

**ONOCERANE I WITNESSES TO DRY CLIMATIC PHASES
AT THE END OF THE LAST GLACIAL MAXIMUM
AND DURING THE YOUNGER DRYAS
IN NORTHERN BRAZIL**

Jérémy JACOB, Jean-Robert DISNAR, Mohammed BOUSSAFIR, Marie-Pierre LEDRU, Abdelfettah SIFEDDINE, Ana Luiza Spadano ALBUQUERQUE and Bruno TURCQ.

CONTENTS

Introduction

Context

Ecology and Limnology
Climate and Paleoclimate

Pentacyclic triterpenes

Goals of the study

Methods

Results

Sediment and Organic Matter composition

Onocerane I

Identification

Previous reports in oils / sediments

Potential biological sources

Variations of abundance along the record

Conclusions

The background of the image is a dark, rich purple color. It is decorated with several thick, wavy, horizontal lines in a slightly lighter shade of purple and magenta. These lines flow across the frame, creating a sense of movement and depth. The overall aesthetic is modern and artistic.

CONTEXT

Geological and ecological context



Geological and ecological context

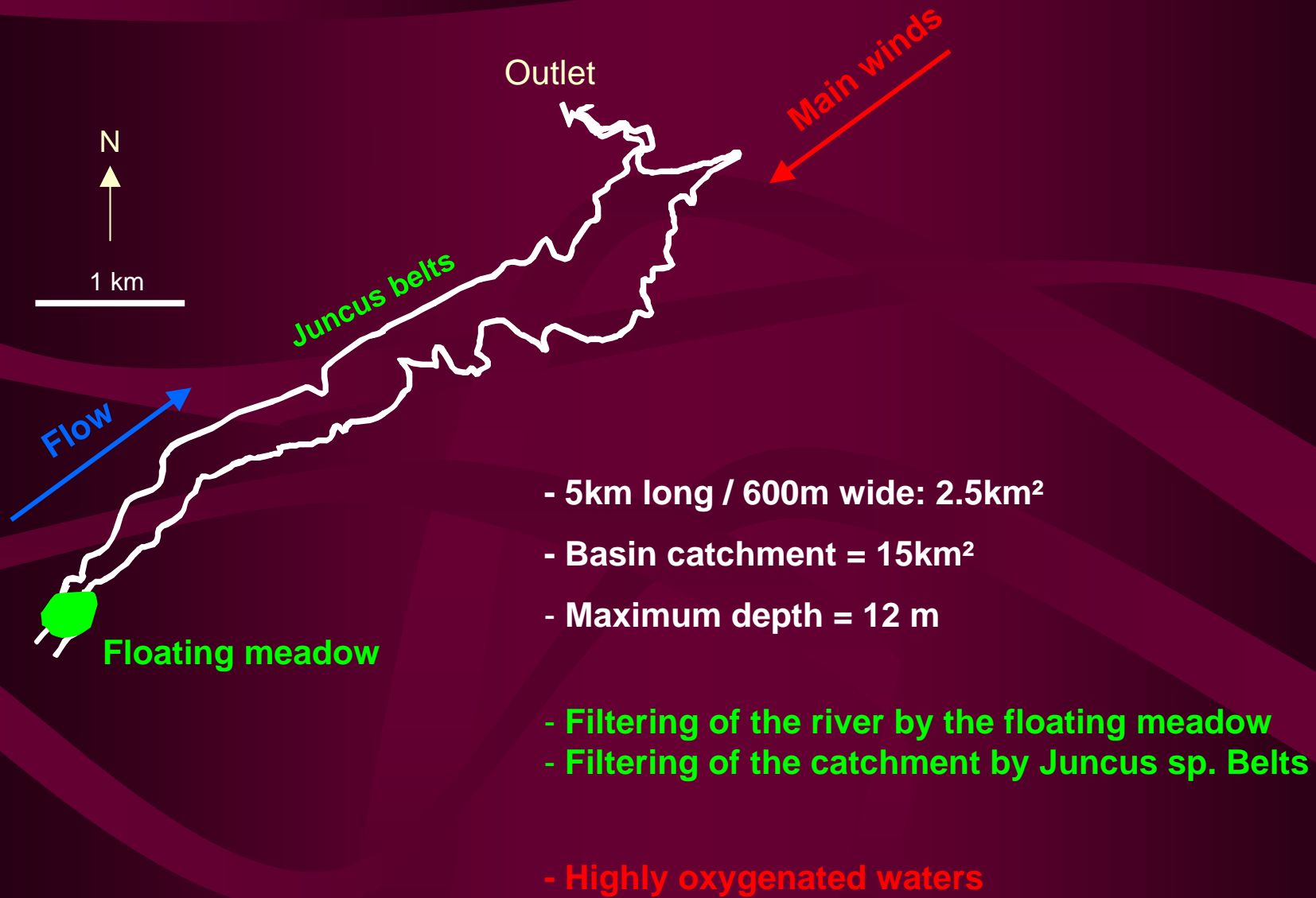


Active dune system

Fossil dune system

Laterites

Limnological context



Limnological context – present day setting

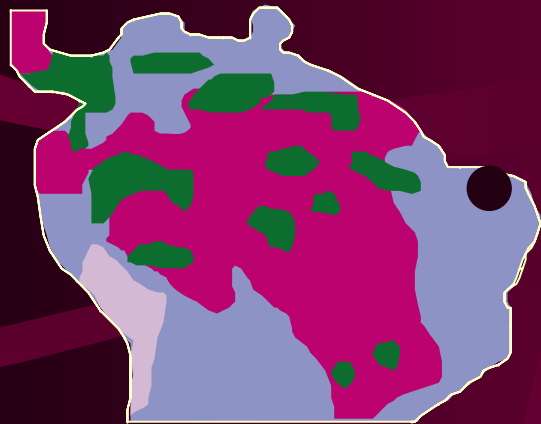
- **Oligotrophic lake**
- **Few phytoplanktonic contribution**
- **Mainly higher-plant derived OM**
- **Strong degradation of OM**

Paleoclimates in South America – Last Glacial Maximum

18,000 ¹⁴C yrs BP

Often missing records due to sedimentary hiatuses

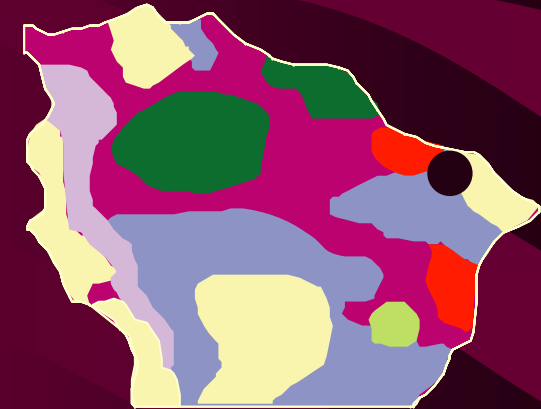
Colder (Stute *et al.*, 1995) and dryer



Van Campo *et al.*, 1993



Crowley, 1995



Adams and Faure, 1998



Turcq *et al.*, 2002

Paleoclimates in South America – Lateglacial

18,000 – 11,000 ¹⁴C yrs BP

Atlantic Margin sediments : Behling *et al.*, 2000

- Influx in fern spores (moisture)
- Elevated Ti/Ca (more erosion onland)

Lake Caço : Ledru *et al.*, 2001 ; Sifeddine *et al.*, 2003

- Pollen evidence for humid and dense forest
- Rises in water level inferred from siderite peaks

Mean wetter climate

Paleoclimates in South America – Younger Dryas

11,000 – 10,000 ^{14}C yrs BP

Cold – Northern Hemispheric event

→ Extension in Tropical South America ?

Colder (1,5 to 3°C) and **drier** in the Andes (El Abra stadial, van't Veer *et al.*, 2000)

Lake Caço : Ledru *et al.*, 2002; Sifeddine *et al.*, 2003 :

- Water-level drops
- AP/NAP decreases
- Increase in forest fires

} Reduction of humid forest

Mean dryer climate

Paleoclimates in South America – Holocene

10,000 ¹⁴C yrs BP - Present

Relatively stable (Dansgaard *et al.*, 1993)

Lake Caço : Ledru *et al.*, 2001

Increase of AP/NAP

Increase in Mimosaceae and *Astronium sp.*

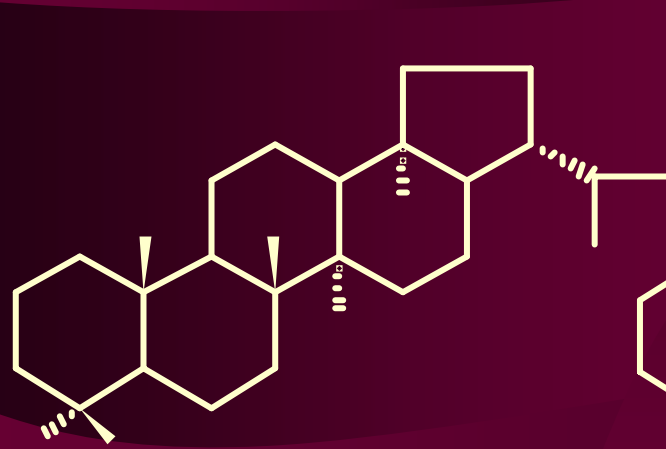
Establishment of present day setting



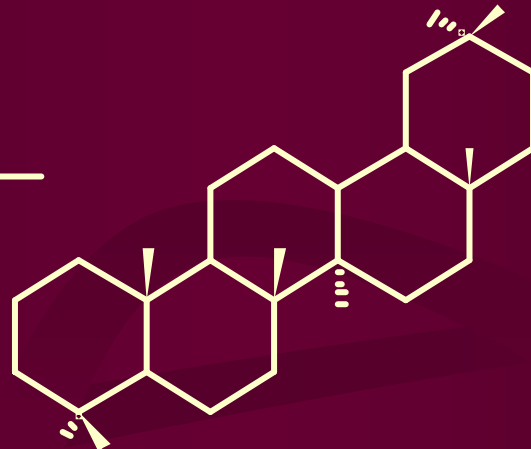
BIOMARKERS

Pentacyclic triterpenes

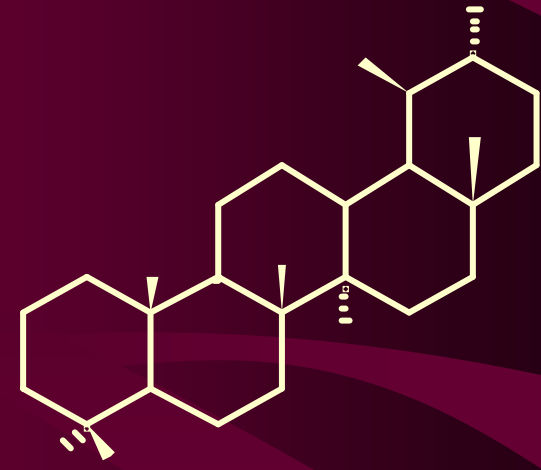
Pentacyclic triterpenes – Basic structures



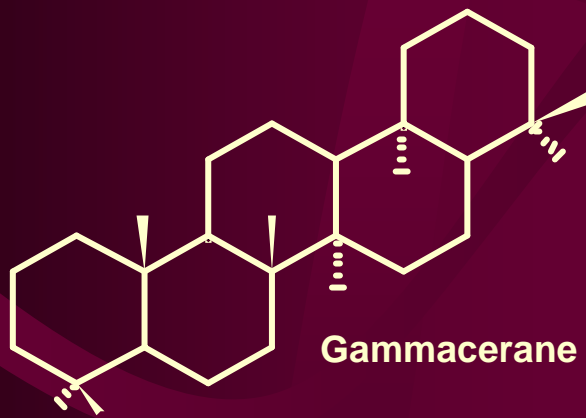
Hopane



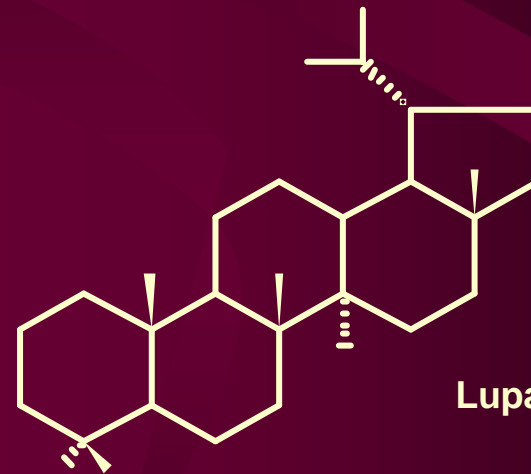
Oleanane



Ursane



Gammacerane



Lupane

Pentacyclic triterpenes – Structural diversity

The structural diversity of PT results from :

- Basic structures
- Position and isomerism of methyl groups
- Rings conformation
- Possible double bonds
- Associated functional groups

One of the most diversified chemical family in Nature

Pentacyclic triterpenes – Conclusion

Structural diversity



Taxonomic value



Potential paleoenvironmental proxies

Poorly used in organic paleoclimate studies

Indicate higher-plant input to the sediment

MAIN OBJECTIVES

Main Objectives

Geological, limnological, ecological/botanical context



Identify new biomarkers

Pentacyclic triterpenes



New proxies for past climate changes in continental settings ?

4 contrasted climatic phases



OM sensibility to these contrasted conditions

METHODS

Methods – Identification and quantitation

Identification by GC-MS: Trace GCQ Polaris (Finnigan)

Mass spectra

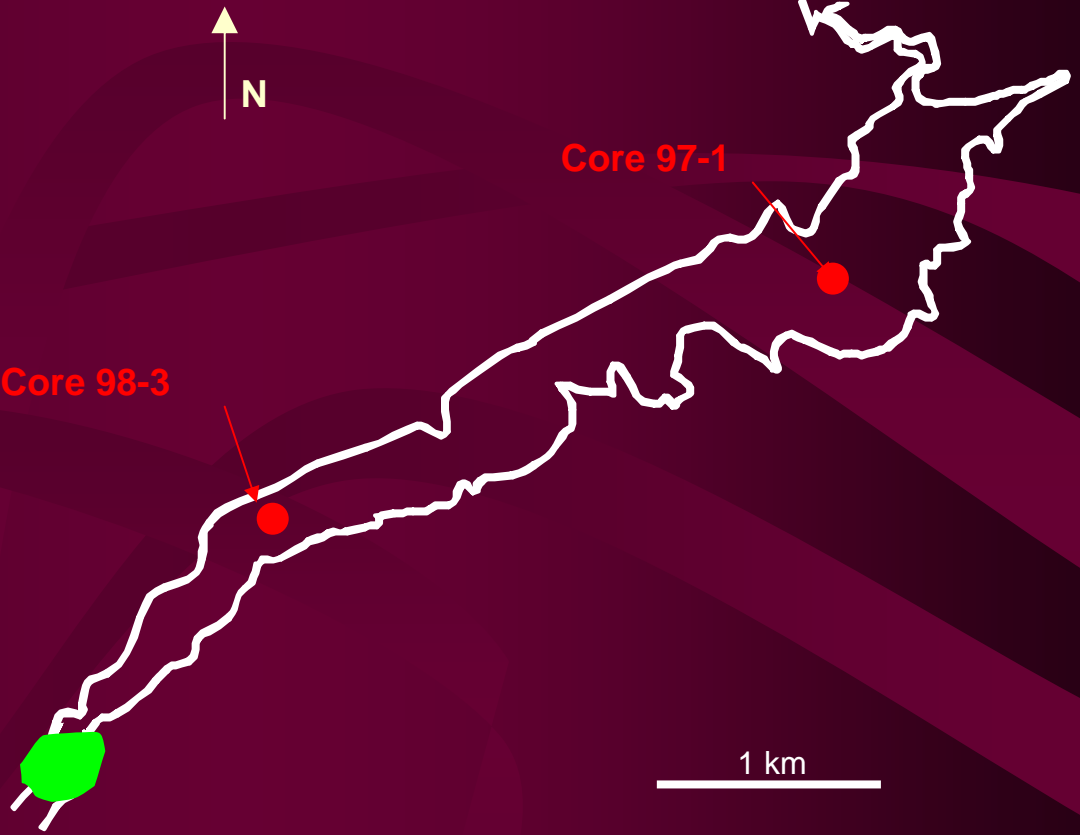
Retention times

Quantitation by GC-MS

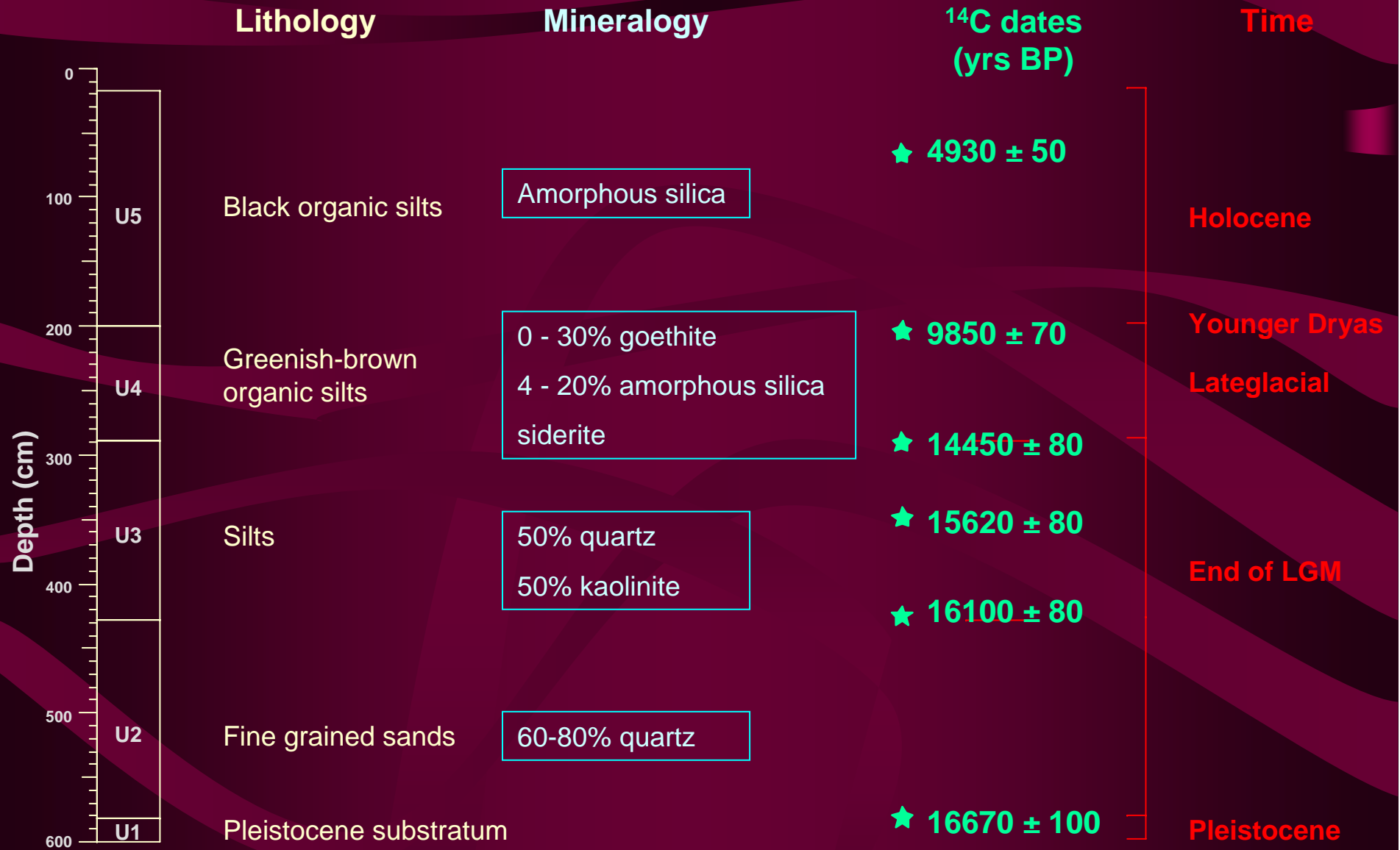
On the chromatograms, comparison of the peak area of ions m/z 414, 191, 123 for onocerane with the area of 5α cholestane (internal standard) on the TIC.

RESULTS

Results



Results



OM: General features

Bulk geochemistry and organic petrography:

Higher-plant in origin

- U2 and U3: Well preserved,
- U4 and U5: Refractory OM,

Molecular analyses:

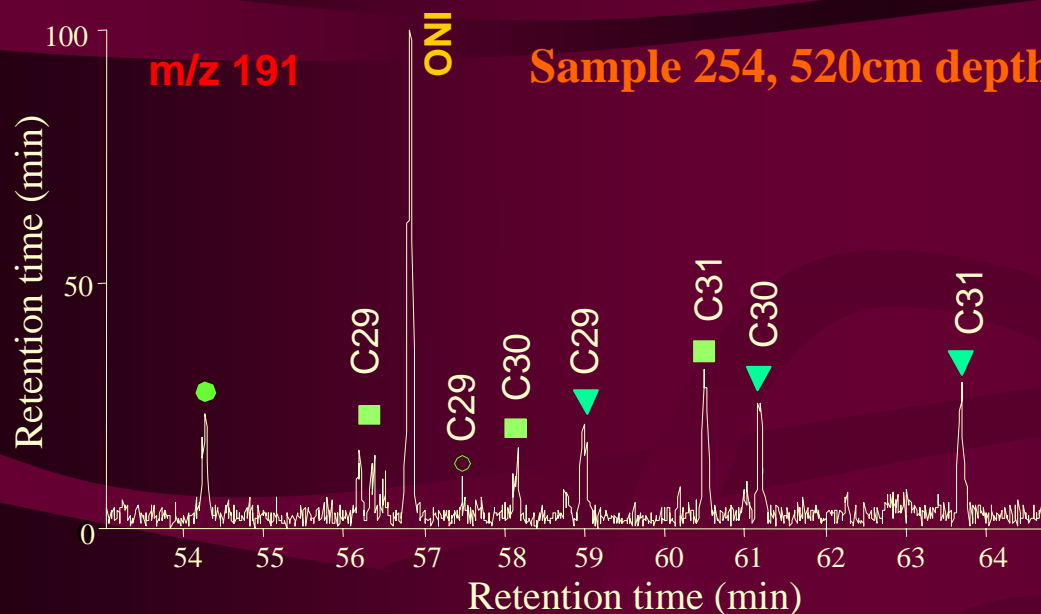
Abundant :

- hopanoids
- higher-plant pentacyclic triterpenes
- degraded triterpenes:
 - des-A-triterpenes
 - aromatics derived from pentacyclic triterpenes
- Few n-alkyl compounds
- No evidence for any phytoplanktonic biomarker in the studied fractions

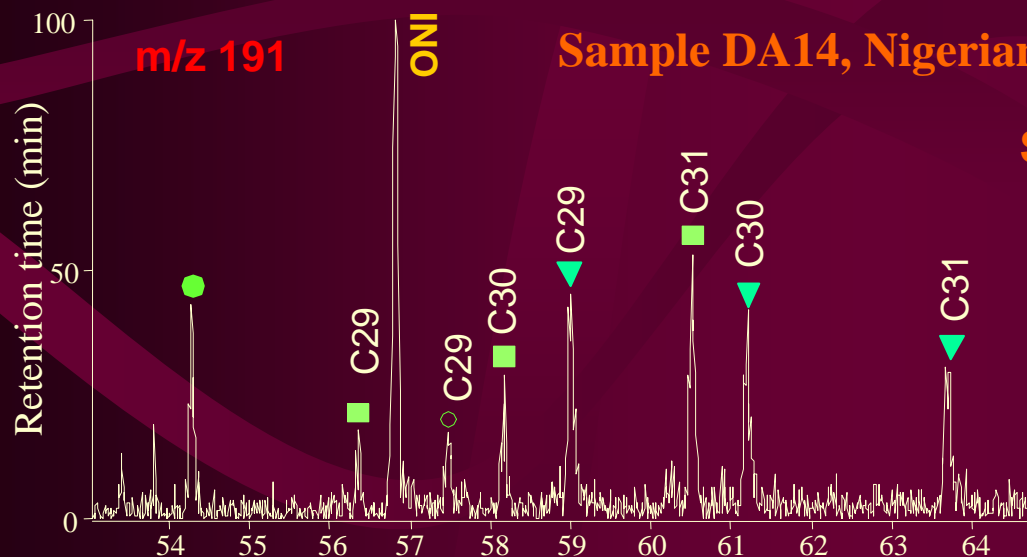


ONOCERANE I

Onocerane I – Identification

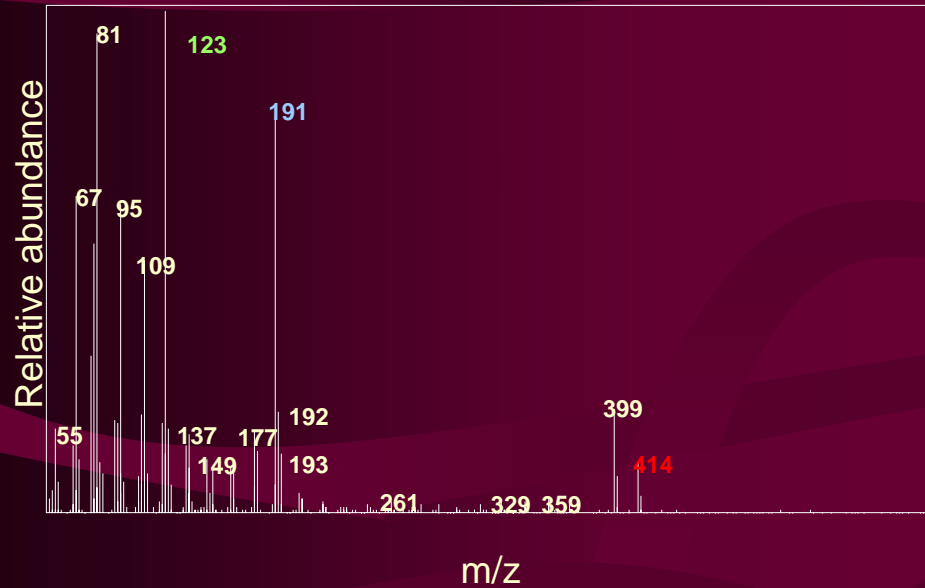


- 17 β Trisnorhopane
- ▼ 17 β ,21 β hopane
- 17 α ,21 β hopane
- 17 β ,21 α hopane

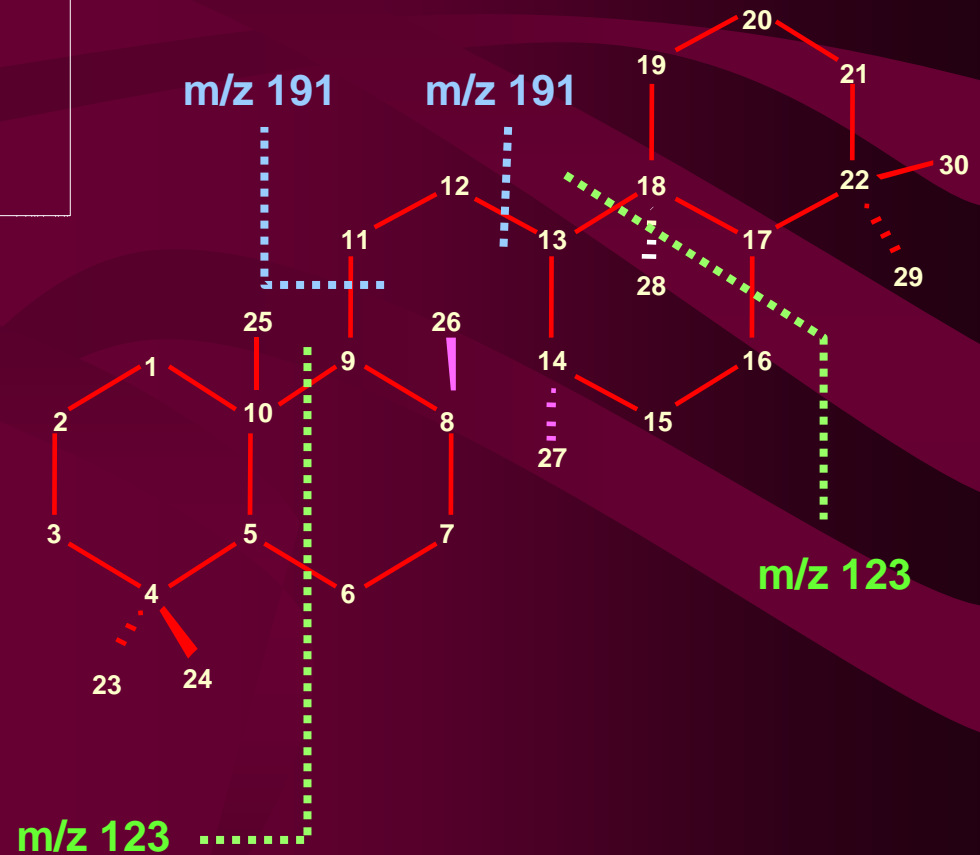


Sample provided by Pr. M.J. Pearson

Onocerane I – Identification



ONOCERANE I



Three onocerane isomers (I, II, III)

- Isomerism at C(8) et C(14) positions,
- Relative abundance of m/z 191 and 193.

Kimble *et al.*, 1974

Onocerane I – Previous reports in sediments / oils

Paleozoic		Mesozoic			Cenozoic		
Carb.	Permian	Triassic	Jurassic	Cretaceous	Paleo.	Neo.	Q.

Onocerane I

- Miocene (Idaho) : Giannasi and Niklas, 1981.
- Oligocene (Montana) : Curiale, 1988.
- Paleogene (China) : Fu Jiamo *et al.*, 1988.
- Oligocene (China) : Wang Tieguan *et al.*, 1988.
- Up. Cretaceous (Nigeria): Pearson et Obaje, 1999.

Since the Upper Cretaceous

Angiosperms ?

Onoceranes II and III

Carboniferous, Jurassic (China) : Wang Tieguan *et al.*, 1988.

Tsuda *et al.*, 1964 : Isomerisation between onoceranoids and serratanoids

Onocerane II and III could derive from serratene-type compounds ? Pteridophyts

Onocerane I – Biological origin

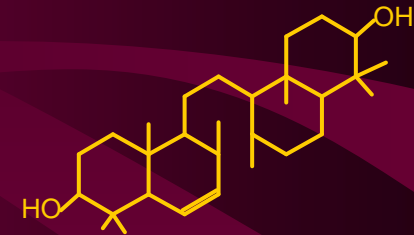
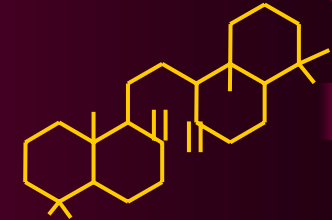
Pteridophyts

Lemaphyllum sp., *Colysis sp.* (Ferns) : Ageta *et al.*, 1982.
Lycopodium sp. (Lycophyts) : Habaguchi *et al.*, 1968.

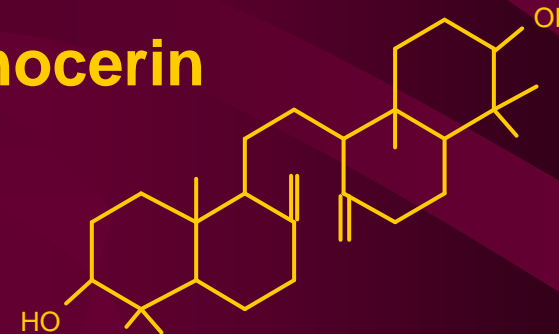
Angiosperms

Lansium domesticum (Meliaceae)
Cissus quadrangularis (Vitaceae)

Ononis sp. (Papillionaceae)

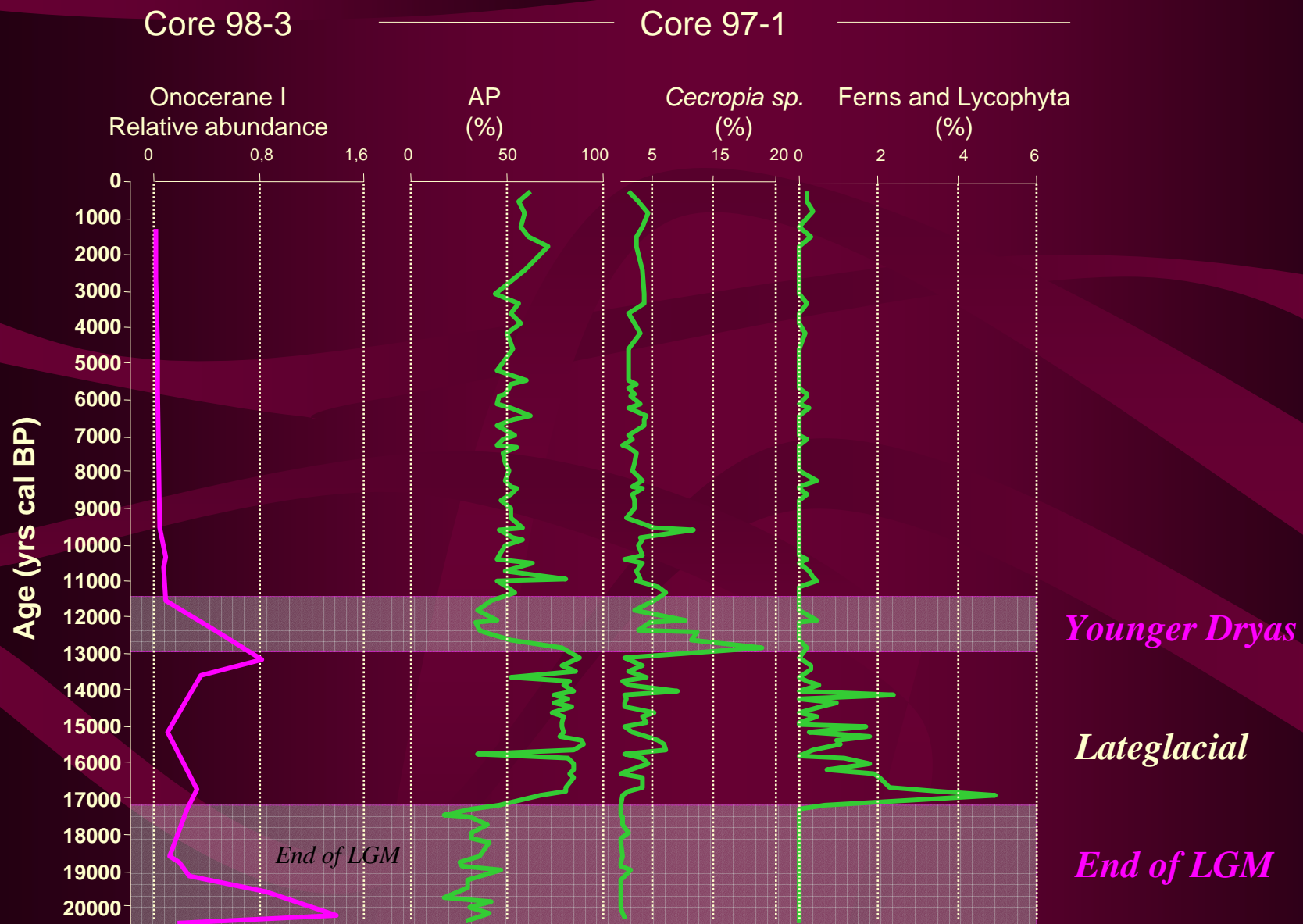


Onocerin



Favors water transport in roots
Adapted to water-depleted media
Sean Mayes / Peter Dean (pers. com.)

Onocerane I – Variations of abundance

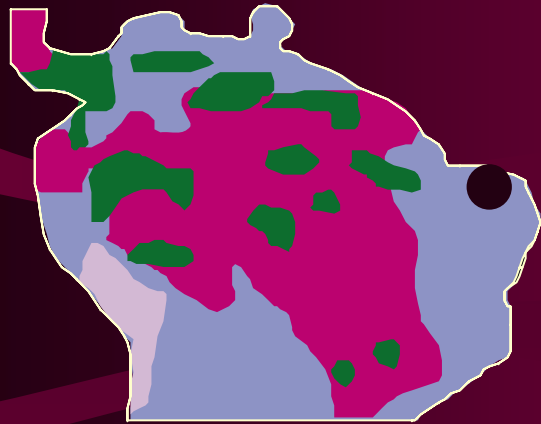


CONCLUSIONS

Conclusions: Palaeoclimatic implications

Onocerane I is abundant during the two driest periods that suffered this region:

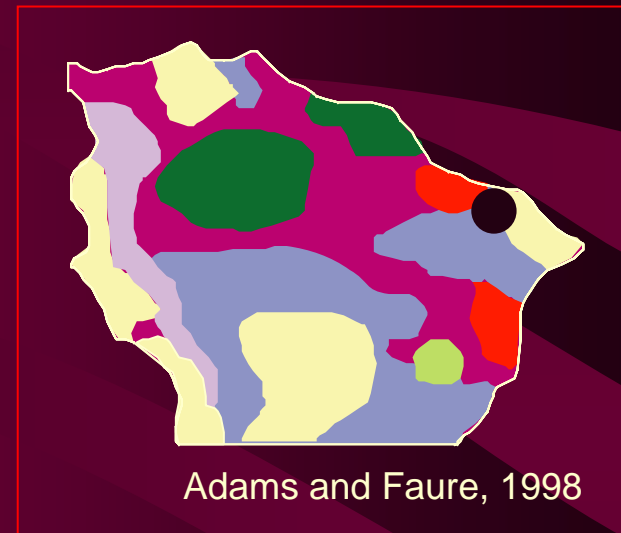
- The end of LGM



Van Campo *et al.*, 1993



Crowley, 1995



Adams and Faure, 1998

The region of Lagoa do Caço was most probably of semi-arid type.

No information about the fragmentation of rainforest but evidences for the reduction of its surface.

Conclusions: Palaeoclimatic implications

Onocerane I is abundant during the two driest periods that suffered this region:

- The Younger Dryas

Started with a dry event that allowed the development of onocerane I producers and the reduction of the Lateglacial humid forest.

Palynological and molecular analyses provide the southernmost record of Younger Dryas in South America and confirm the relative dryness of this episode.

Conclusions: onocerane I

- First report of onocerane I in Quaternary sediments
- Onocerane I was not produced by ferns or lycophyts in this setting
- Onocerane I testifies to the development of a plant well-adapted to dryness, probably close to the *Ononis* genus.

The *Ononis* genus has not yet been reported in South America

Conclusions: new proxies for vegetation changes ?

The sediments of Lagoa do Caço contain specific pentacyclic triterpenes :

Onocerane I and PTME (poster PII/096)

Each of them probably attest to the development of a **single species** in the catchment area.

These molecules can complement palynological studies

Due to their specificity, they are designed targets for CSIA analyses.

Acknowledgments

Peter Dean (Cambio, UK) and Sean Mayes (Cambridge)

Conseil Régional du Centre (Phd grant)

Research support:

ISTO-IRD convention

IRD-CNPq (Brazil) convention

Departamento do Geoquimica – Universidad Federal Fluminense

