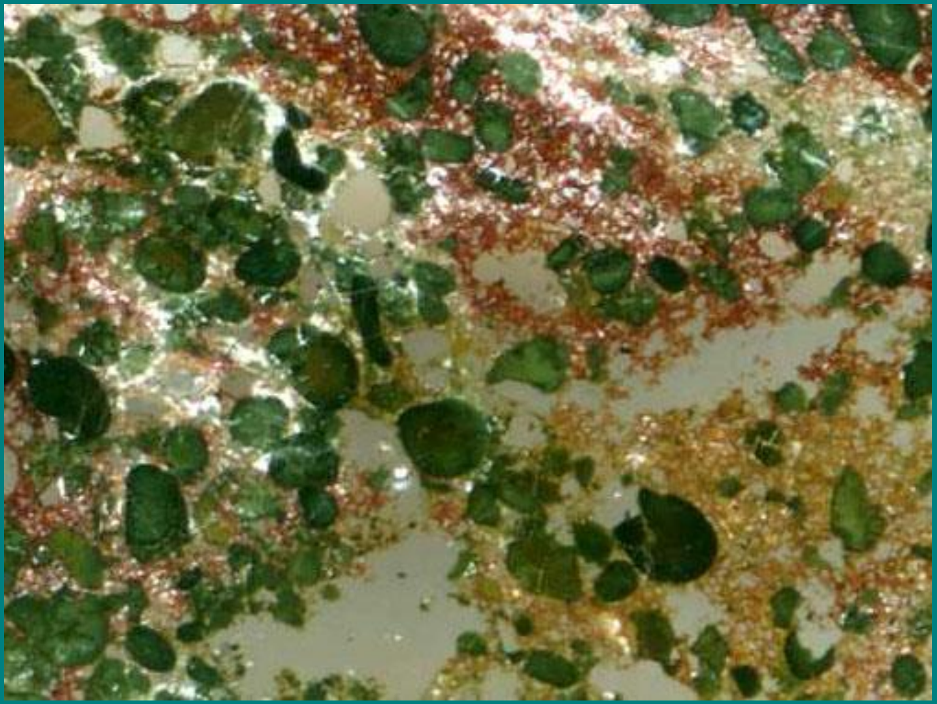
Green Clays: uses and pitfalls



Jenny Huggett
Petroclays

Green clays

- Glauconite
  - Glauconite-smectite
- Nontronite
- Celadonite
- Chlorite
  - Chamosite
  - Berthierine
  - Odinite
  - Verdine

Recent green granules

:

- Verdine - 7Å (phyllite V), ferric chlorite (phyllite C)
-
- Glaucony - glauconite and smectite-glauconite

Mineralogy of ancient green granules

- Verdine: odinite & berthierine
- Glaucony: glauconite, glauconitic smectite

Nontronite

- Possibly the immediate precursor of all or many glauconitic and chloritic clay assemblages
- Nontronite is an Fe-rich smectite which is increasingly being identified in a range of environments, though quantitatively it is most abundant in deep ocean sediment.

Glaucony

- Includes all glauconitic clays: glauconite-smectite (olive-brown) through to end member glauconite (green, Fe-rich mica).
- Glauconite in faecal pellets replaces all the other clays present, hence numerous mixed layers are possible.
- Glauconitisation ceases after burial to > 20cm
- Formation is slow, estimated at 10^6 years for complete replacement.

Glauconite defined

- A potassium and ferric iron-rich mica
- Occurs as granules, thin films and occasionally as ooids
- Associated with periods of slow deposition and invertebrate burrows

Glaucony distribution

- 50° N - 50° S
- Water temperature <20° C (?<15° C)
- Water depth *typically* 100-300m
- M-Coarse sand, hiatus, TST
- Redox boundary position in sediment

Data from Odin 1988; Rao et al. 1995; VanHouten and Purucker, 1984

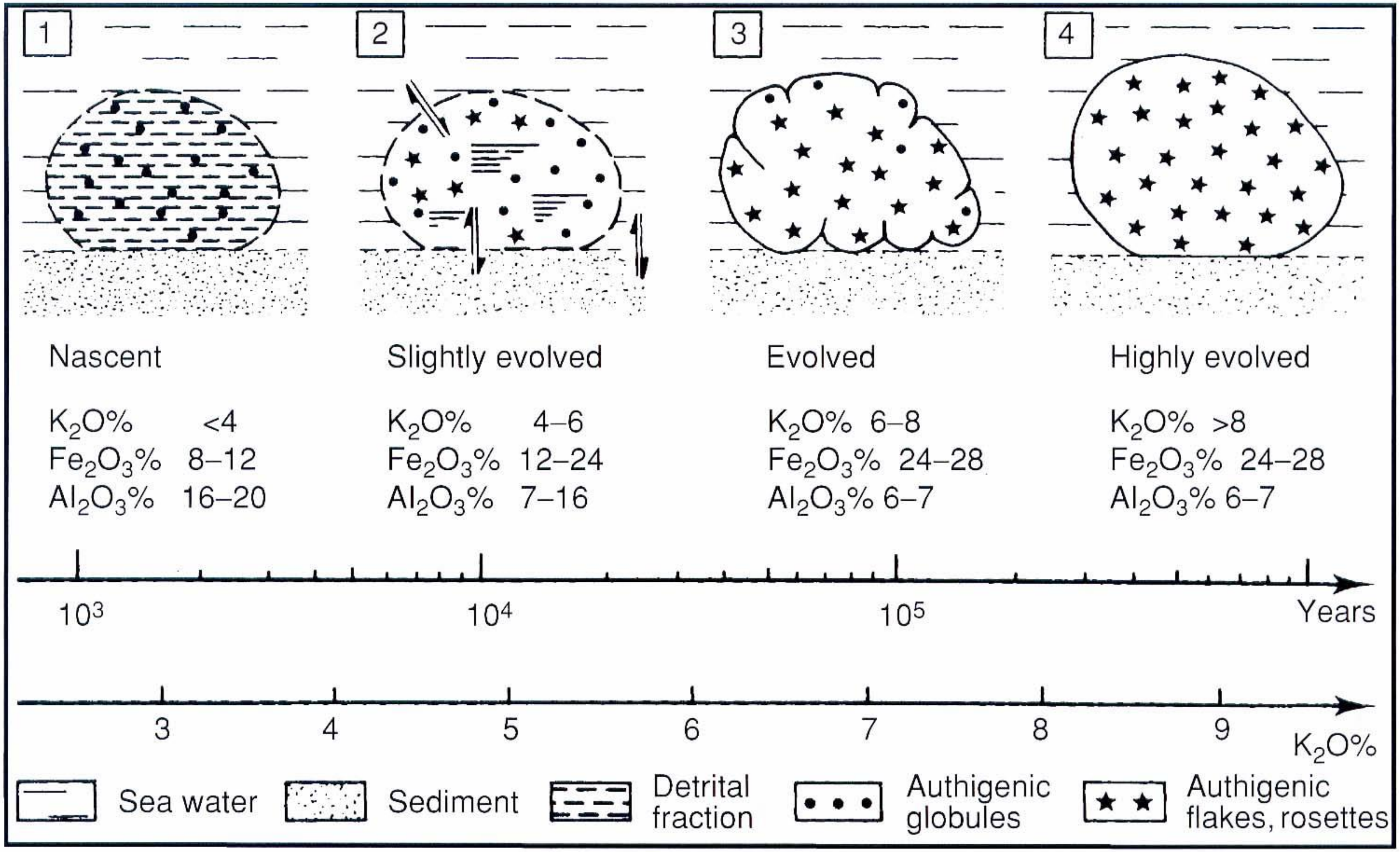
Criteria for identifying in situ glauconite

Pellets are concentrated in burrows

Fragile fractured grains are present

Grain-size distribution does not correspond to the overall grain-size distribution of the rock

Soft immature pellets present



(adapted from Odin & Matter, 1981)

Criteria for identifying reworking of glauconite

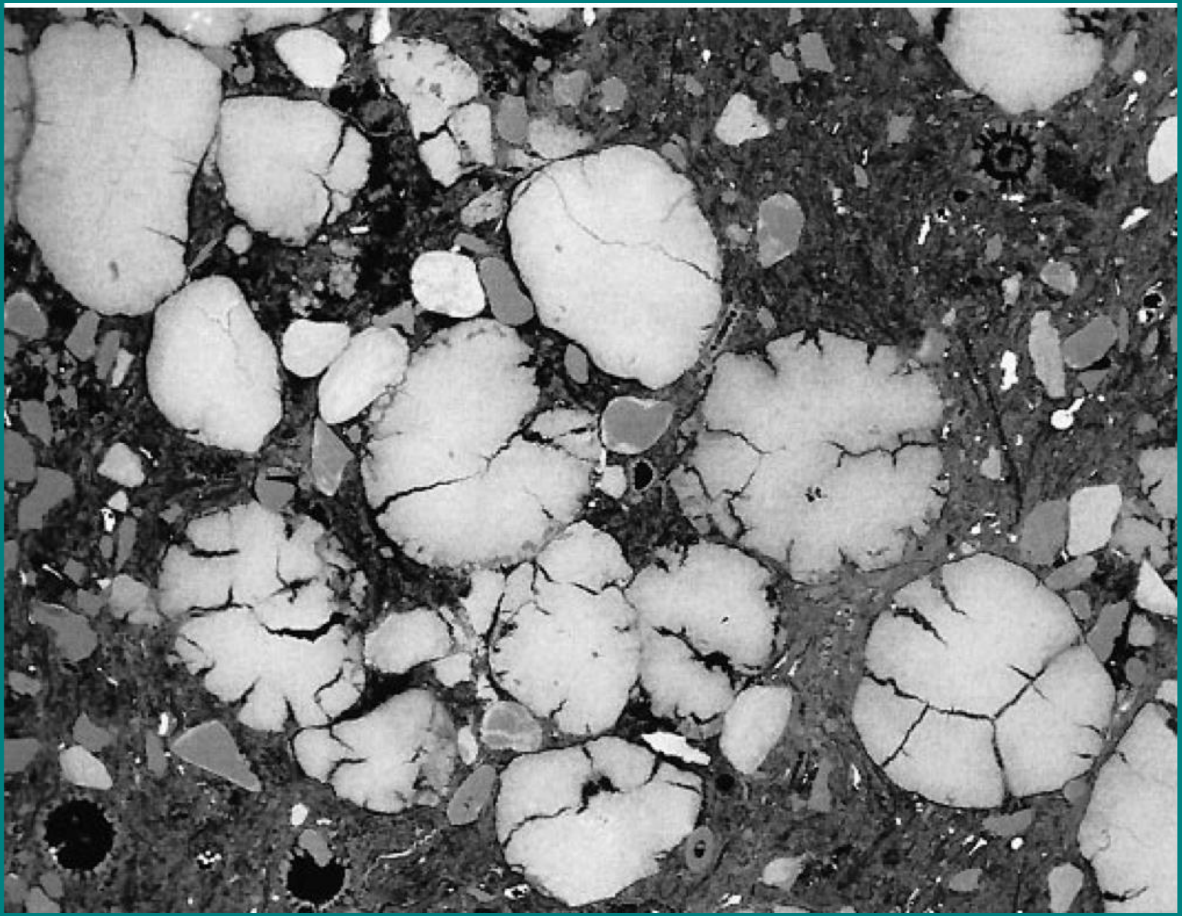
Pellets are grain-size sorted along with the rest of the sediment

Fragile fractured but intact grains are absent

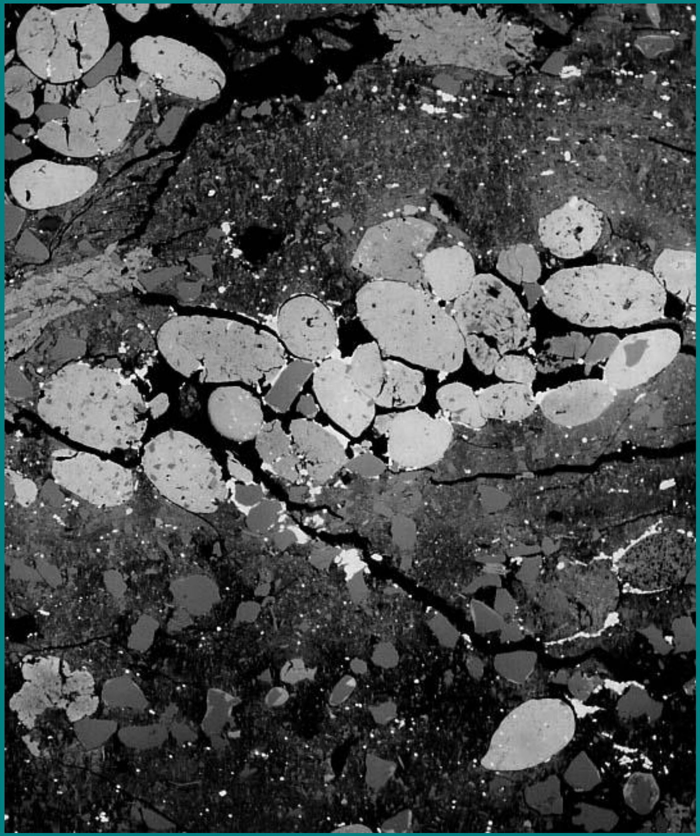
Angular fragments are present

Pellets are enclosed in clay ooids

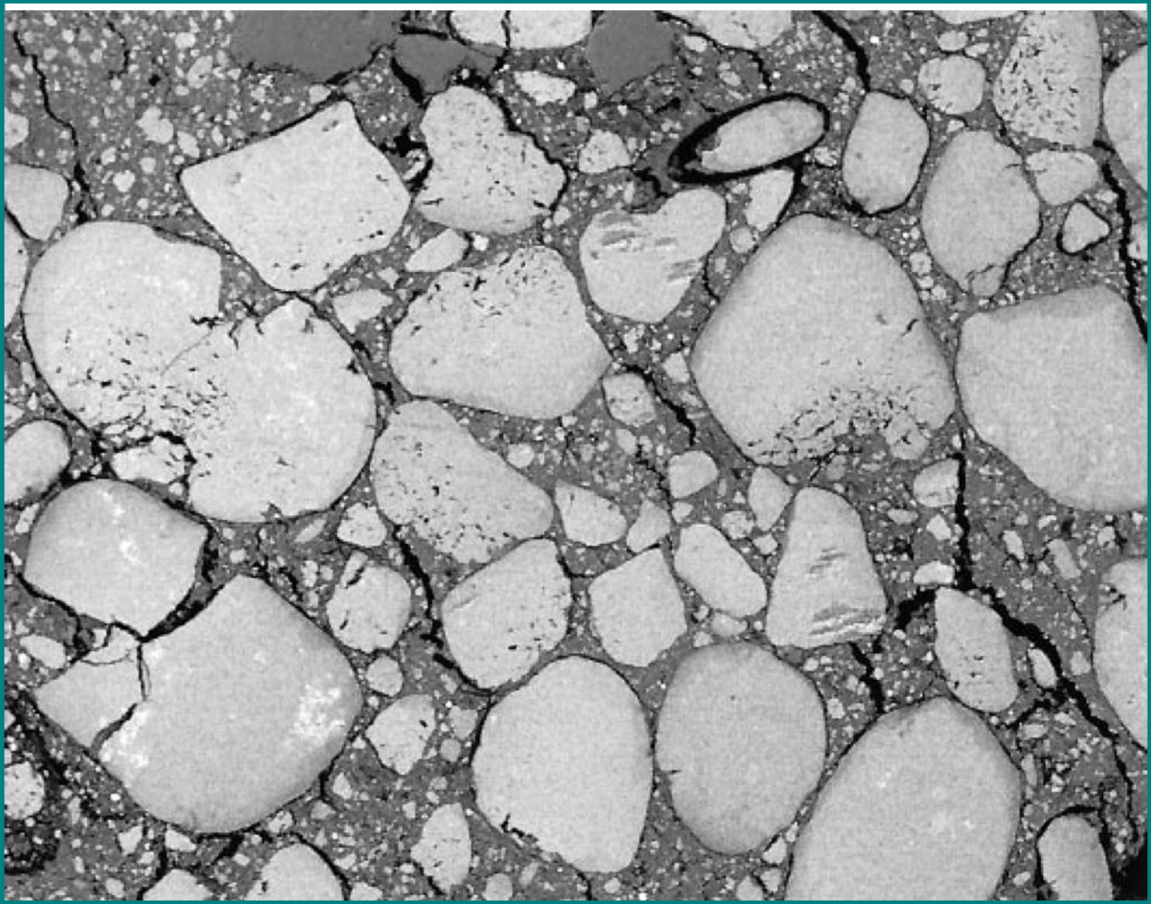
In situ glauconite pellets



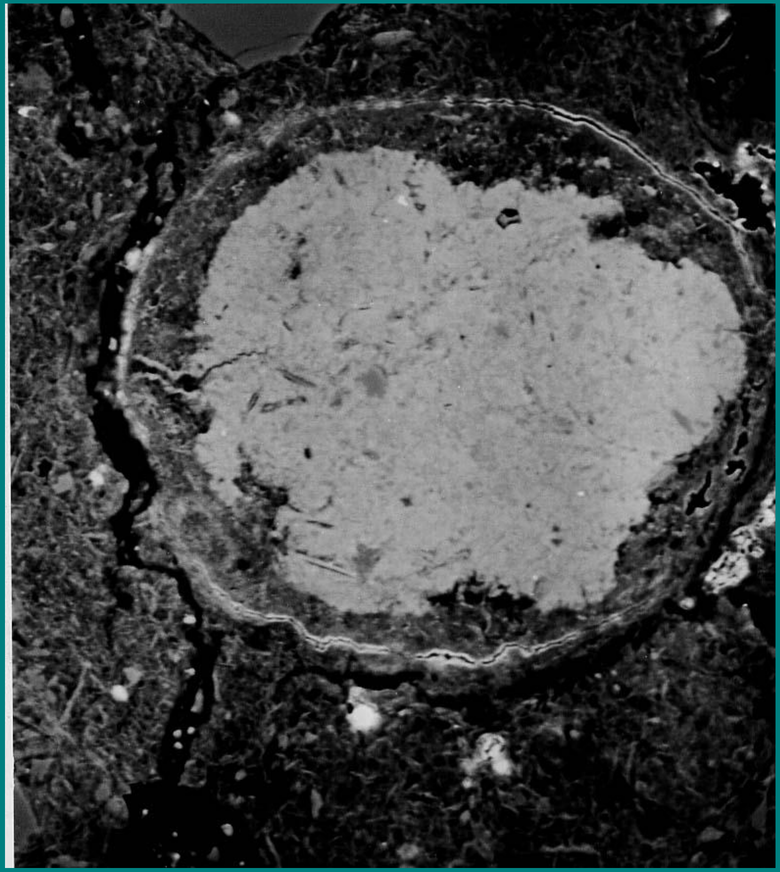
Burrow-filling glauconite

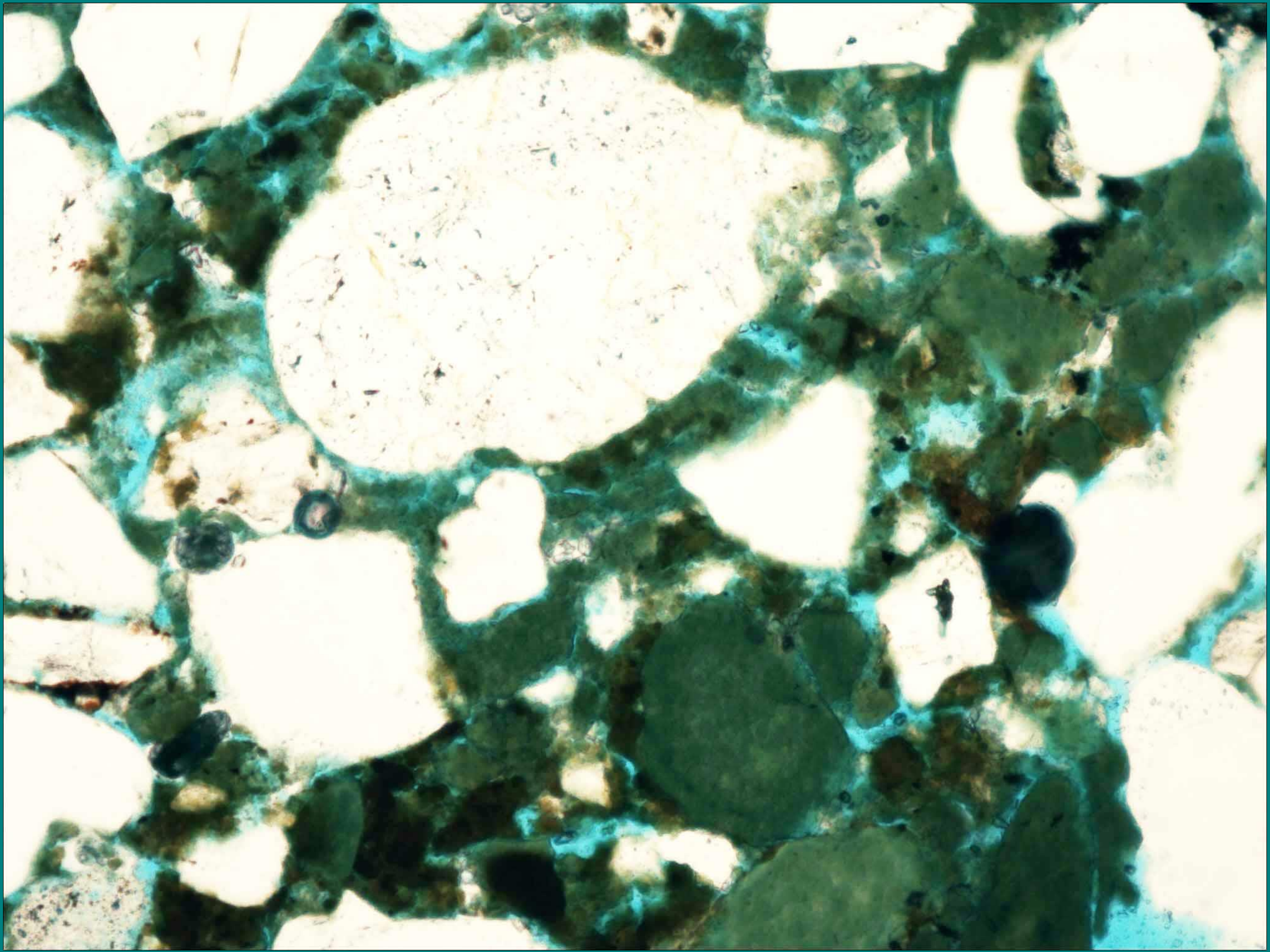


Reworked glauconite pellets

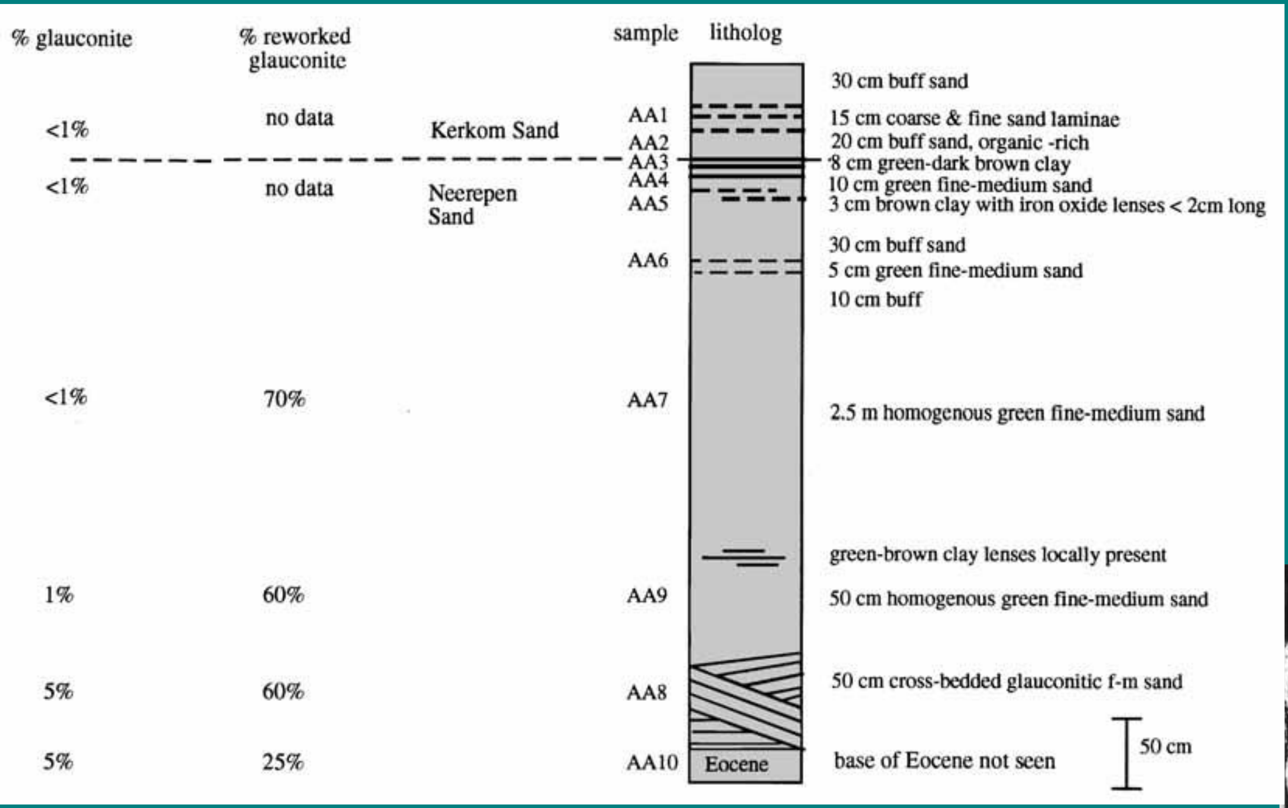


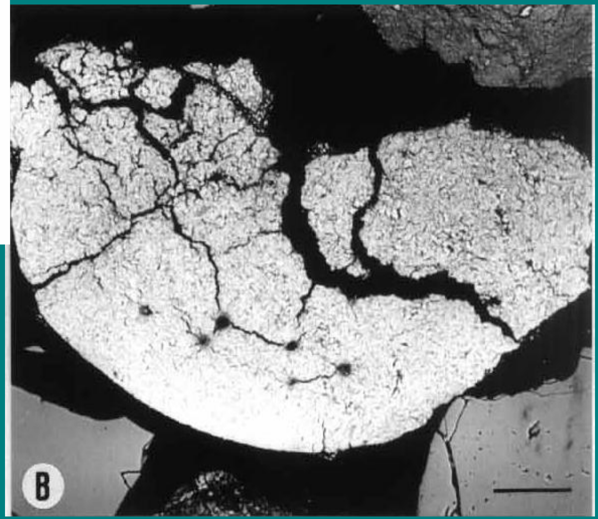
Glauconite reworked with ooid of later clay



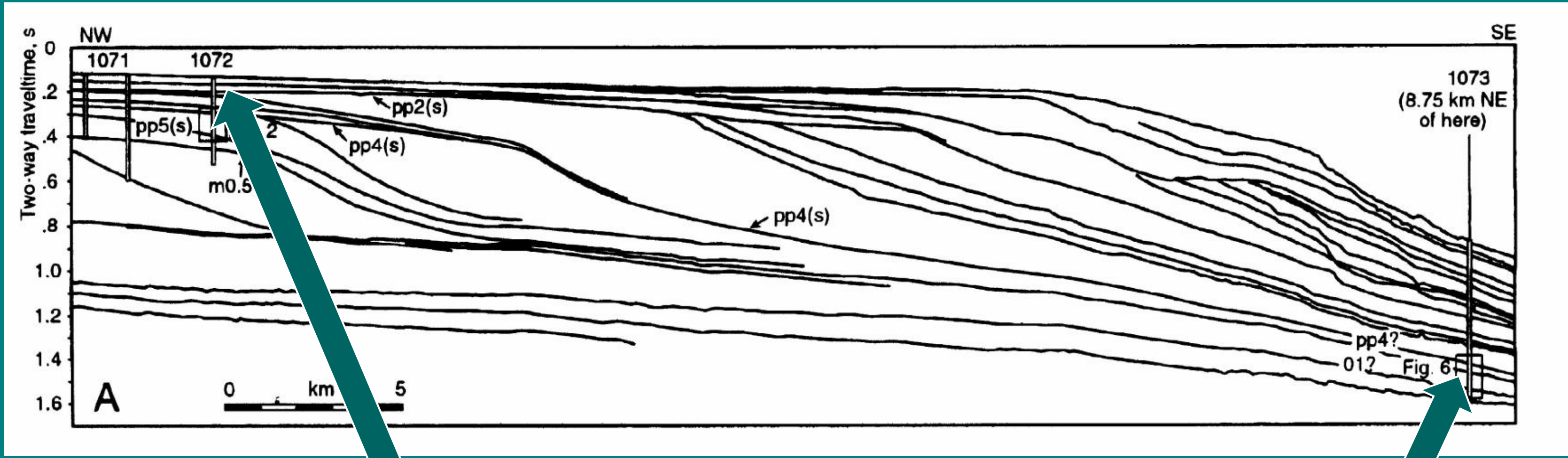


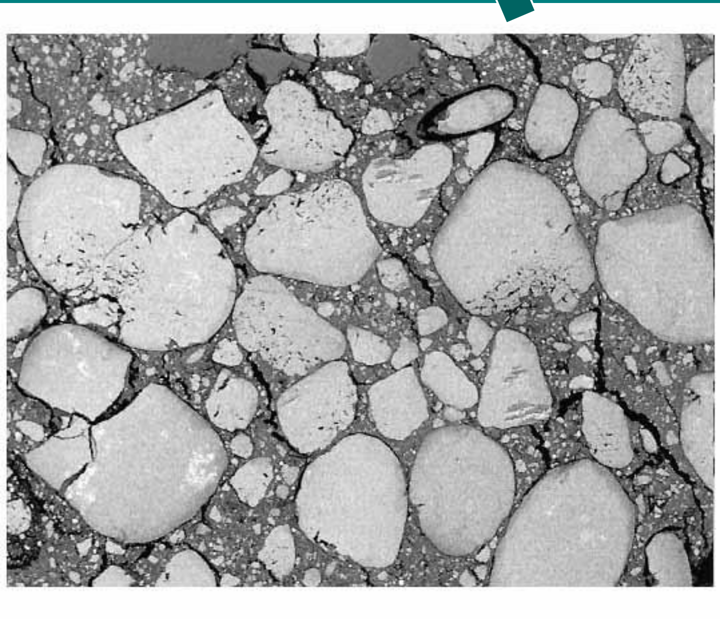
Glauconite in brackish & lacustrine sediment, Oligocene, Belgium

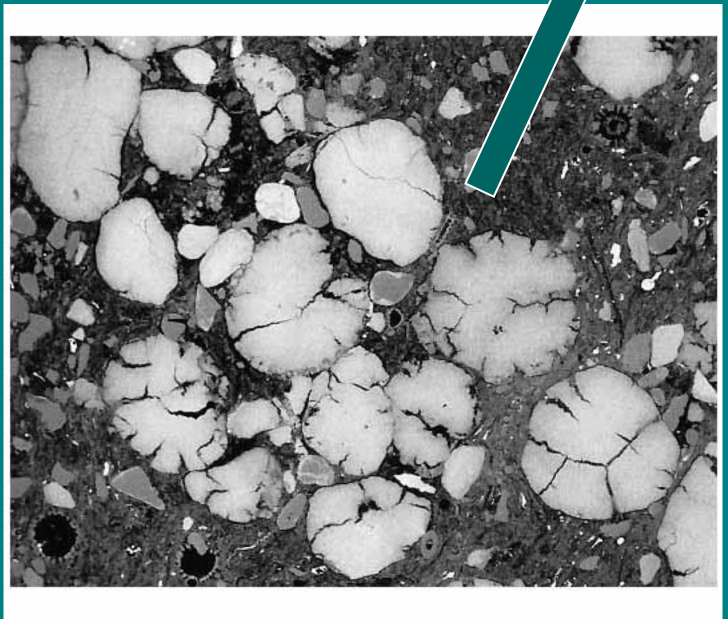




New Jersey Margin, shallow & deep water glauconite shallow



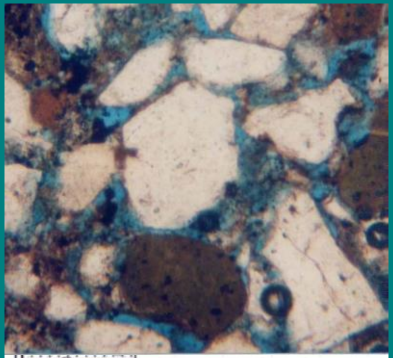


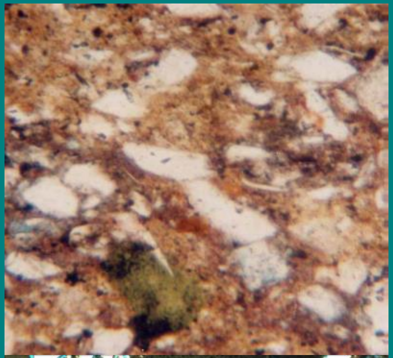


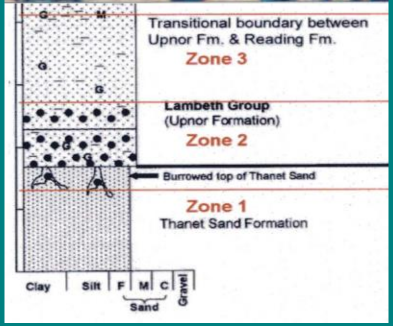
Glauconite in shallow marine sediment

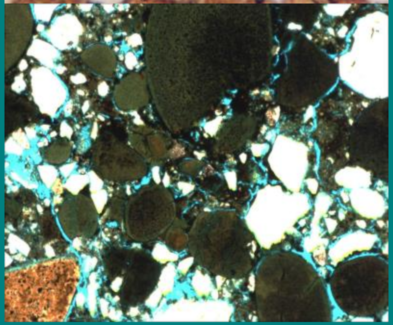
London Clay Fm

Upnor Fm

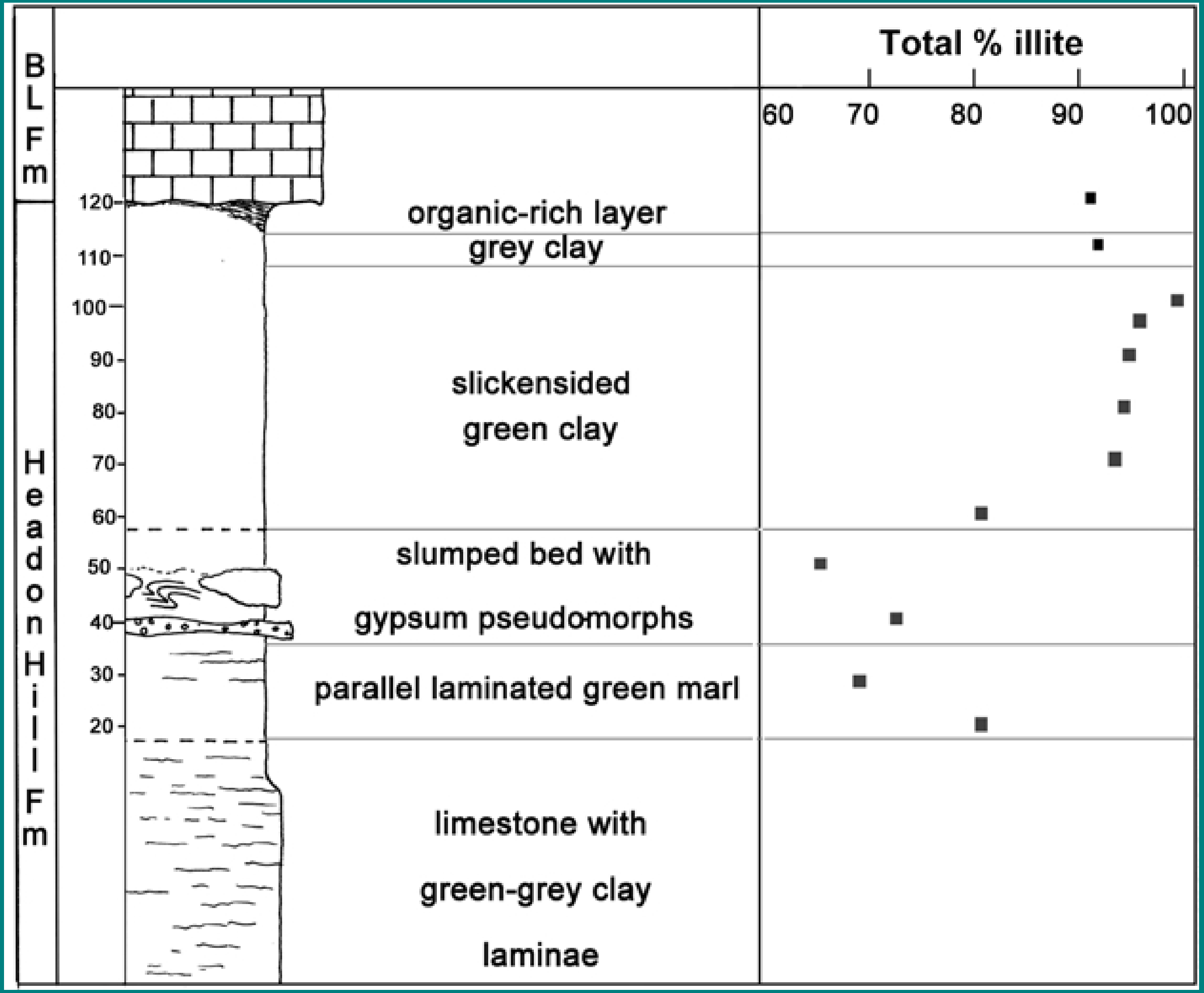






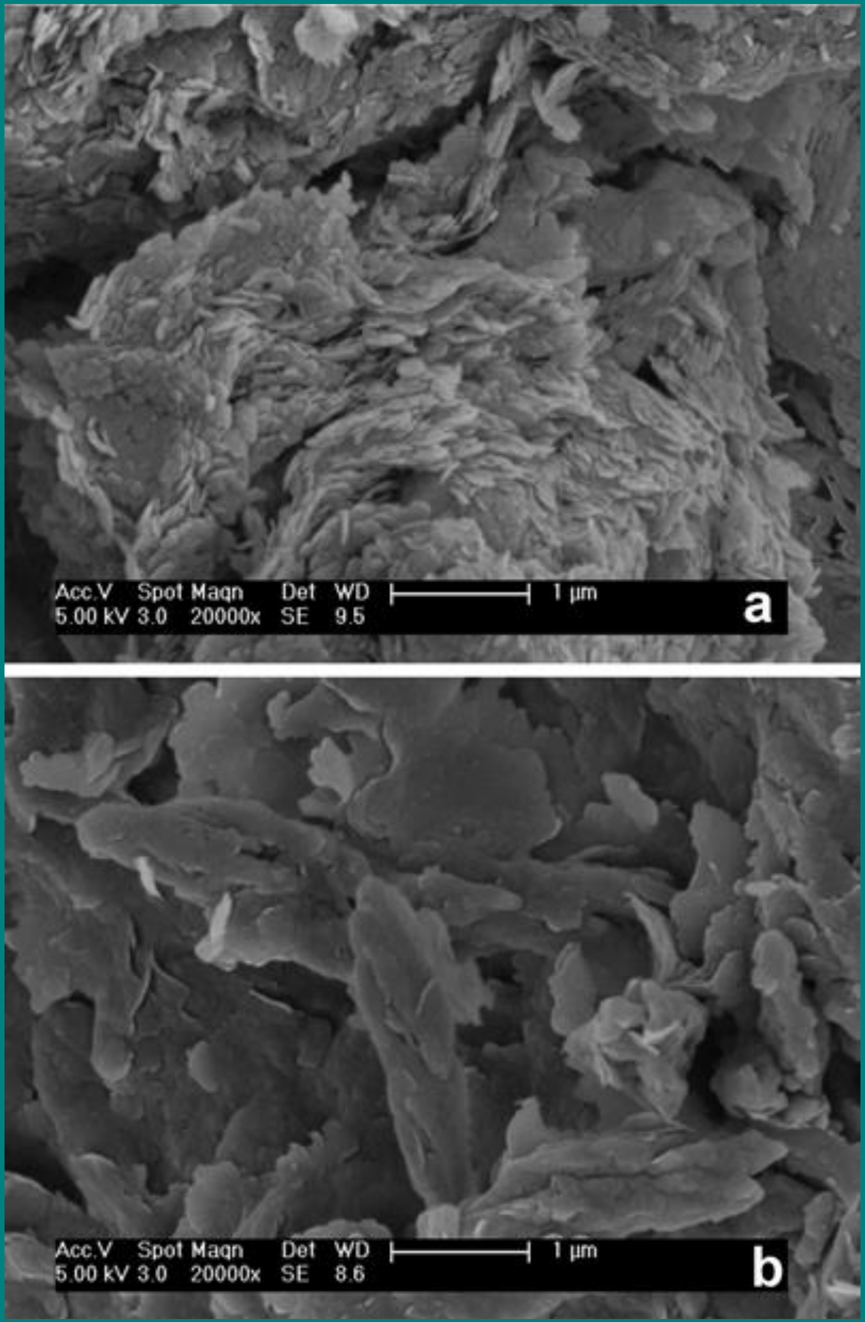


“Illitisation” in a palaeosol



Mechanism

- Hypersaline lake
  - Uptake of K^+, Fe^{3+} and Mg^{2+}
- Lake dries up, seasonal wetting and drying occurs
  - Particle size is mechanically reduced and Fe^{3+} is reduced to Fe^{2+}

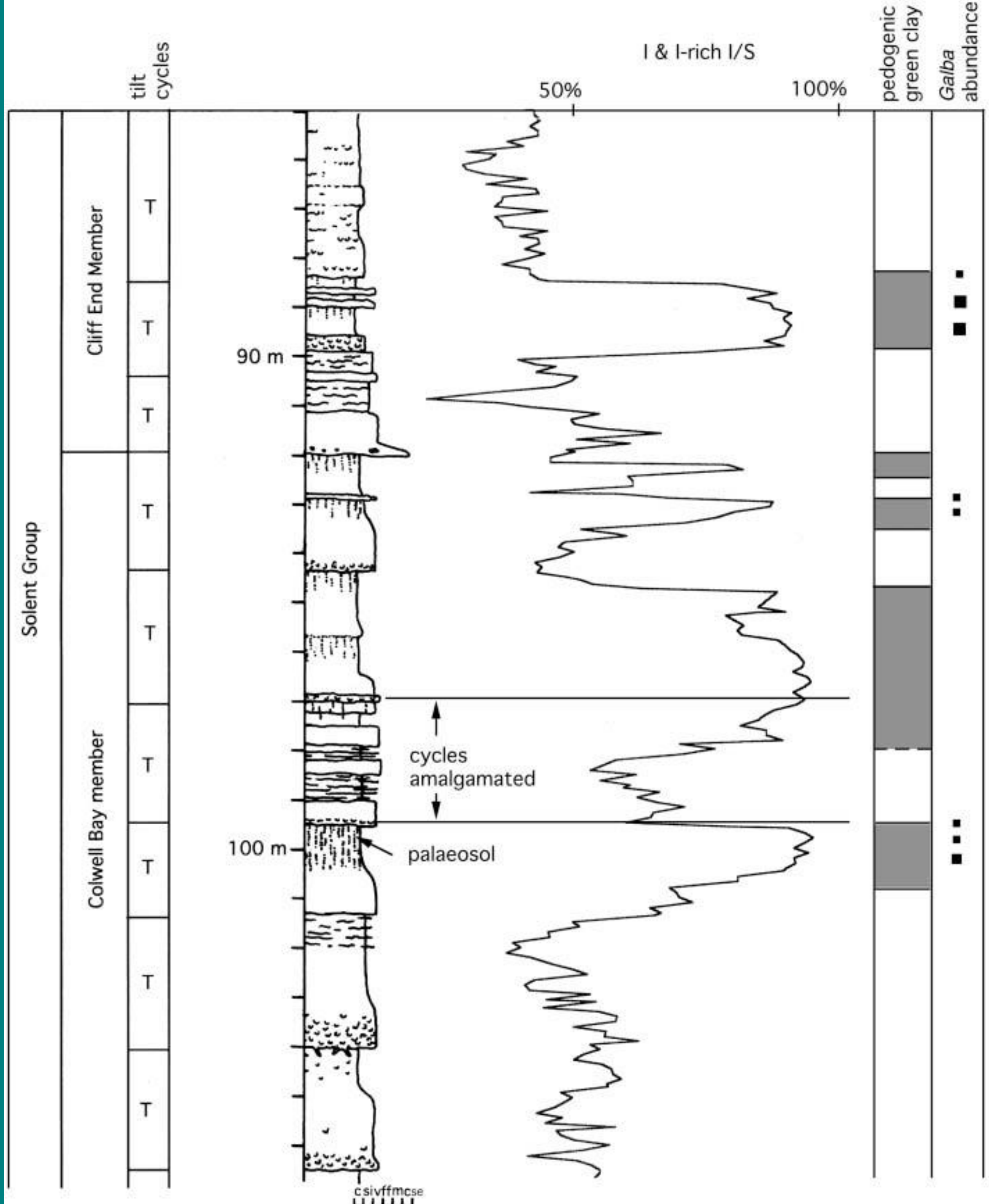


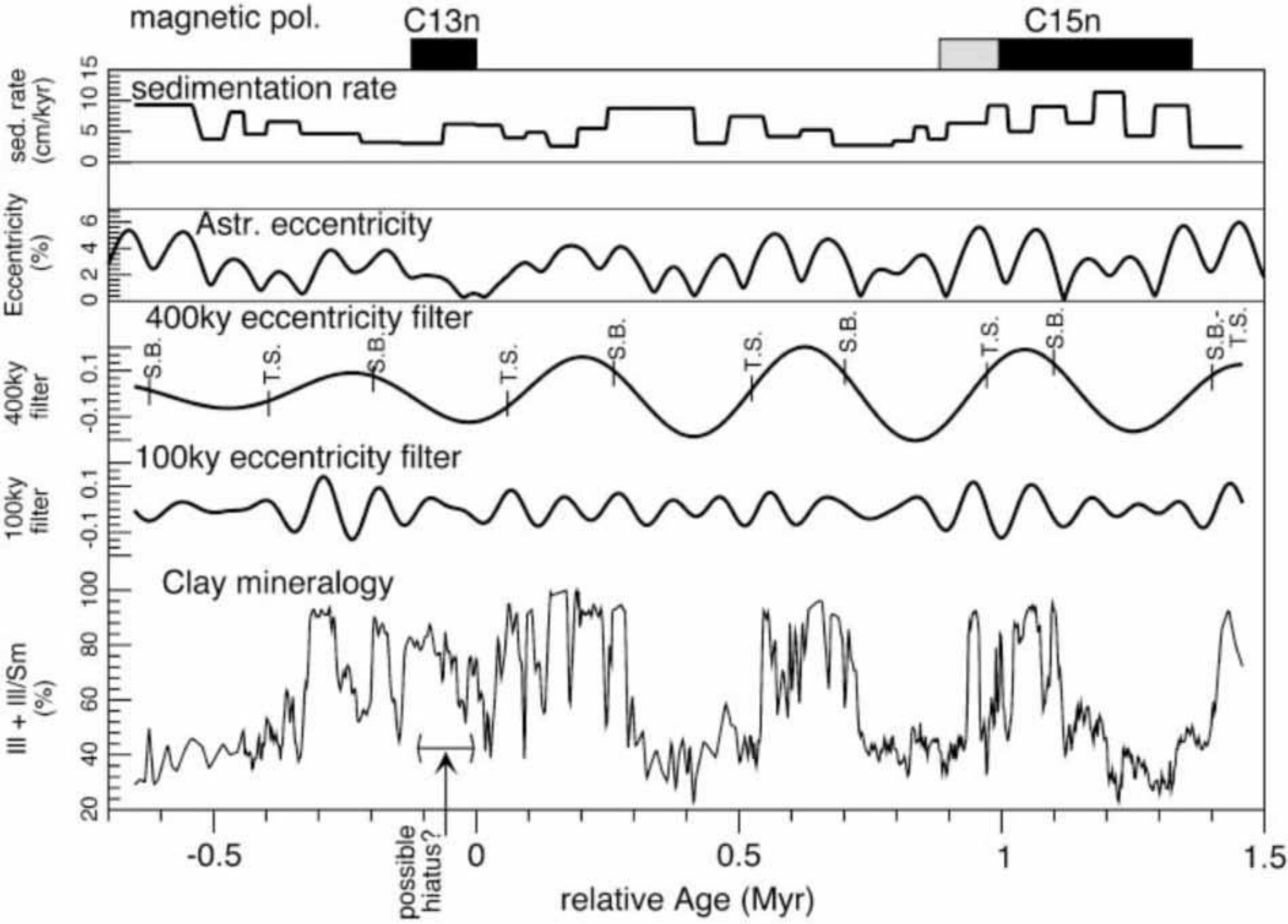
Particle size reduction is caused by the wetting and drying process

Ferric illite or glauconite?

- Less Fe-rich, more Al-rich than glauconite for any given %K
- Not known to occur as pellets
- Only known from non-marine environments

Glauconite as a proxy for Milankovitch Cyclicity





magnetic pol.
C13n
C15n
sedimentation rate
sed. rate (cm/kyr)
Eccentricity (%)
Astr. eccentricity
400ky eccentricity filter
400ky filter
S.B.
T.S.
S.B.- T.S.
100ky eccentricity filter
100ky filter
Clay mineralogy
Ill + Ill/Sm (%)
possible hiatus?
relative Age (Myr)

Glauconite age dating

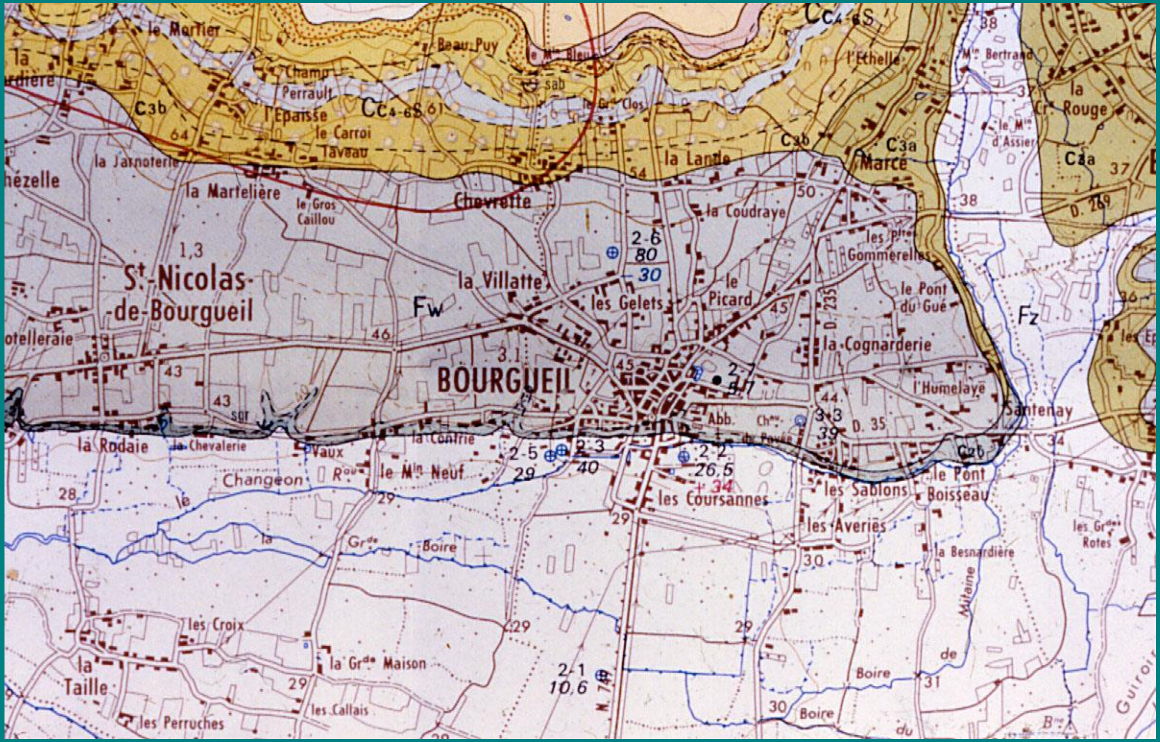
An excellent tool for dating

But

Contamination by particles of illite and K feldspar within the pellets

Reworking

????



St-Nicolas-de-Bourgueil
BOURGUEIL
la Villatte
les Gelets
la Coudraye
Chevrette
la Martelière
la Jarnoterie
la Lande
la Cognarderie
l'Humelaye
Santenay
les Coursannes
les Sablons
les Averies
le Pont Boisseau
la Besnardière
la Rodaie
Changeon
le Mln Neuf
la Confrie
Vaux
les Croix
la Taille
les Perruches
les Callais
Boire
Fw
Fz

14Å & 7Å sedimentary green clays

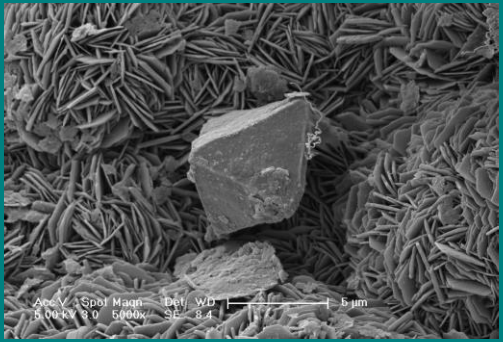
- 14Å – iron-rich chlorite (usually chamosite)
- 7Å – also called the serpentine group though this includes metamorphic phyllosilicates
- Berthierine is ferrous iron-rich
- Odinite is ferric iron-rich
- Verdine is a term used in the same way as glaucony: to describe an assemblage of imprecisely known composition

14Å & 7Å green clays

Iron-rich chlorite and berthierine usually occur as platelets rimming grains in a radial arrangement or as ooidal coatings on grain

- Odinite/verdine in recent sediments *typically* occur as pellets

- Though as green pellets are often assumed to be glauconite and ooidal coatings/radial rims are assumed to be chlorite, the distinction may not be so clear.



Verdine distribution

- 20° N - 20° S
- Water temperature >20°
- Water depth 10-60m
- Offshore from mangroves, swamps, major riverine input

Data from Porrenga, 1967; Odin 1988

Diagenesis of the verdine-chlorite family of clays

Odinite in recent sediments ->
berthierine in Mesozoic ironstones ->
chamosite in Palaeozoic ironstones

suggests the possible diagenetic sequence: odinite -> berthierine -> chamosite

Berthierine distribution

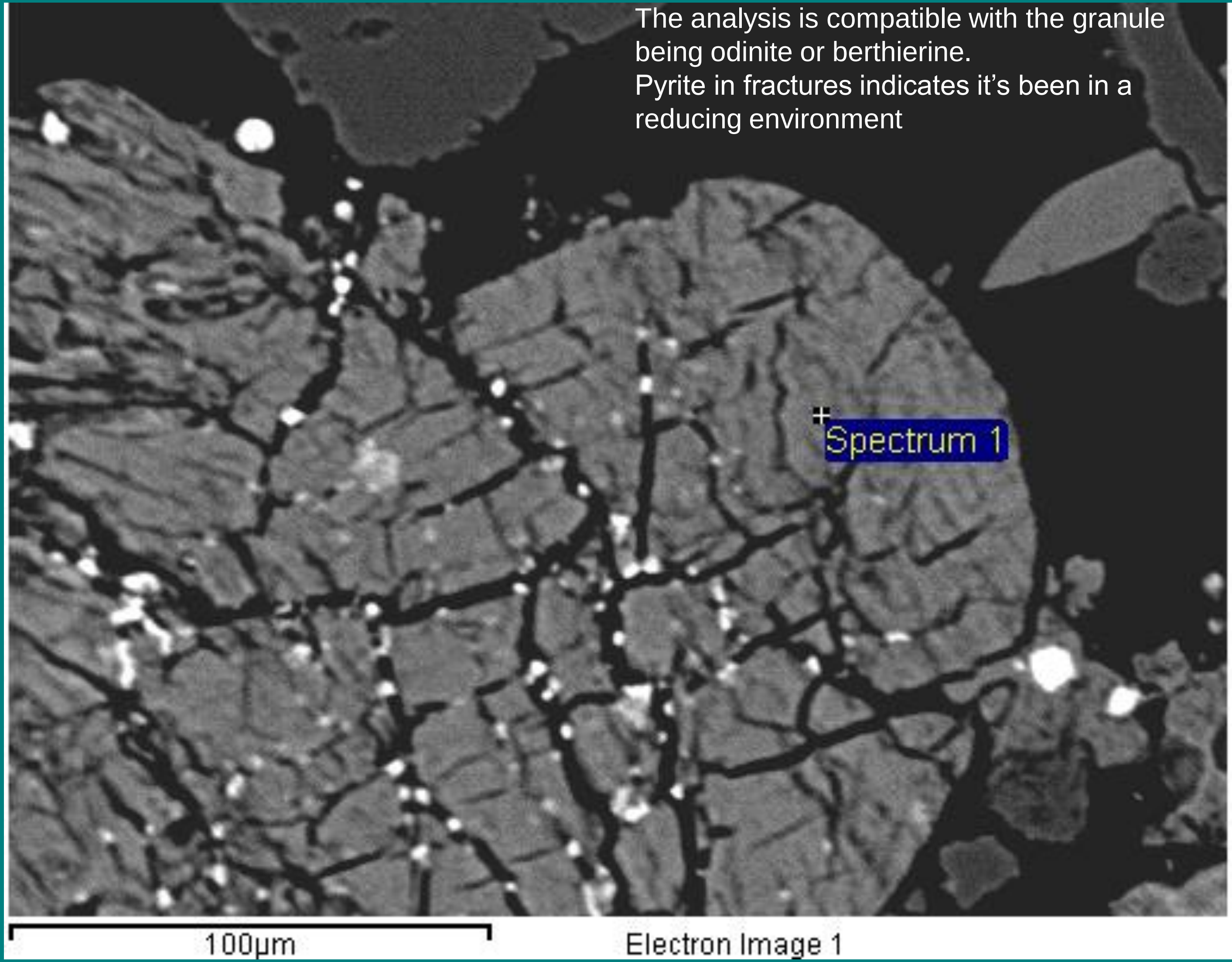
- Most berthierine is associated with sediments deposited in warm shallow seas
- BUT berthierine granules have been reported from a cold water estuary (Rohrlich et al., 1969)
- warm? water estuaries (Odin and Letolle, 1980)

Gulf of Cambay

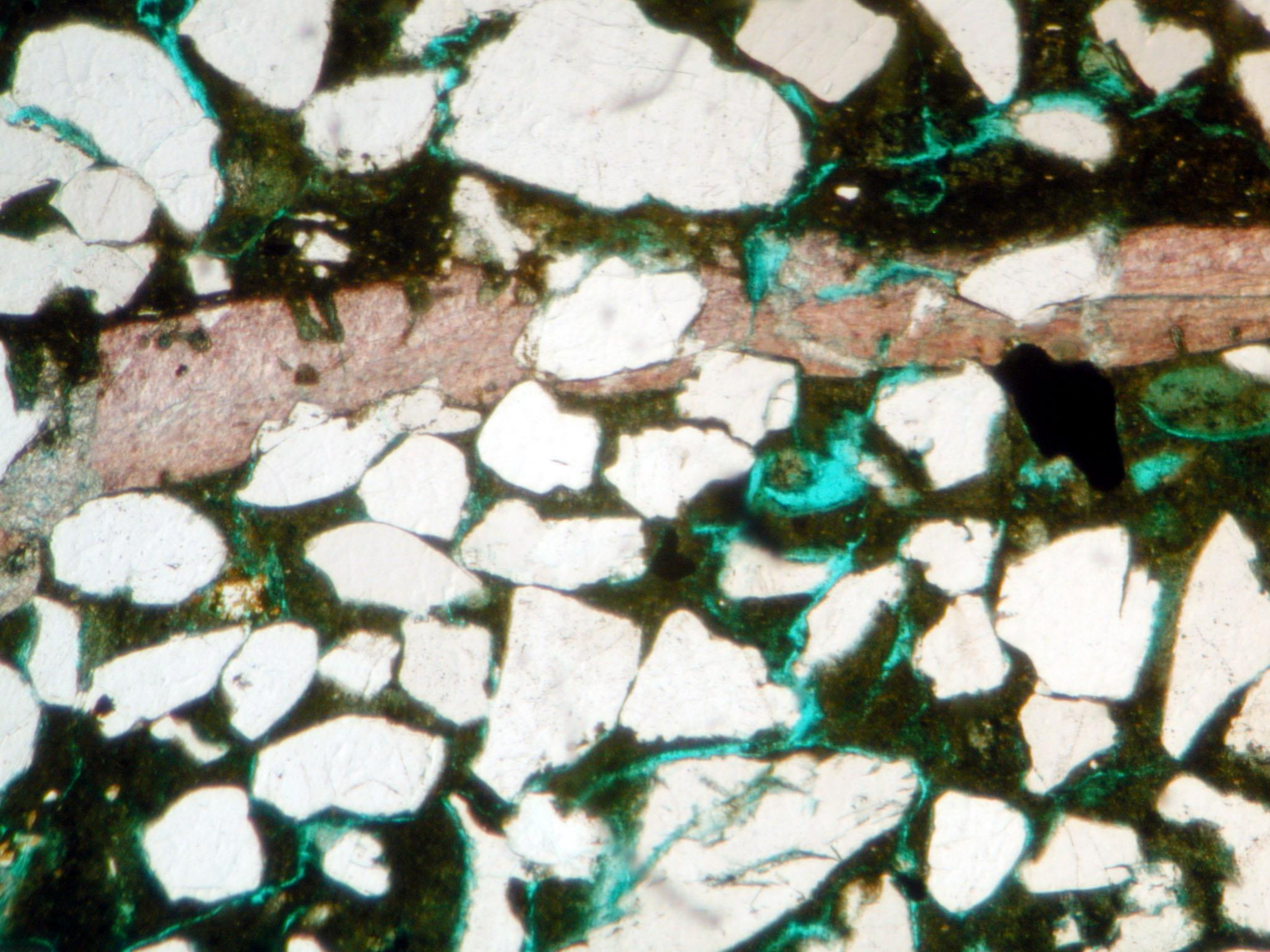
- Verdine in recent sediments at ~55m water depth, glaucony at >330m (Thamban & Rao, 2000)
- Brown/olive pellets in beachrock (~6k years) are predominantly Fe Smectite-rich I/S
- Olive green pellets in Holocene
- Chlorite with ~10% vermiculite layers & Fe^{2+}/total Fe of 0.65 in Oligo-Miocene

	MgO	Al_2O_3	SiO2	$FeO+Fe_2O_3$
Oligo-Miocene	6.92	23.90	34.17	35.00
Holocene	15.16	14.26	42.00	24.53
Odinite	11.45	14.41	42.51	30.33
Vermiculite	23.81	14.15	45.10	11.30

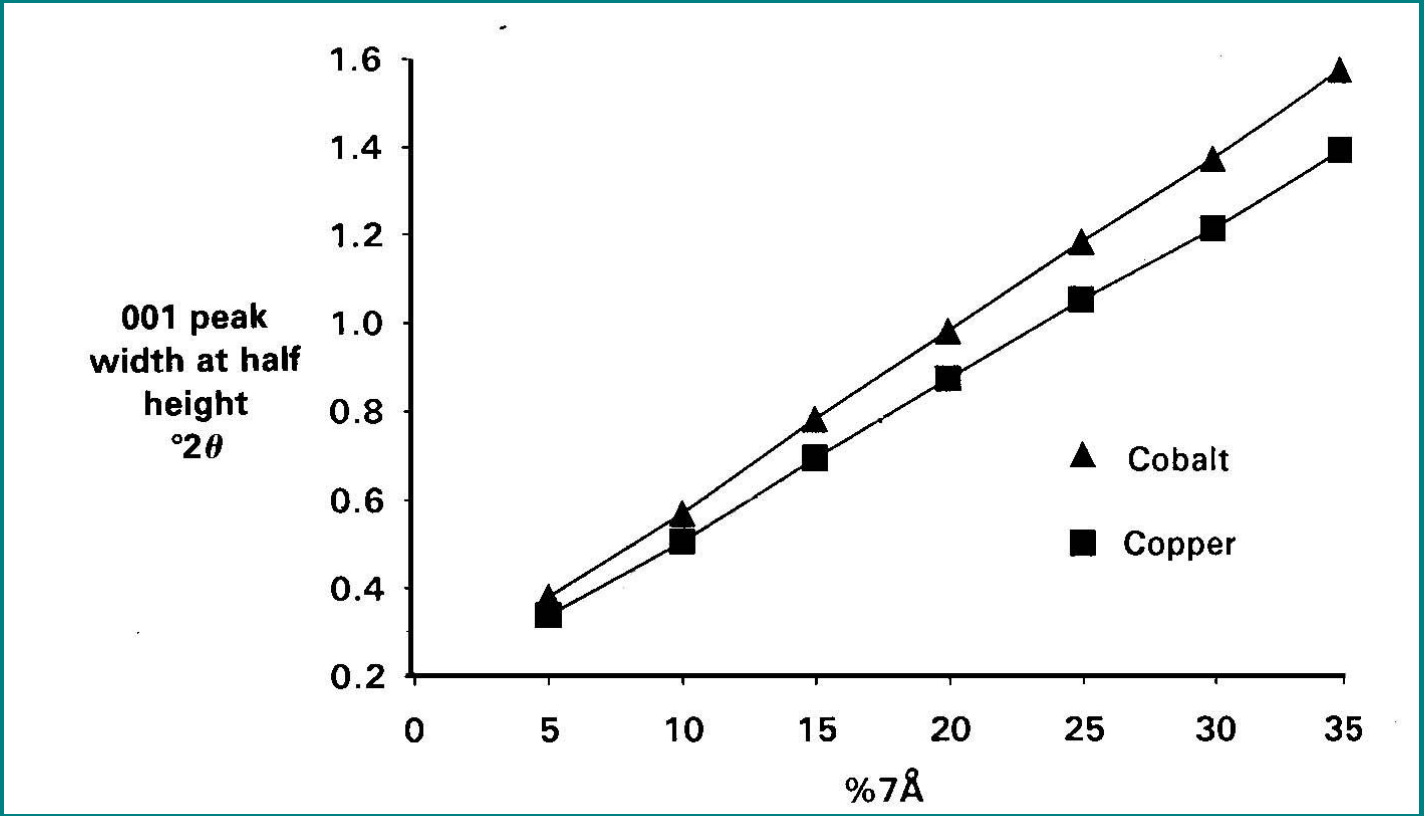
The analysis is compatible with the granule being odinite or berthierine.
Pyrite in fractures indicates it’s been in a reducing environment



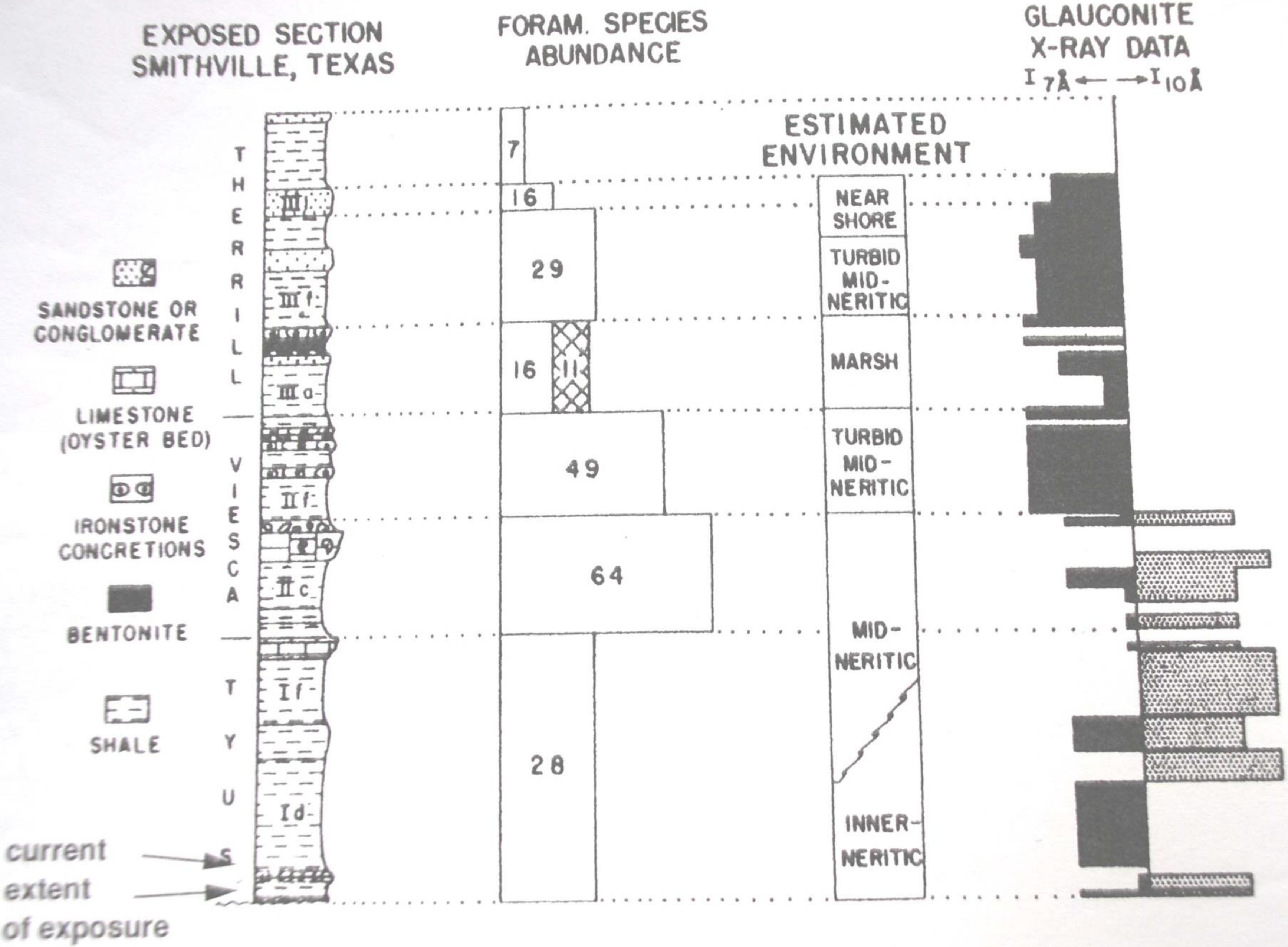
Mg	Al	Si	Ca	Fe	O
9.42	7.63	19.48	0.61	21.33	41.53



Determination of %7Å clay in chlorite



Calculated from Newmod™ by Hillier & Velde (1992)



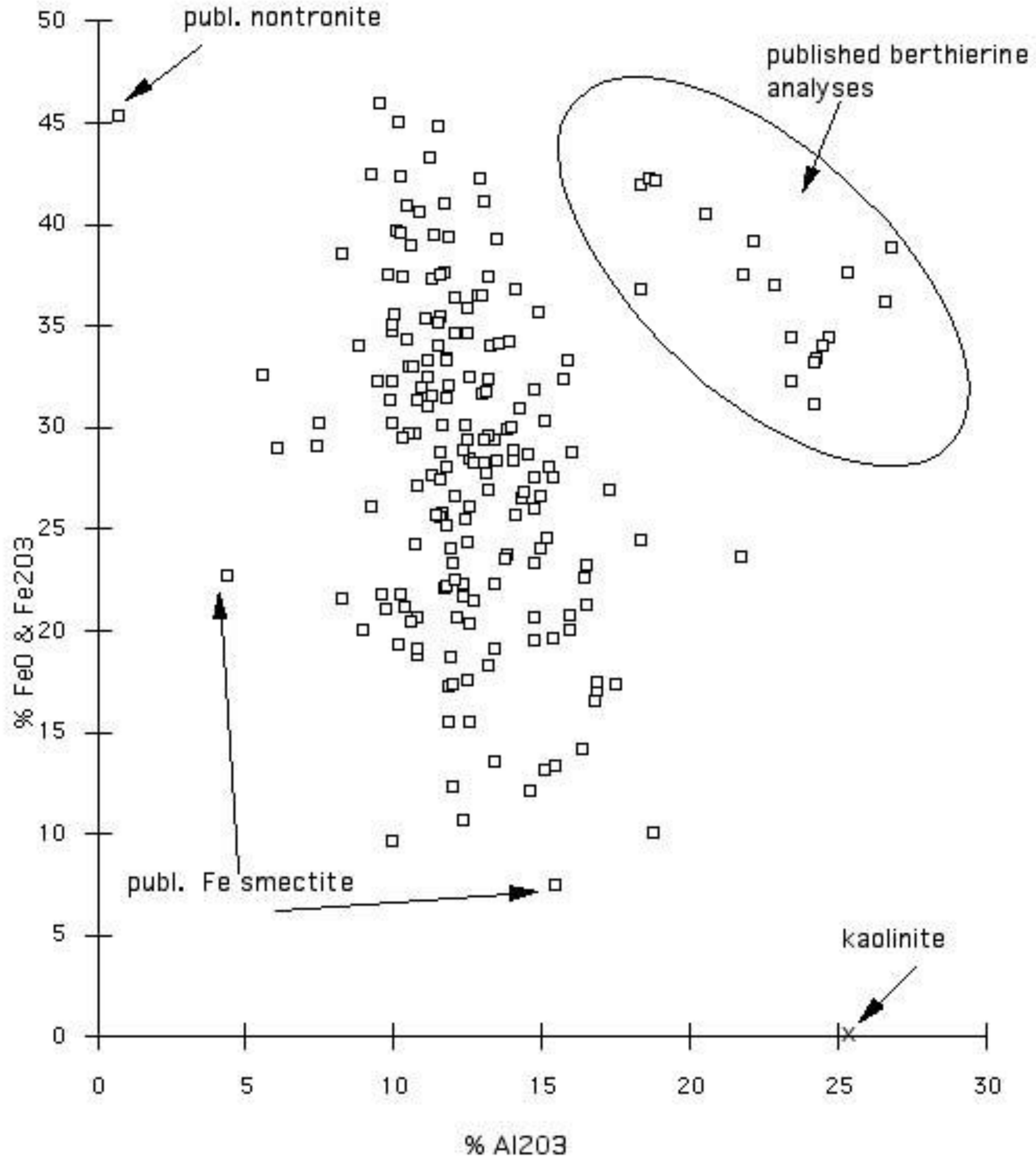
Comparison of foraminiferal and clay data from Weches Formation, Smithville, Texas
Adapted from Burst (1958).

Claiborne Group, Eocene Texas

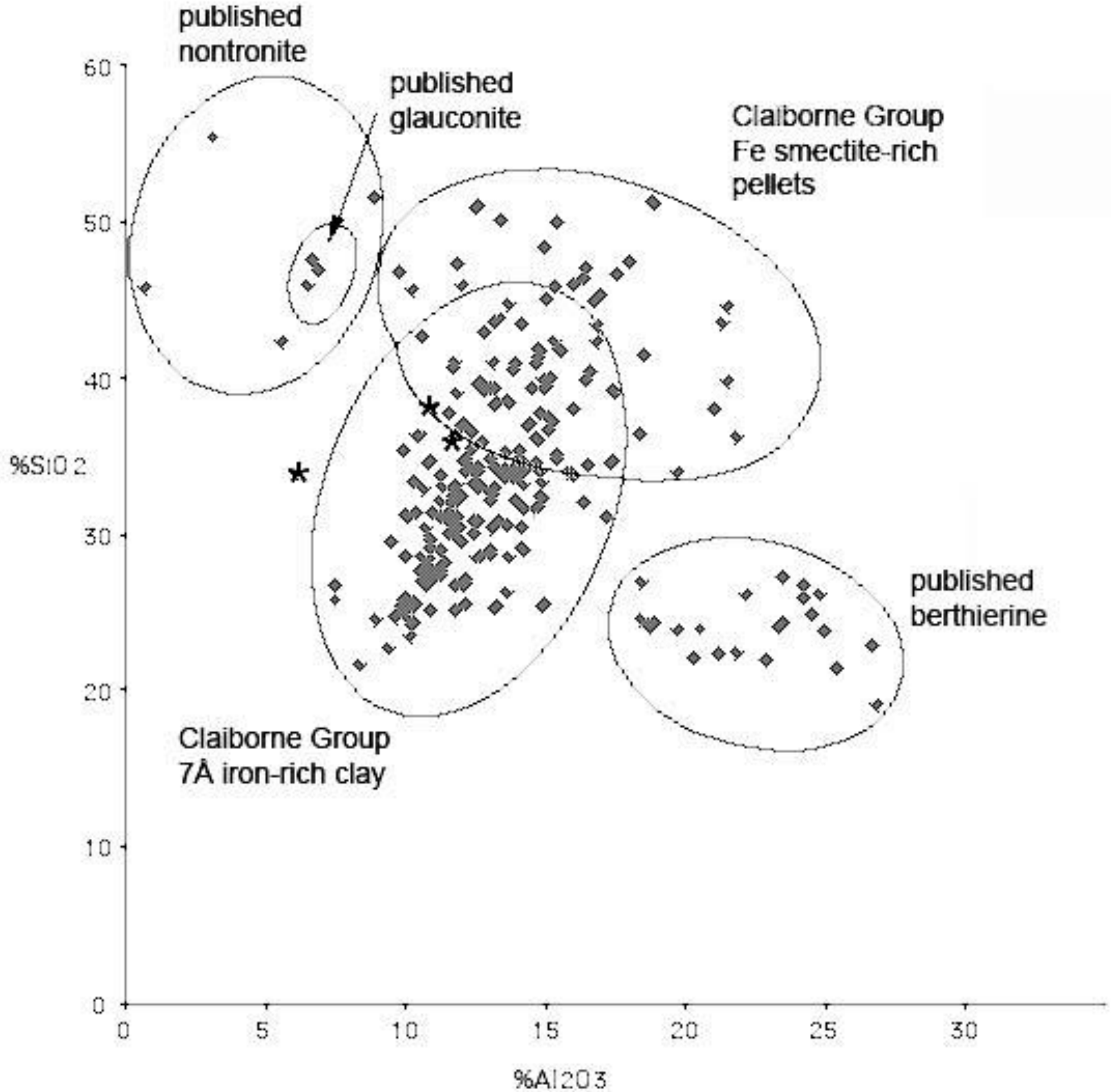
- Fe smectite-dominated (immature, soft, brown) to 7Å clay (mature, hard, green) pellets

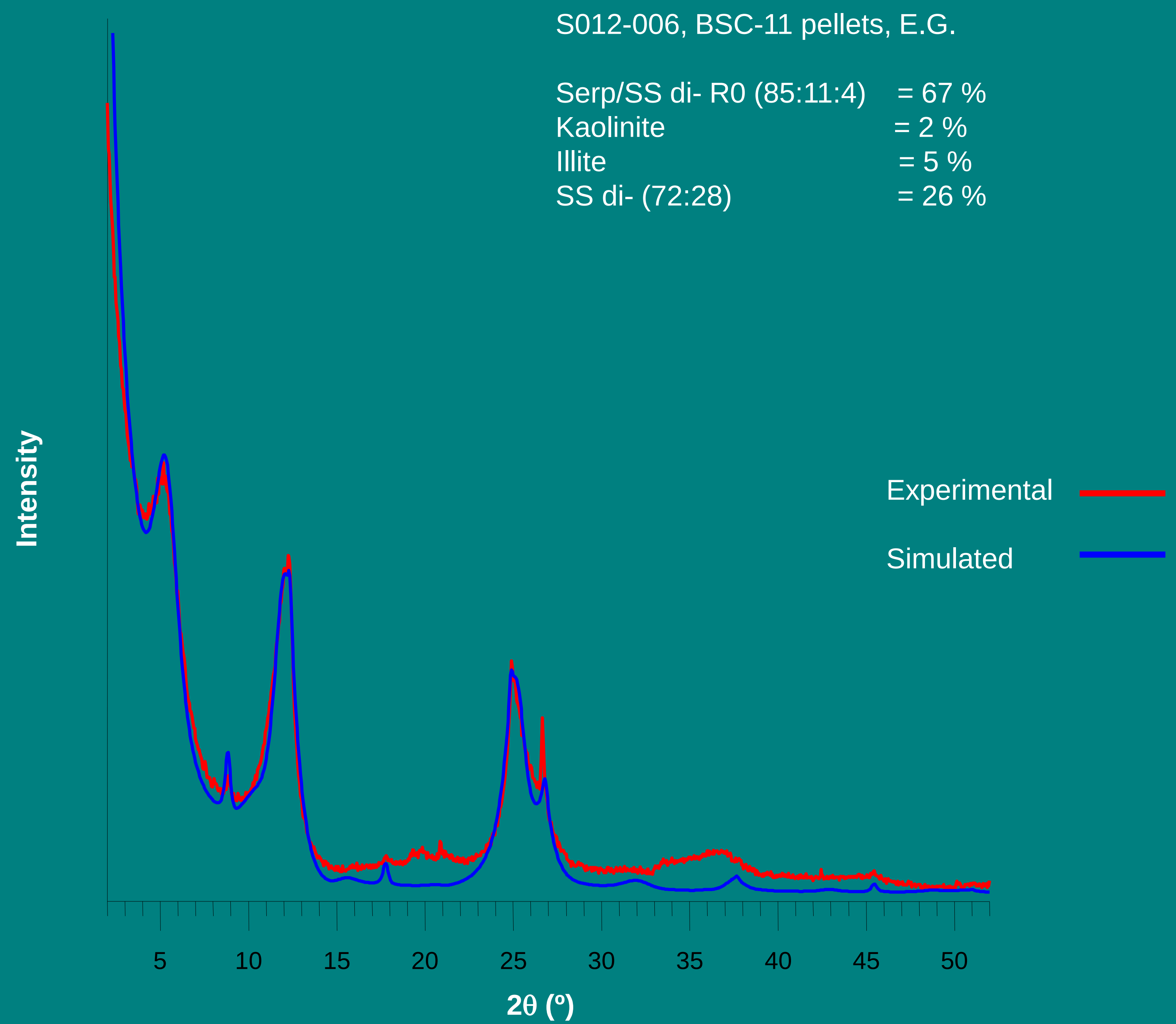
- Br-N-V with a wide range of compositions (N->V->O->Br?)

- Most of the Fe^{3+} is assigned to the exp. clay, hence Fe^{2+} is concentrated in the 7Å layers, i.e. it is closer to berthierine than odinite

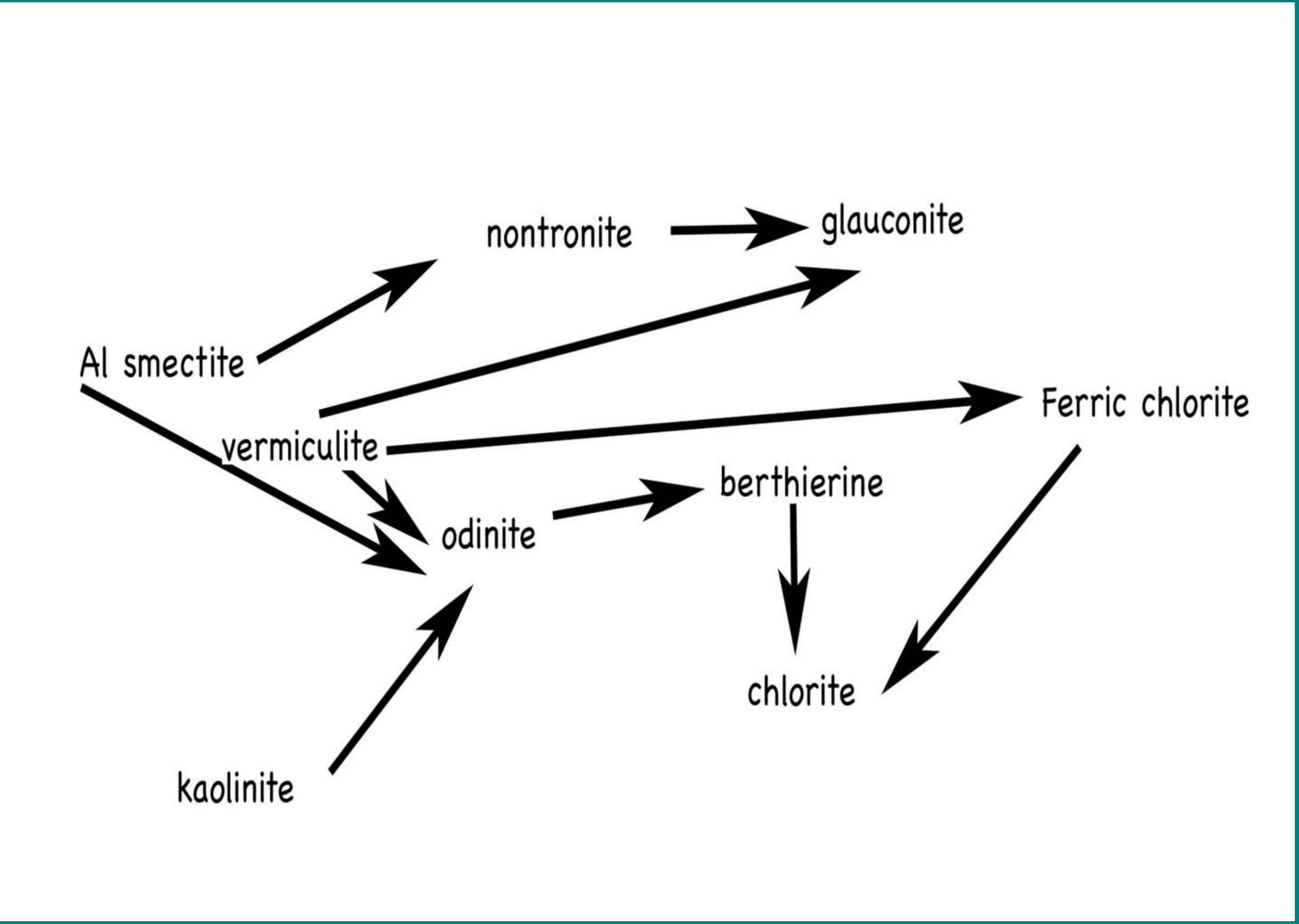


publ. nontronite
published berthierine analyses
% FeO & Fe2O3
% Al2O3
publ. Fe smectite
kaolinite
50
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30


published
nontronite
published
glauconite
Claiborne Group
Fe smectite-rich
pellets
published
berthierine
Claiborne Group
7Å iron-rich clay
%SiO2
%Al2O3
0
10
20
30
40
50
60
0
5
10
15
20
25
30


S012-006, BSC-11 pellets, E.G.
Serp/SS di- R0 (85:11:4) = 67 %
Kaolinite = 2 %
Illite = 5 %
SS di- (72:28) = 26 %
Experimental
Simulated
Intensity
5
10
15
20
25
30
35
40
45
50
2θ (º)

Green Clay Mineral Evolution as understood now



What controls the final mineralogy of green granules?

Why does it matter?

Macro-environmental factors

- temperature (depth and latitude)
- salinity
- rate of sedimentation
- detritus

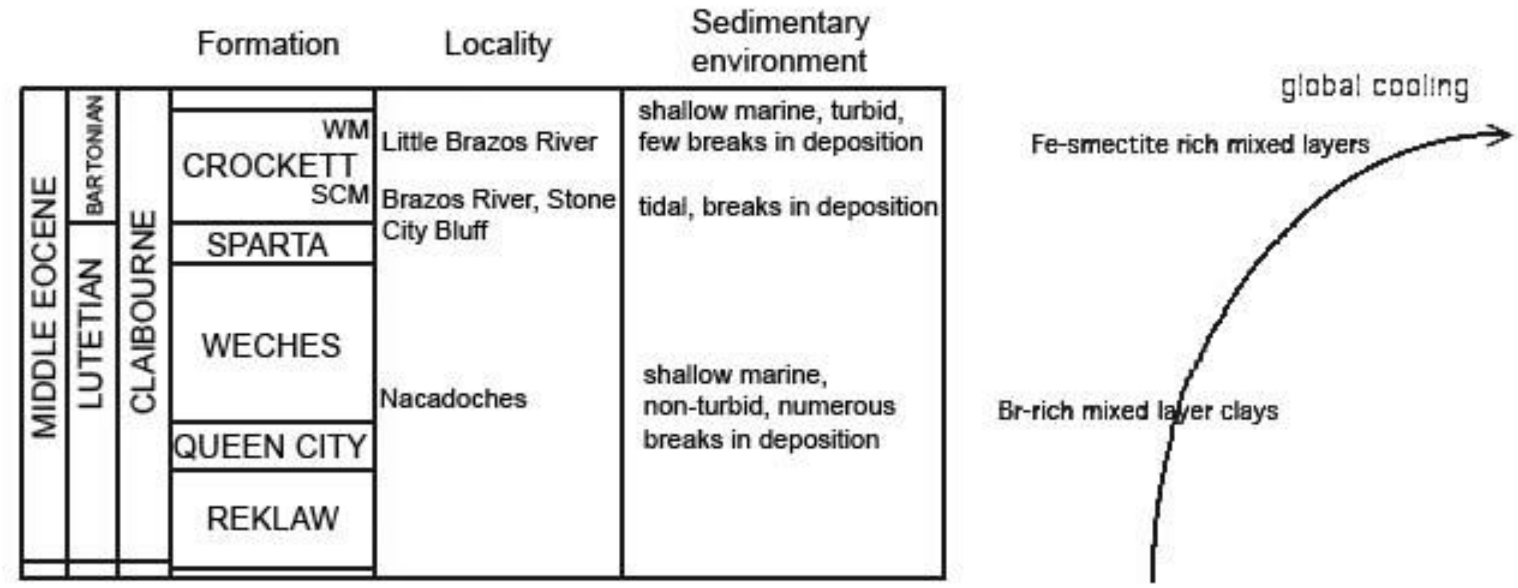
Micro-environmental factors

- pH & Eh
- Bacteria
- invertebrates

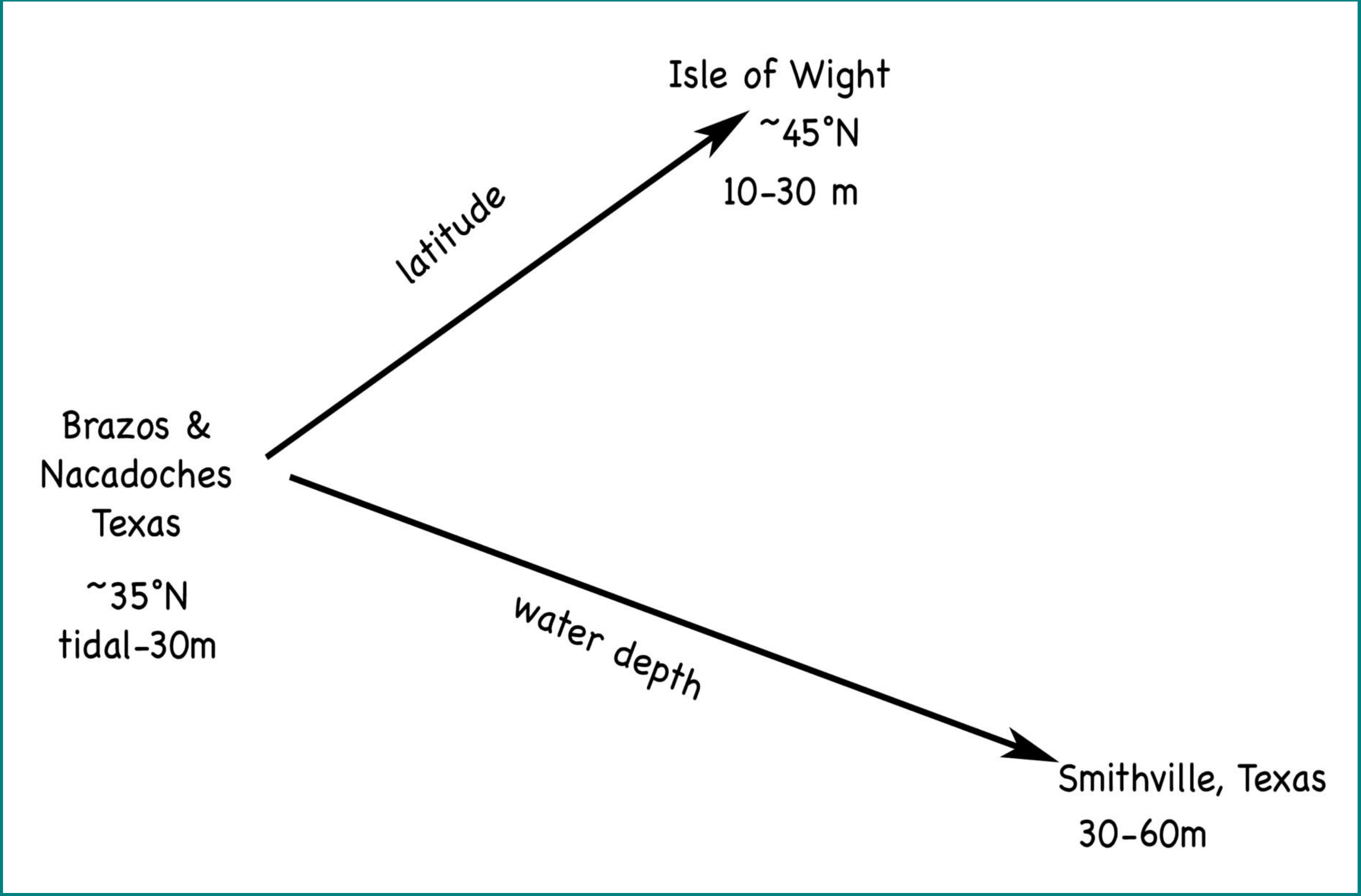
What does the distribution of green granules Tell us about the environment of deposition?

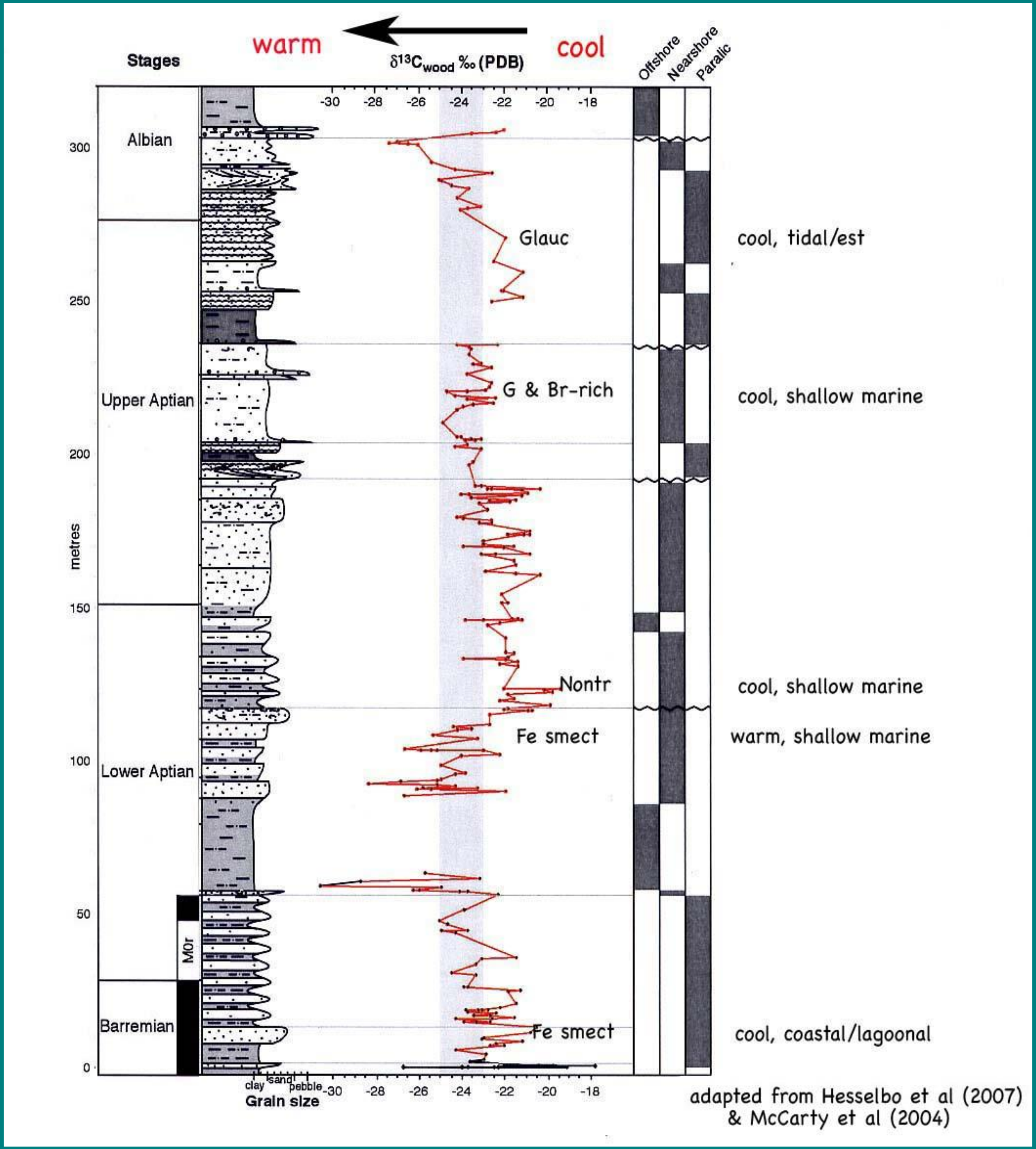
Location	Age	Approx. latitude	water depth	Bottom water t°C	authigenic clay	Ref.
India	Recent	20°N	tidal or shallow mar.	?	O?, Br?	unpubl.
	Holocene	20°N	shallow marine		O?, Br?	unpubl.
India	Oligo-Miocene	10°N	tidal/shallow marine	?	chlorite with V interlayers	unpubl.
New Jersey Margin	Oligo-Miocene	40°N	outer shelf (0.6-1km water depth)	**?**	glauconite	Hesselbo & Huggett 2001
Texas	Eocene	35°N	tidal to ?60m	?-20°	Br& Sm rich mixed layers	Huggett et al 2006
Isle of Wight	Eocene	45°N	10-30m	15-20°	smectitic glauconite & glauconite	Huggett & Gale, 1997
Isle of Wight	Oligocene		ephemeral lake	>20°?	smectitic glauconite & glauconite	Huggett & Cuadros 2010
Isle of Wight	Cretaceous	40°N	tidal/shallow marine	variable	Br & N rich mixed layers, glauconite	McCarty et al 2004

Distribution in time of the Texas sample localities and their depositional environment



Claiborne Group, Texas and Bracklesham Group, IoW, UK (both Eocene) - differences in environmental factors





Comparison of environmental and clay data for the Cretaceous Greensand of the Isle of Wight.

If the verdine = warm/shallow
and glaucony = cool/deep
rule doesn't always apply

can the present still be a key to
the past?

It would seem not….

In ancient sediments berthierine is also found in non-marine sediment

Glauconite can be reworked into non-marine sediments

Glauconite occurs in shallow marine sediments

Glauconite & berthierine occur in the same sediment packets

In ancient sediments glauconite occurs in warm water sediments

Distribution in Time

- During the Phanerozoic there have been 2 main periods of iron-rich clay accumulation:
- 1) The early Palaeozoic 2)Mesozoic-Cainozoic
- Both episodes were characterised by:
- temperate to warm climates world-wide
- sea level rise and associated transgression
- Dispersed cratonic blocks, leading to a high proportion of shelf seas
- Intervals of low sediment flux
  - (from Van Houten and Purucker, 1984)

Conclusions

- Evolution of detrital clay to form green clays is complex and may follow more than pathway of transformation

- Until we understand what really controls how green clays form and the sediments they are found in they cannot be reliably used as palaeo-environmental indicators

Glauconite defined

- Tetrahedral Al usually >0.2 atoms per O10(OH)2 unit formula
- Octahedral R3+ >1.2
- Octahedral Fe>>Al
- Octahedral Mg^{2+}>Fe^{2+}
- D060 >1.510Å