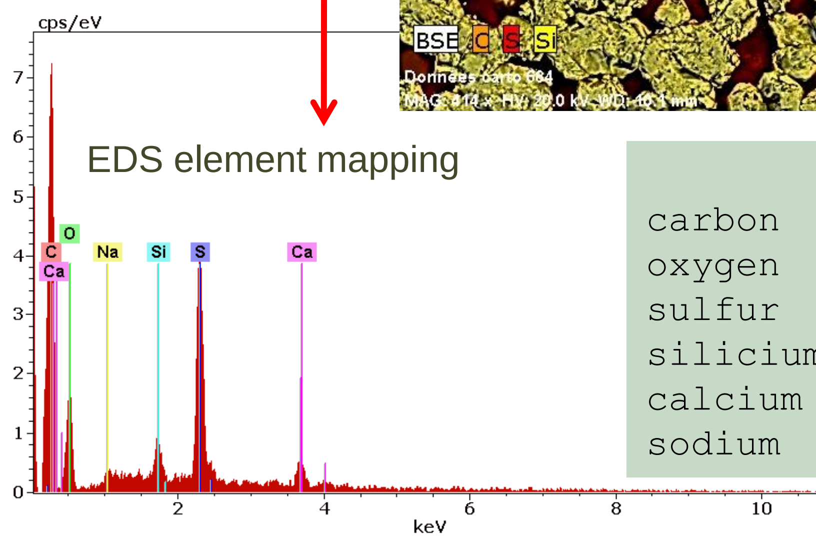






Organic matter

EDS element mapping



	wt%
carbon	77.45
oxygen	13.70
sulfur	6.00
silicium	0.83
calcium	1.42
sodium	0.59

Constituents

- Quartz (Q)
- Organic material

▪ **ICPS-MS Analysis**: Dark-gray Sandstone

Wt%	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	MgO	MnO	P_2O_5	TiO_2	H_2O	LOI	Total
AVE.	85.24	0.16	0.27	0.14	0.02	0.15	0.26	0.003	0.01	0.003	3.03	12.26	98.18

Nearly pure silica — enriched in organic matter

ppm	As	Ag	Au	Ba	Be	Bi	Br	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er
AVE.	1.8	0.3	0.02	10	0.1	0.1	3.6	0.5	3.01	1	11	0.1	3.7	0.05	0.03

ppm	Eu	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Lu	Mo	Nb	Nd	Ni
AVE.	0.03	1	0.07	0.5	0.02	0.12	0.04	0.1	5	48	0.09	2	0.2	2	3.7

ppm	Pb	Pr	Rb	Sb	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	Tl	Tm	U
AVE.	3	0.2	1	0.2	0.16	3	0.11	1	11	0.01	0.13	0.08	0.05	0.00	0.39

ppm	V	W	Y	Yb	Zn	Zr
AVE.	0.05	0.5	0.5	0.04	7.4	1.3

Wt%	C	S	N	H
AVE.	7.56	0.51	0.12	0.47

➢ICPS-MS analyses: Rejected Lignite

Proximate	Wt% (daf)
Moisture	7.67
Ash	4.10
Volatile Matter (VM)	45.89
Fixed Carbon	42.43
Ultimate	
Carbon	62.32
Hydrogen	6.26
Nitrogen	1.60
Oxygen	20.43
Pyritic sulphur	0.04
Sulphate sulphur	0.17
Organic sulphur	5.08
Total sulphur	5.29

Trace elements	ppm
As	184
Ba	419
Cd	1
Co	10
Cr	75
Cu	56
Hg	0.024
Mn	205
Mo	146
Ni	81
Pb	100
Rb	83
Sb	6
Se	3
Sr	7092
Zn	145
Zr	3
V	94

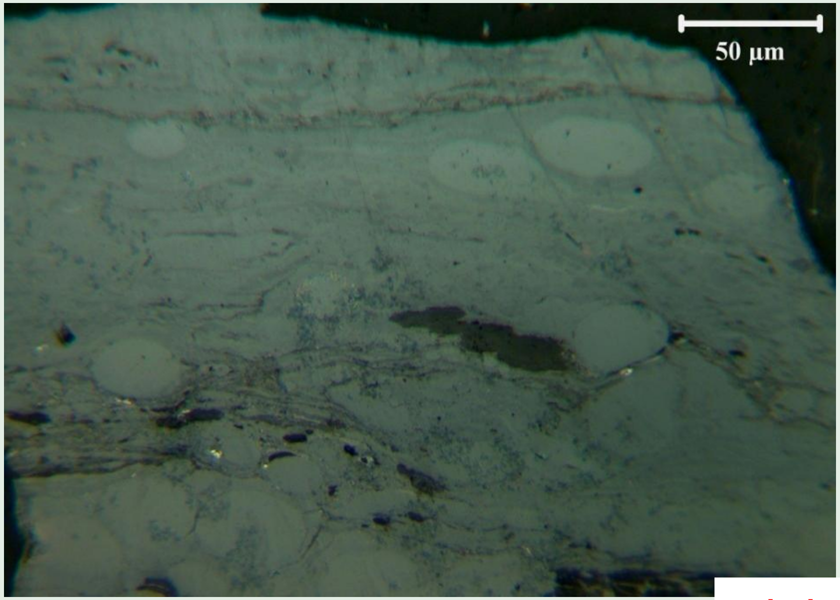
Mineral matter (wt%)

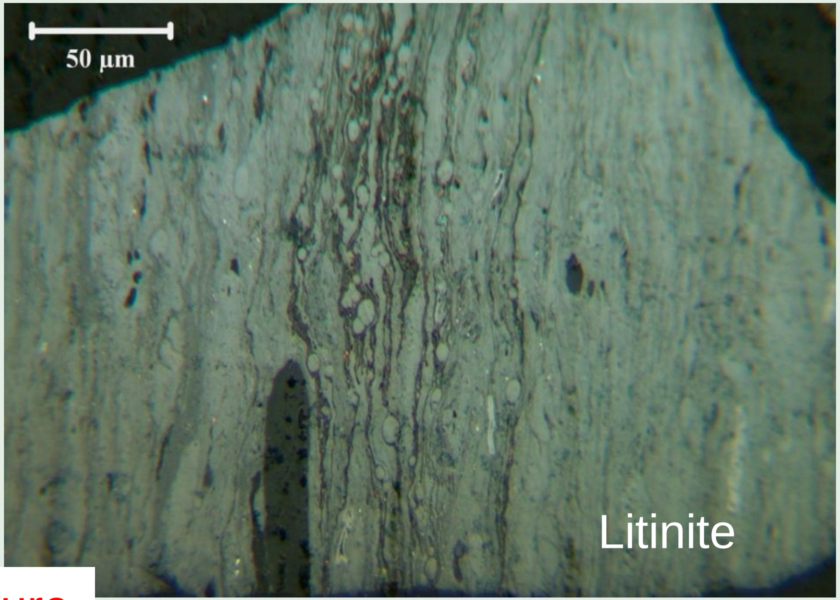
SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3*	MgO	P_2O_5	TiO_2	SO_3**
19.26	12.41	22.80	0.46	0.60	4.26	6.92	1.68	0.31	29.62

*Total **"Fe"** expressed as Fe_2O_3
** Total **"S "**expressed as SO_3

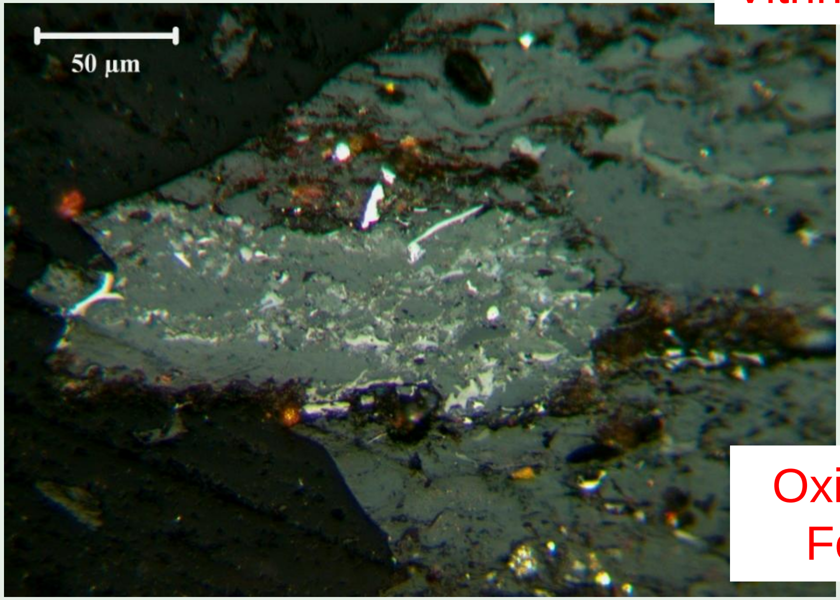
Mineral assemblages: Kaolinite, Gypsum, Pyrite / Marcasite, Calcite, Dolomite

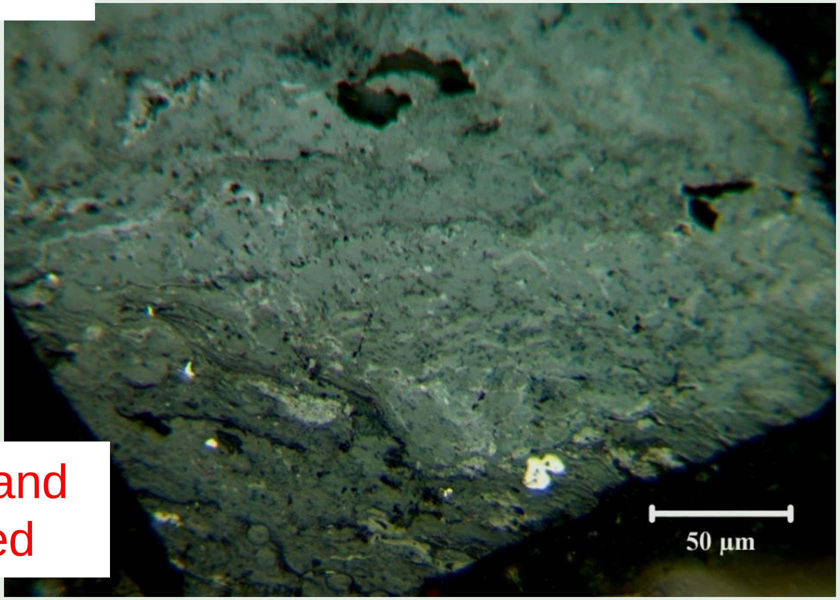
➢ Organic Petrography & Reflectance of the macerals





Vitrinite texture





Oxidized and Fossilized

- Organic petrography
  - small size maceral groups
    - liptinite (cutinite and liptodetrinite)
    - inertinite (fusinite and semi-fusinite)

- The reflectance values of macerals

R_{random}	0,38	st.dev	0,03
R_{max}	0,40	st.dev.	0,03

Indicating low reflectance, corresponding to **subbituminous C** to **lignite** in rank

- Hand specimens

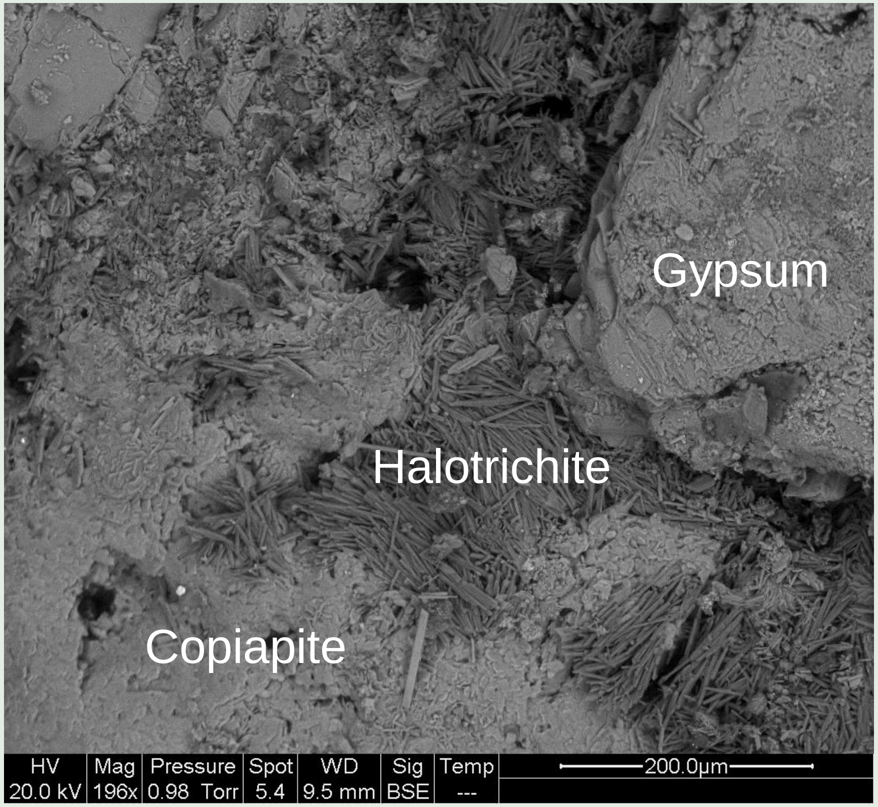
  Gastropods” are visible fossils , which are enriched in **Aragonite ($CaCO_3$)**

- Prone to oxidation

  Pyrite /marcasite oxidation in contact with air

➢ Sulphide oxidation: Secondary by- Products

Waste heap n 1



Copiapite: $Fe^{2+}Fe^{3+}4(SO_4)_6(OH)_2{\cdot}20(H_2O)$
Halotrichite: $Fe\ Al_2\ (SO_4)_4.22H_2O$
Gypsum: $(CaSO_4)_2.2H_2O$

➢ Pyrite / Marcasite (FeS_2) Oxidation and sulphate formation

$4FeS_2 + 7O_2 + H_2O \rightarrow 2Fe^{2+} + 4SO_4^{-2} + 4H^+$

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$

(Acidithiobacillus Ferroxidants)

$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15Fe^{2+} + 2SO_4^{-2} + 16H$

$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H_3$

T ≥ 22 C
1 atm.
pH 3- 4

- **Early oxidation stage**

$5Fe^{2+}SO_4\ .7H_2O_{(s)} + H_2SO_4 + O_2 \rightarrow Fe^{2+}Fe^{3+}4(SO_4)_6(OH)_2{\cdot}20(H_2O) + 11\ H_2O$

Iron sulphate (melanterite) — Iron sulphate (Copiapite)

$Fe^{2+}\ SO_4.7H_2O_{(s)} \rightarrow Fe^{2+}SO_4.4H_2O_{(s)} + H_2O$

Iron sulphate (melanterite) — Iron sulphate (rozenite)

$5Fe^{2+}SO_4.4H_2O_{(s)} + H_2SO_4 + O_2 \rightarrow Fe^{2+}Fe^{3+}4(SO_4)_6(OH)_2{\cdot}20(H_2O) + 11\ H_2O$

Iron sulphate (rozenite) — Iron sulphate (Copiapite)

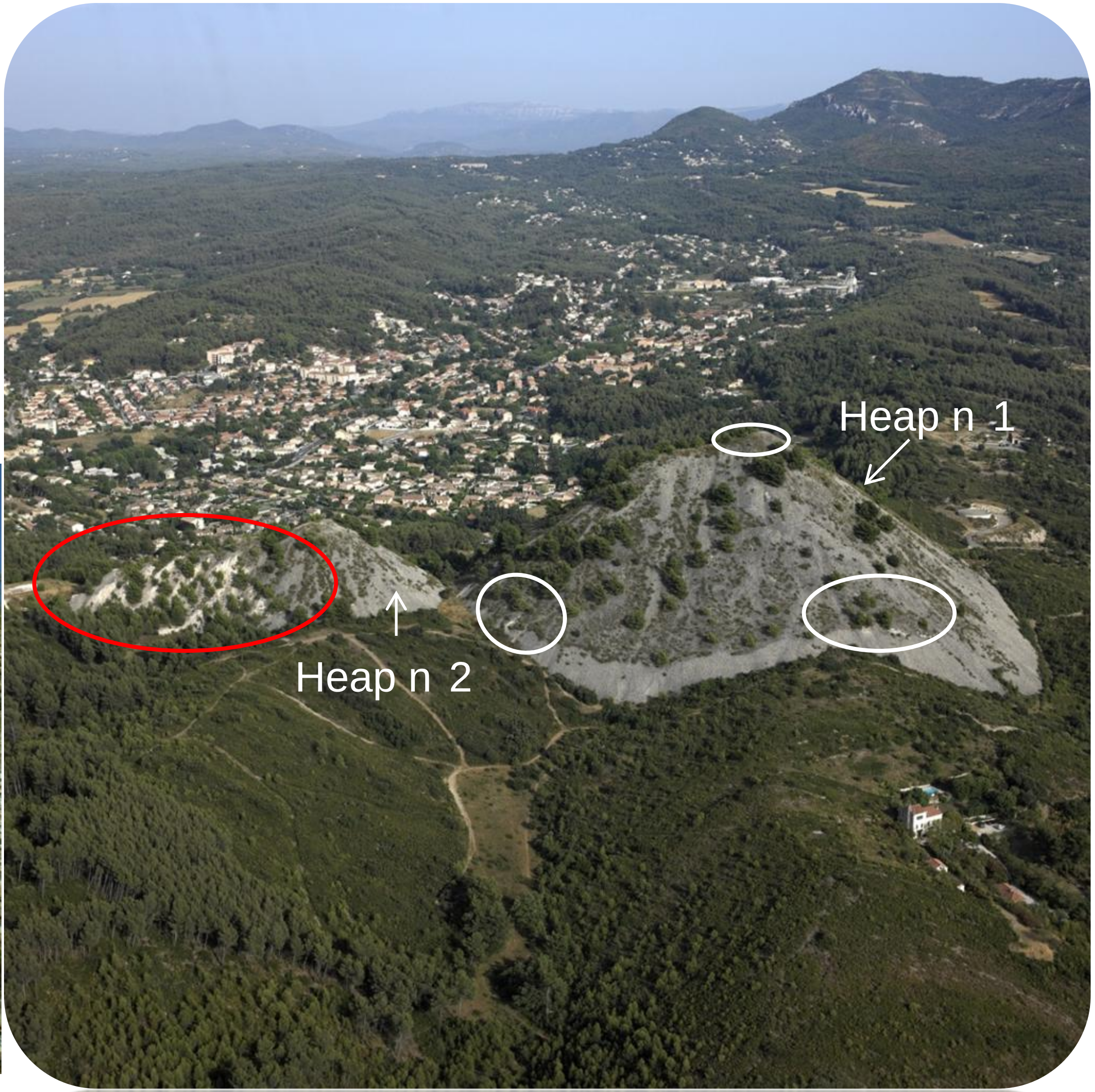
- **Late oxidation stage: decrease in Fe^{2+} : Al ratio**

$Fe^{2+} + 4SO_4^{\ 2-} + 2Al^{3+} + 22H_2O \rightarrow Fe\ Al_2\ (SO_4)_4..22H_2O$

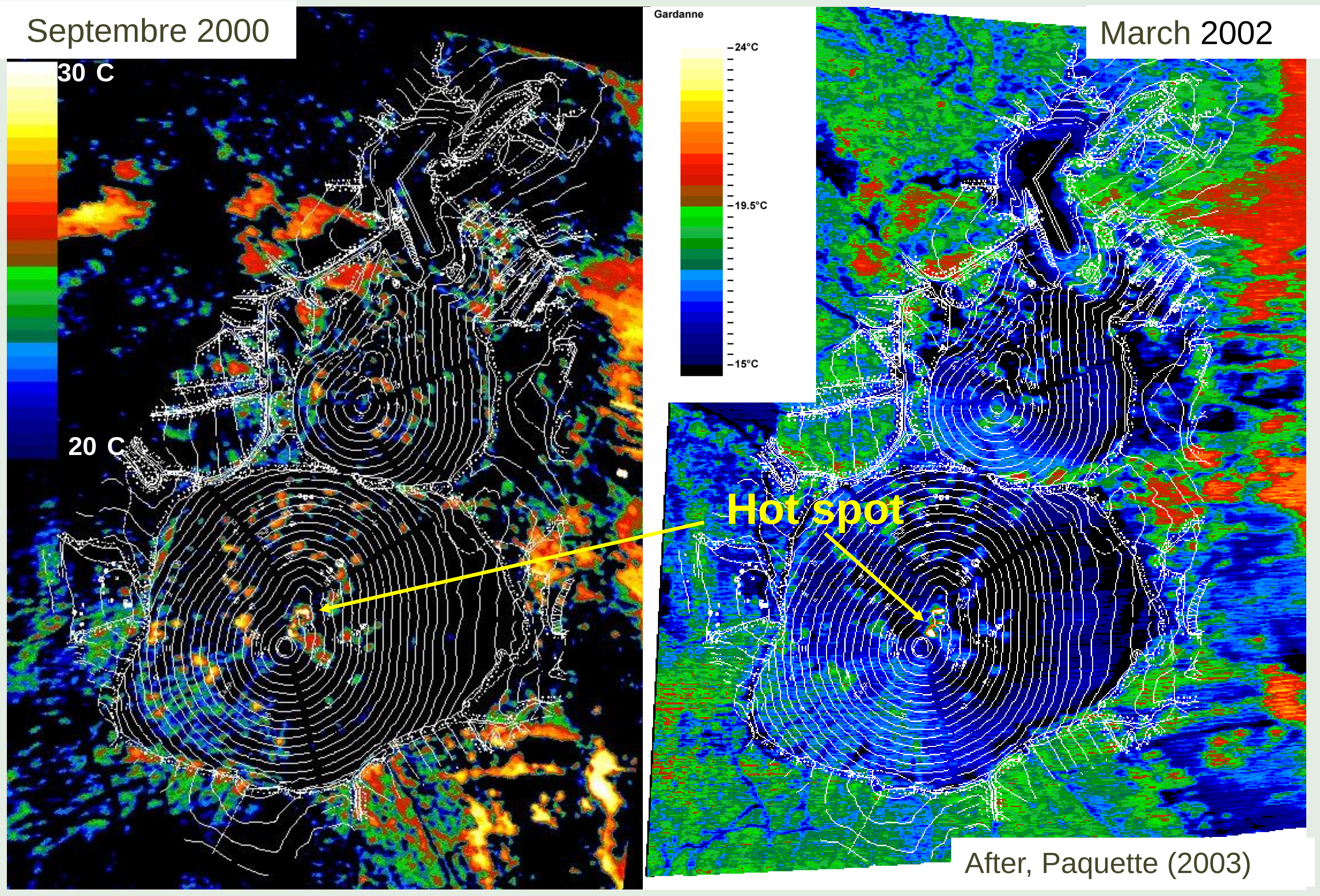
Aluminium-iron-sulphate (Halotrichite)

COAL FIRES

- Both heaps have undergone spontaneous combustion
- Combustion initiated within the slopes and the crest



➢ Infrared thermographic analyses



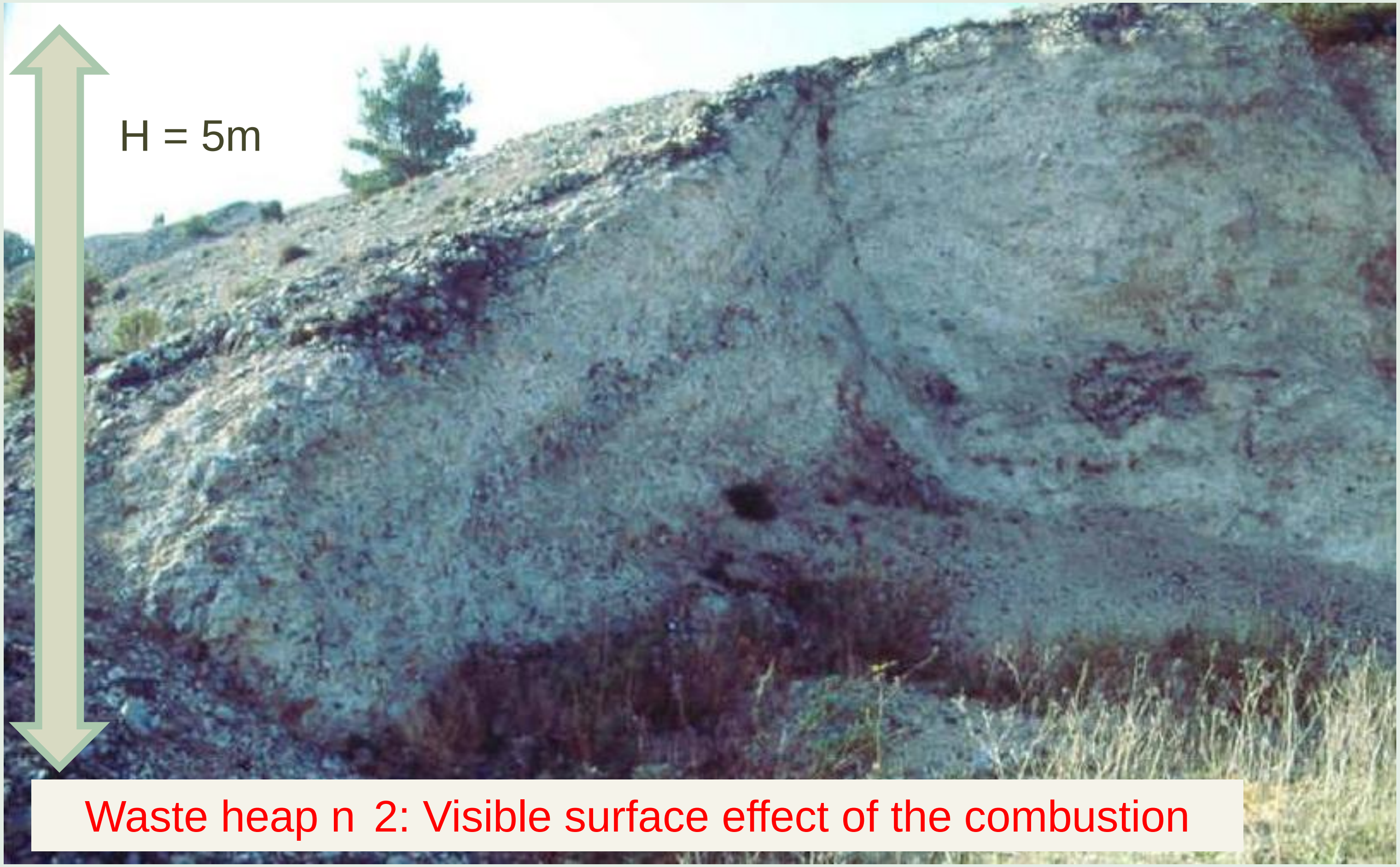
After, Paquette (2003)

➢ Effects of combustion on the sites' materials

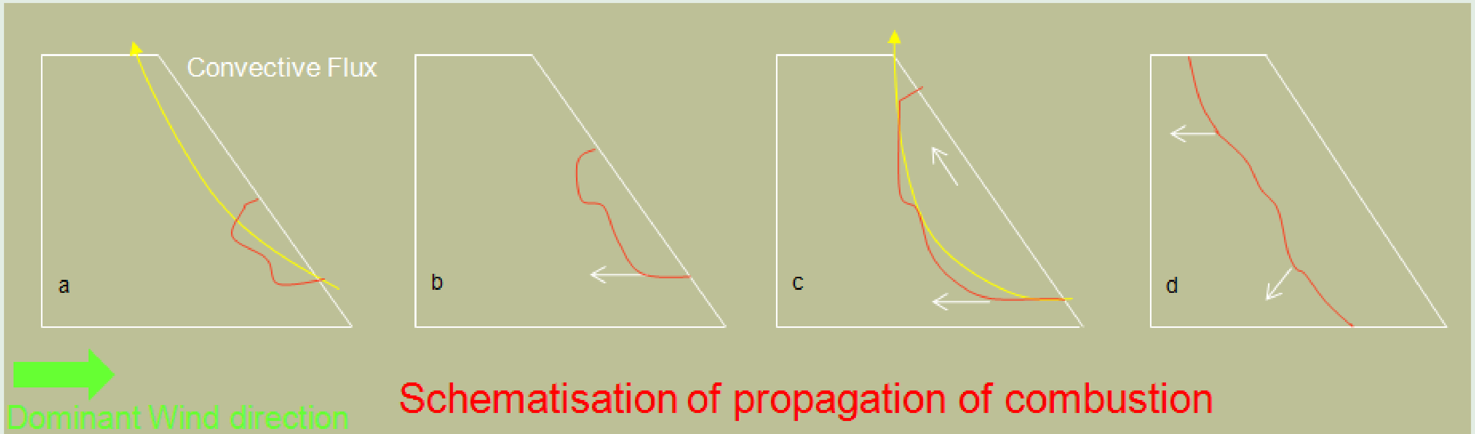
- Strength,
- Chemical composition,
- Mineralogical components,
- Coherence and
- Colour

Rock debris along the slope of the waste heap n 1 (south section) had undergone backing, then was transformed into more coherent debris.

Dominant
Wind direction

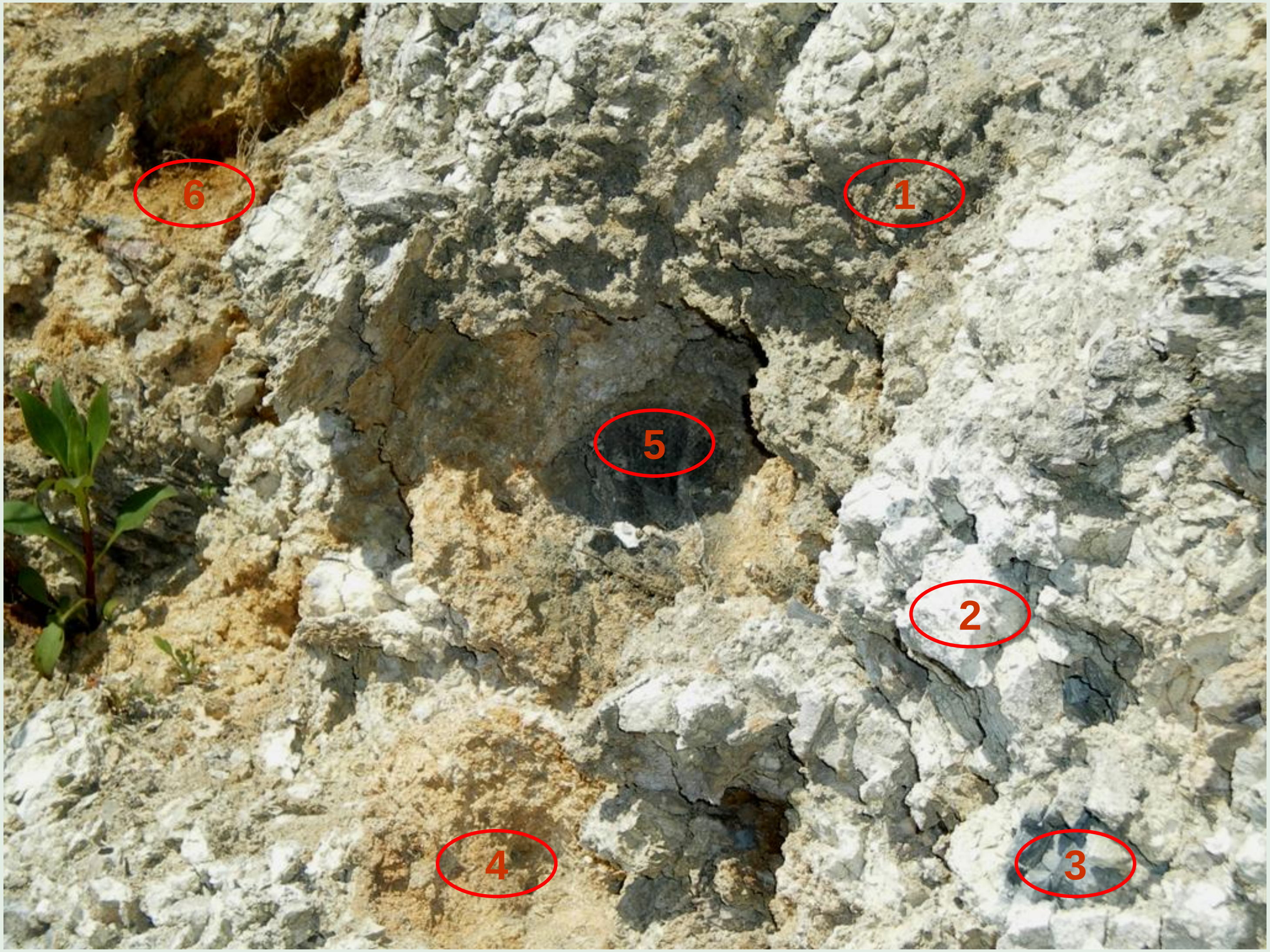


Waste heap n 2: Visible surface effect of the combustion



Schematisation of propagation of combustion

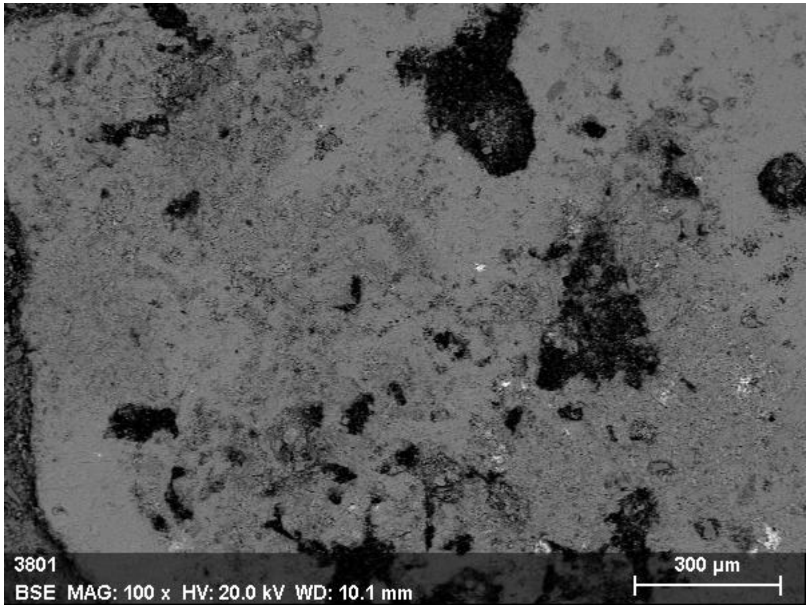
➢ Mineralogy & Composition of « Clinkers »

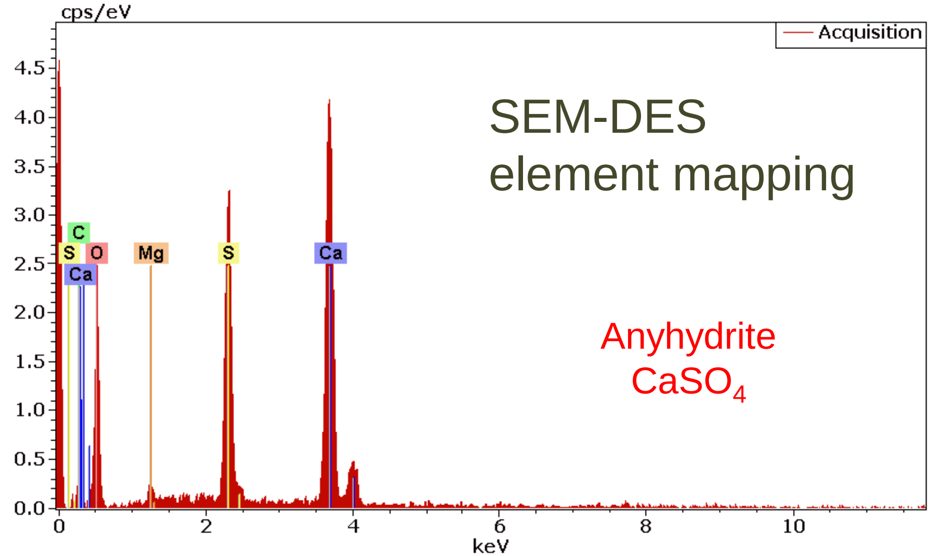


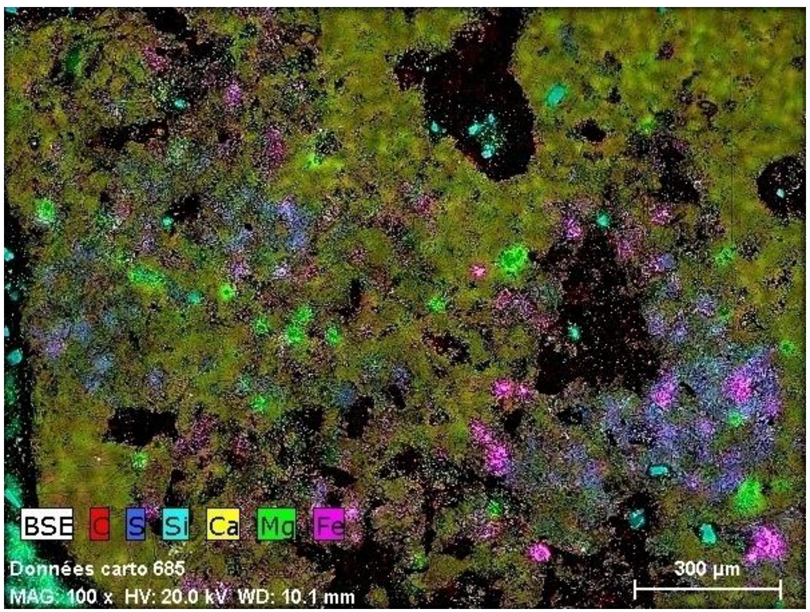
1,3 & 5: Calcite, Anyhydrite, Hematite, Quartz

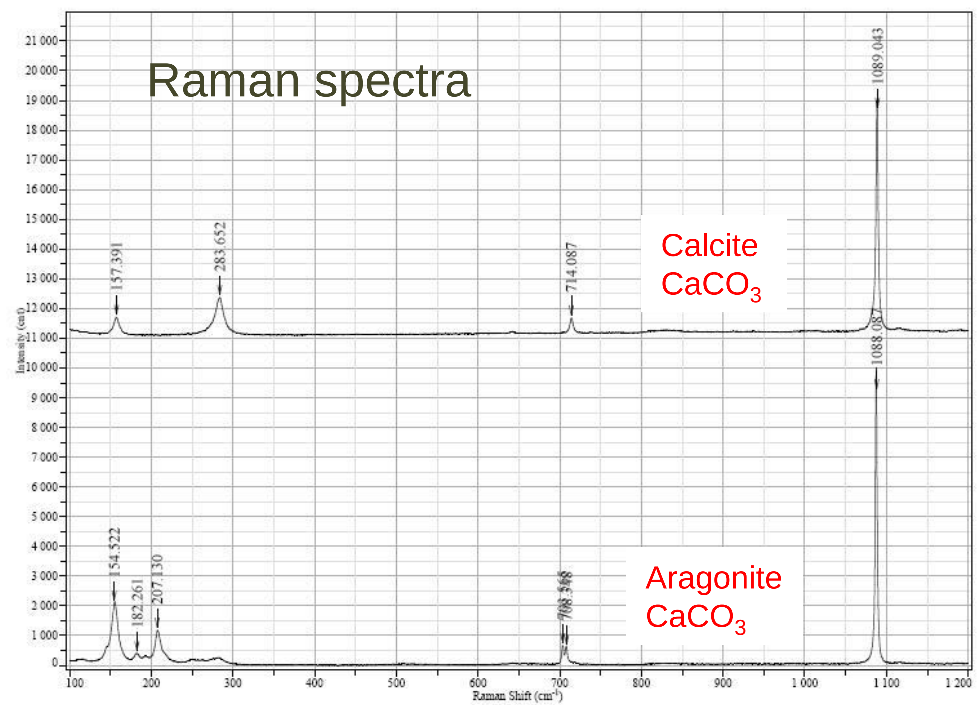
2: Calcite, Anyhydrite, Aragonite, Hematite, Quartz

4 & 6: Hematite, Calcite, Gypsum, Quartz



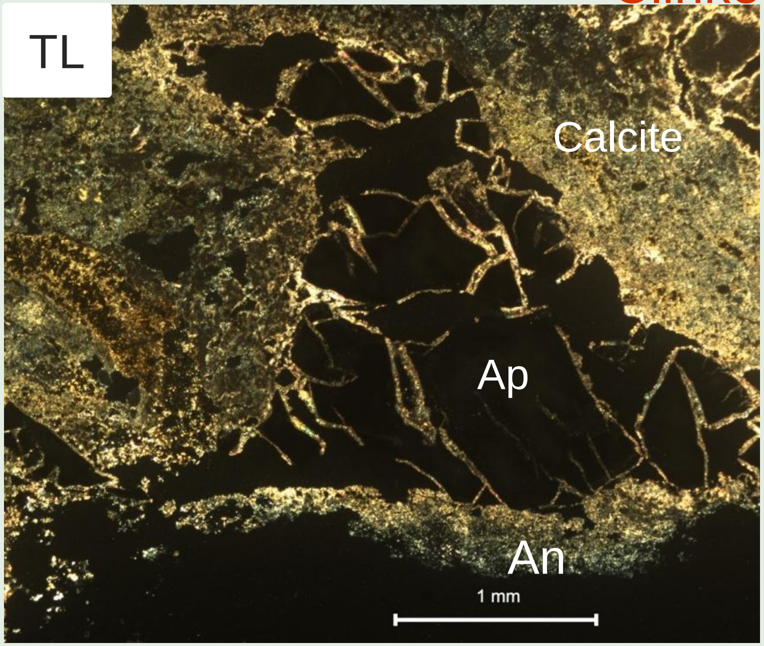


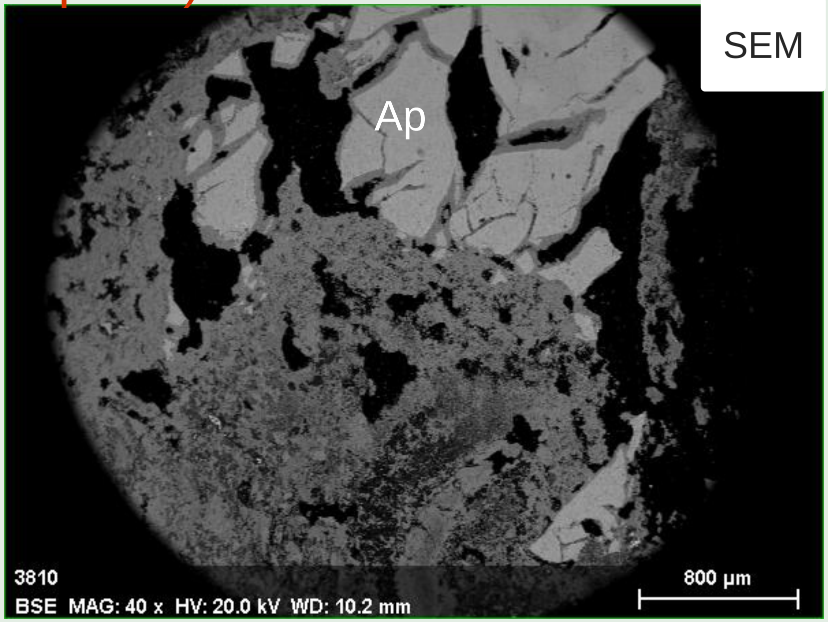




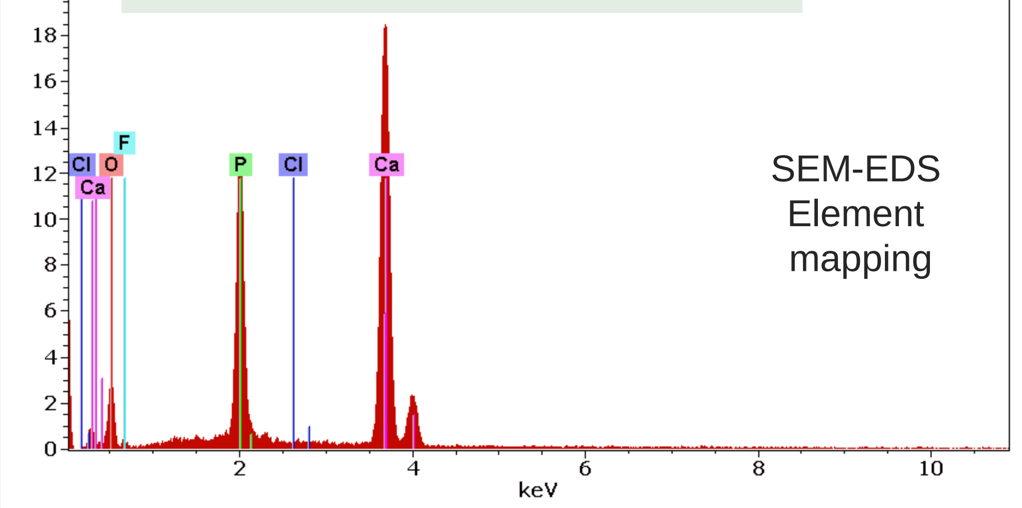
Clinker sample n 2

Mineral assemblage: Apatite - Calcite - Hematite - Anyhydrite - Quartz
Clinker (waste heap n 1)

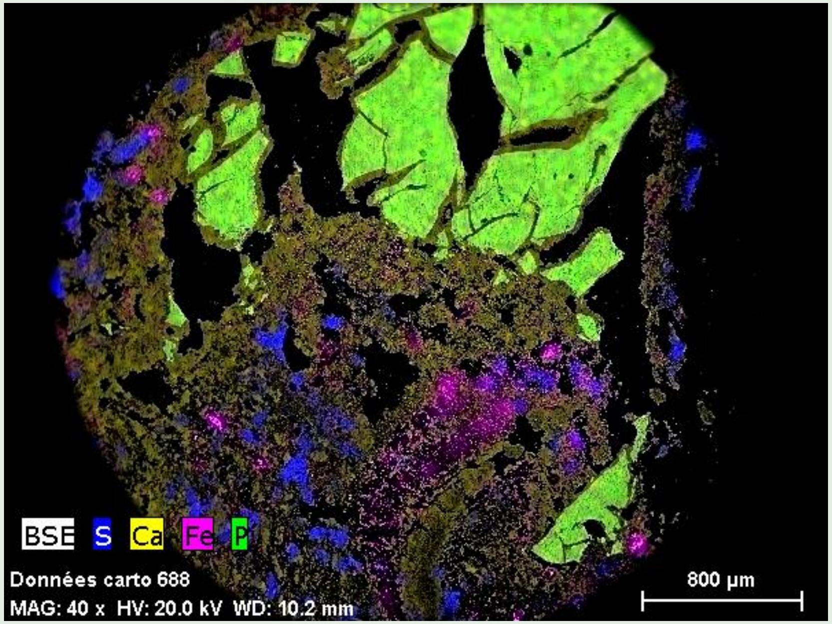




Oxygen	33.47	50.49		0.00
Phosphate	12.58	9.80	P_2O_5	28.82
Chlorine	0.00	0.00		0.00
Fluorine	10.80	13.72		10.80
Calcium	43.15	25.99	CaO	60.38



SEM-EDS Element mapping



ICPS-MS Analyses: Baked debris « Clinkers »

Wt%	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	MgO	MnO	P_2O_5	TiO_2	H_2O	LOI	Total
N 2	0.14	0.11	61.73	L.D	L.D	L.D	1.09	0.06	0.08	L.D	11	38.37	101.5

ppm	As	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu
N 2	1.43	61.9	L.D	L.D	0.00	1.01	1.00	L.D	L.D	5.73	0.09	0.06	0.03

ppm	Ga	Gd	Ge	Hf	Hg	Ho	In	La	Lu	Mo	Nb	Nd	Ni
N 2	L.D	0.106	L.D	0.032	0.00	0.023	L.D	7.63	0.008	0.65	0.086	0.52	4.32

ppm	Pb	Pr	Rb	Sb	Se	Sm	Sn	Sr	Ta	Tb	Th	Tm	U
N 2	0.90	0.152	L.D	0.17	L.D.	0.107	L.D	628.4	0.011	0.017	0.068	0.01	0.60

ppm	v	W	Y	Yb	Zn	Zr
N 2	**1.40**	**LD**	**0.81**	**0.05**	**L.D**	**1.38**

Wt%	C	S	N
AVE.	8.11	0.26	0.12

Wt%	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	MgO	MnO	P_2O_5	TiO_2	H_2O	LOI	Total
N 6	4.84	2.27	43.24	0.04	0.14	7.80	1.29	0.10	0.28	0.11	7.29	36.43	96.52

ppm	As	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu
N 6	122.4	146.4	0.00	0.00	0.00	17.63	7.32	20.74	0.71	8.11	2.02	1.00	0.59

ppm	Ga	Gd	Ge	Hf	Hg	Ho	In	La	Lu	Mo	Nb	Nd	Ni
N 6	4.15	2.32	0.38	0.48	0.003	0.371	0.00	7.63	0.130	4.01	1.51	11.01	25.67

ppm	Pb	Pr	Rb	Sb	Se	Sm	Sn	Sr	Ta	Tb	Th	Tm	U
N 6	2.28	2.80	4.83	3.02	L.D	2.53	0.764	717.2	0.146	0.367	1.601	0.141	10.21

ppm	v	W	Y	Yb	Zn	Zr
N 6	**28.26**	**0.22**	**11.52**	**0.90**	**21.37**	**17.51**

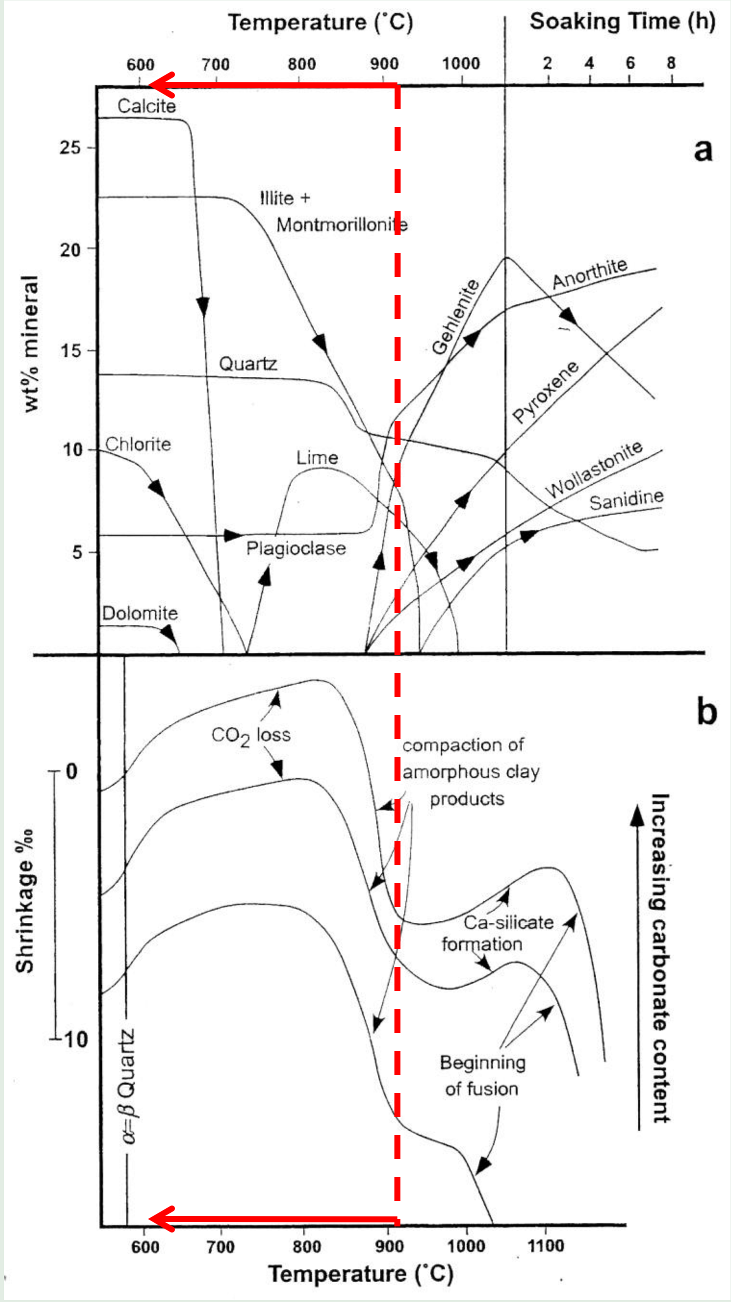
Wt%	C	S	N
N 6	8.05	1.51	0.14

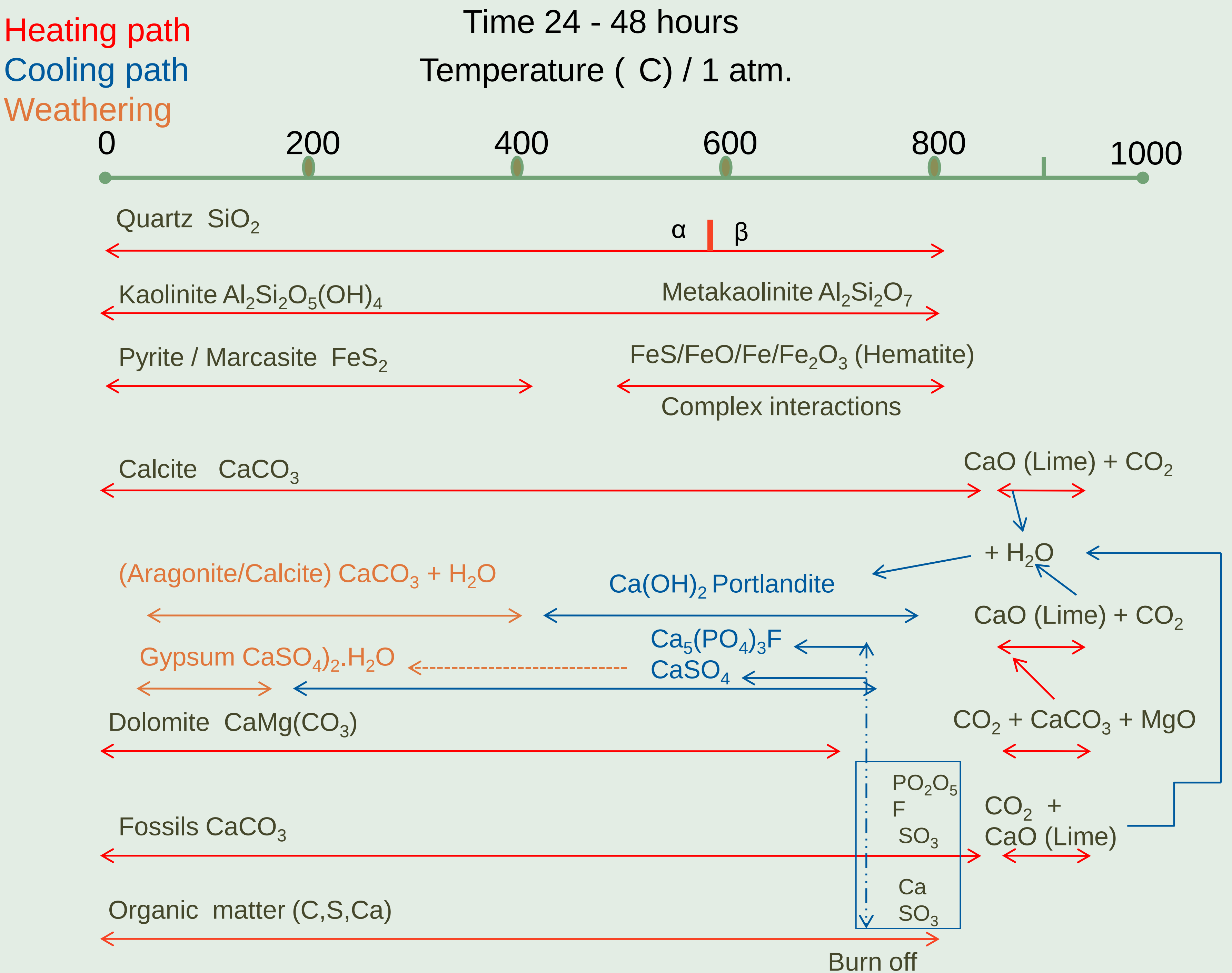
Thermal decomposition
Mineral phase transformation

Components in unburnt debris	Components in clinkers
Quartz SiO_2	Quartz SiO_2
Calcite $CaCO_3$	Calcite $CaCO_3$
Dolomite $CaMg(CO_3)_2$	Aragonite $CaCO_3$
Pyrite FeS_2	Anhydrite $CaSO_4$
Marcasite FeS_2	Hematite Fe_2O_3
	Gypsum $(CaSO_4)_2.2H_2O$
Kaolinite $Al_2Si_2O_5(OH)_4$	Apatite $Ca_5(PO_4)_3F$
Fossils	
Organic matter	

Heating path → T C 65 - 900 → Cooling path → T C 400 - 30 → Weathering

➢ Thermal decomposition during combustion




Heating path
Cooling path
Weathering
Time 24 - 48 hours
Temperature (C) / 1 atm.
0
200
400
600
800
1000
Quartz SiO_2
α
β
Kaolinite $Al_2Si_2O_5(OH)_4$
Metakaolinite $Al_2Si_2O_7$
Pyrite / Marcasite FeS_2
$FeS/FeO/Fe/Fe_2O_3$ (Hematite)
Complex interactions
Calcite $CaCO_3$
CaO (Lime) + CO_2
+ H_2O
(Aragonite/Calcite) $CaCO_3$ + H_2O
$Ca(OH)_2$ Portlandite
CaO (Lime) + CO_2
$Ca_5(PO_4)_3F$
$CaSO_4$
Gypsum $CaSO_4)_2.H_2O$
Dolomite $CaMg(CO_3)$
CO_2 + $CaCO_3$ + MgO
PO_2O_5
F
SO_3
CO_2 +
CaO (Lime)
Fossils $CaCO_3$
Ca
SO_3
Organic matter (C,S,Ca)
Burn off

➢ EMP-WDS: Ponctual trace element analysis (ppm)

		As	Co	Cu	Hg	Ni	Pb
SS							
	Org.matter	16.7	N.D.	1.7	N.D.	N.D.	N.D.
	Quartz	20	N.D.	10	N.D.	N.D.	N.D.
LM							
	Calcite	119	N.D	3.4	N.D	N.D	N.D
	Pyrite ●	234	283	62	151	59	1
	Pyrite ■	623	53	92	29	98	1
	Org.matter	36.2	16.8	12.2	8.2	4.4	15.6
Clinker *							
	Calcite	3	25	10	110	3.4	13.4
	Hematite	97	266.7	44.5	51.75	128.5	83

● Pyrite framboidal ■ Pyrite cubic * Clinker n 6

➢ Primary causes of spontaneous combustion in Molx waste heaps

Factors:

- **Chemical**
  - **Lignite**
    - *petrographic constituents: high in the reactive vitrinite*
    - *chemical composition*
      - *high in moisture & in sulphur (pyrite, marcasite, organic)*
  - **Rock debris' composition**
    - *high in sulphur (pyrite, marcasite) & carbon*
  - **Fly ash composition**
    - *enriched in lime, available sulphur (e.g. anyhydrite, pyrite)*
- **Physical**
  - *granulometry, compaction, geometry (size & shape)*
  - *permeability & porosity of the rock debris*
- **Environmental**
  - *Atmospheric conditions: available air, wind direction, ambient temp. solar radiation*
- **Others:** ***Lightining & grass fire***

Spontaneous combustion: exothermic reactions

- If the heat is dissipated, the temperature of the coal will not increase
- If the heat is not dissipated then the temperature of the coal will increase

Lignite (40 - 250 C)

Coal + oxygen → Coal-oxygen complex + heat
Coal-oxygen complex → $CO + CO_2 + H_2O$ + heat
$C + O_2 \rightarrow CO_2 + 394\ kJ\ mol^{-1}$
$2C + O_2 \rightarrow 2CO + 170\ kJ\ mol^{-1}$

Pyrite/Marcasite (chemical oxidation): in Lignite & Limestone 65 - 400 C

Catalysed by the presence of bacteria «Acidithiobacillus ferrooxidans »

$2FeS_2 + 7O_2 + 16H_2O \rightarrow 2H_2SO_4 + 2FeSO_4.7H_2O + 1324\ kJ\ mol^{-1}$
$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2H_2SO_4 + 2FeSO_4 + 260\ kJ\ mol^{-1}$
$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + SO_2\uparrow + 3412\ kJ\ mol^{-1}$

A layer of coarser particles at the base and edges of waste heap resulted in increased ventilation passing through the inner part. The situation was particularly aggravated by prevailing hot, moist winds, and led to a higher risk of spontaneous combustion most probably in the summer months

Thank you for your attention