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A Sulfuric Acid Speleogenesis in the Northern Pyrenees (France)?

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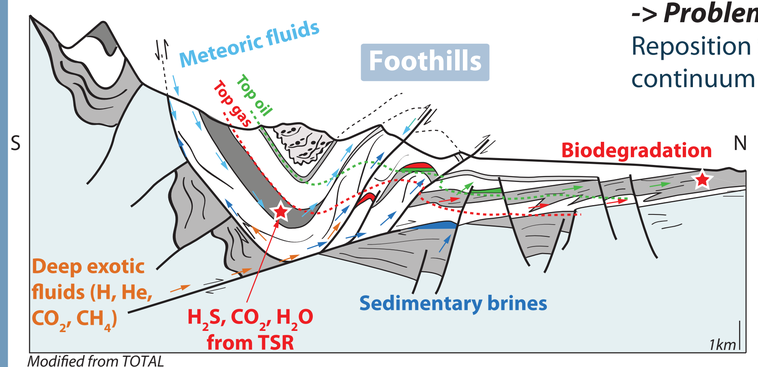
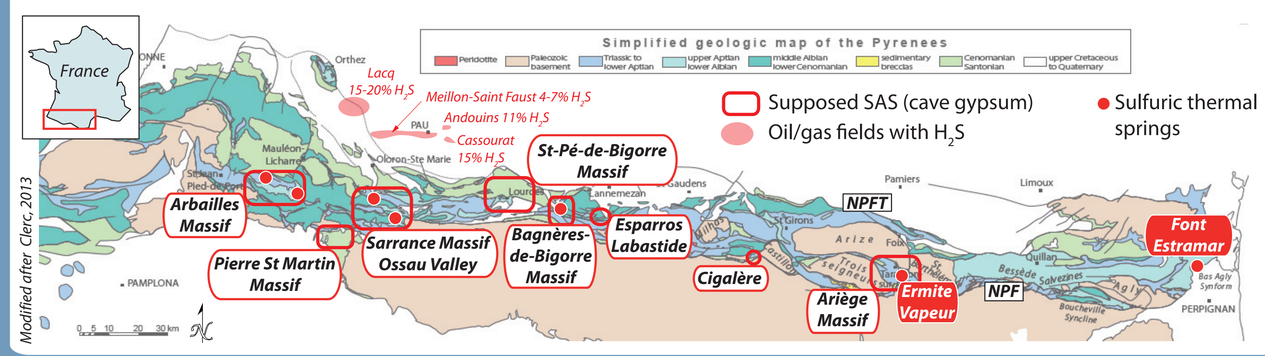
1- Introduction: hypogenic caves in the Northern Pyrenees?



Modified from TOTAL

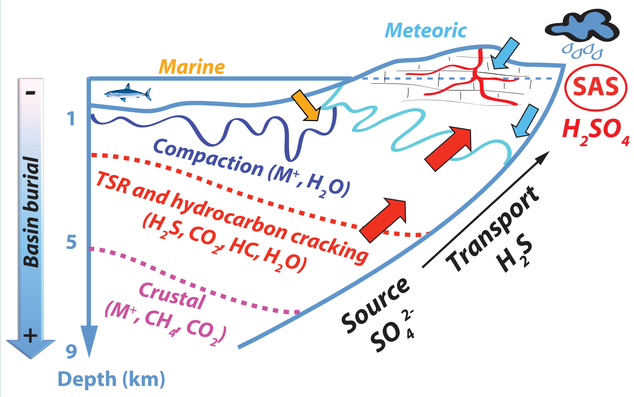
-> Problematic (in Total «Fluid» program):
Reposition Sulfuric Acid Speleogenesis (SAS) in the continuum of fluid-rock interactions in the foothills.

-> Main questions:
- **Timing** of karst formation (hyper-extension, compression…)?
- **Controlling factors** of karst development (structural, geochemical...)?
- **Nature and origin of fluids** involved in the dissolution (CO_2, H_2S, meteoric...)?
- Link with petroleum and ore deposits?



Modified after Clerc, 2013

2- Thermochemical Sulfate Reduction (TSR) and SAS



Thermochemical sulfate reduction:
$CH_4 + SO_4^{2-} \Rightarrow H_2S + CO_2 + 2OH^-$

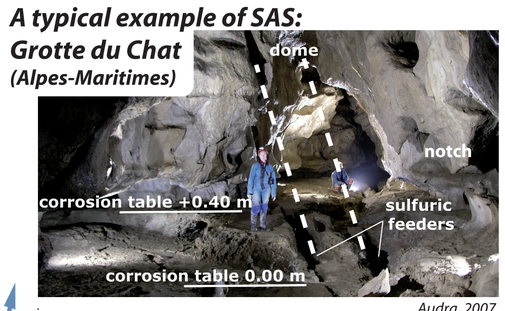
Oxidation of H_2S:
$H_2S + 2O_2 \Leftrightarrow H_2SO_4$ ($SO_4^{2-} + 2H^+$ in solution)

Sulfate precipitation in replacement of carbonate:
$SO_4^{2-} + 2H^+ + CaCO_3 + 2H_2O \Rightarrow CaSO_4\text{-}2H_2O$ (gypsum) $+ CO_2 + H_2O$

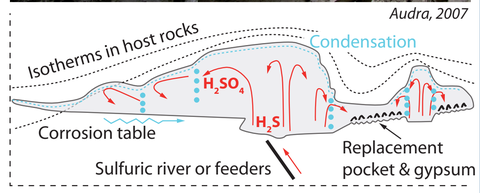
Condensation-corrosion

Corrosion-replacement

A typical example of SAS: Grotte du Chat (Alpes-Maritimes)



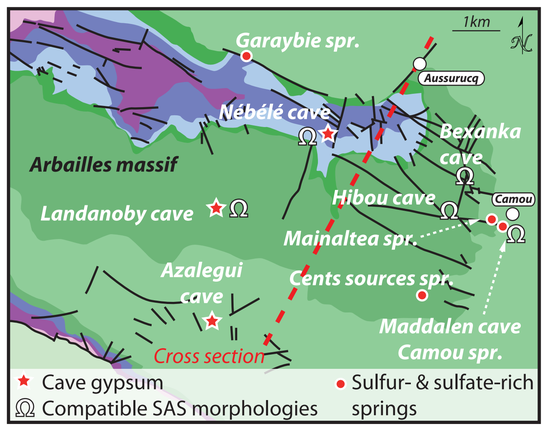
Audra, 2007



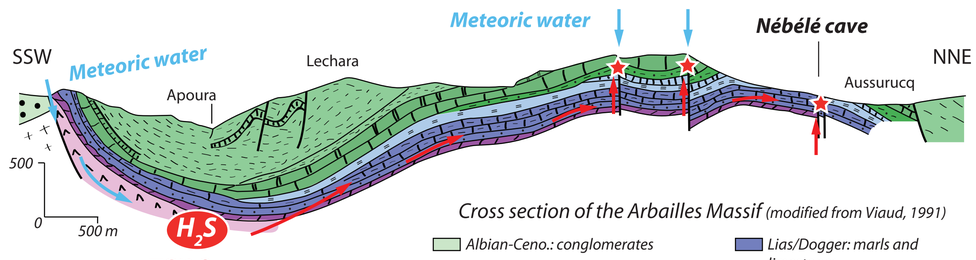
3- Field evidences of cave sulfates in the Arbailles massif: SAS or evaporite leaching ?

The Arbailles Massif, a good candidate for SAS...
-> Numerous caves in Aptian and Dogger limestones
-> Caves located close to regional faults connected to Triassic evaporites
-> Current thermo-mineral springs = sulfate/sulfur-rich deep fluids circulation
-> Gypsum precipitation in karst systems
-> Relative proximity with oil seeps and hydrocarbon fields

... But several processes may be responsible for cave sulfate precipitation:
-> SAS
-> Pyrite oxidation
-> Leaching of sulfate-rich sediments (evaporite, carbonate...)
-> Decomposition of organic matter (guano...)



Geological map of the Arbailles Massif

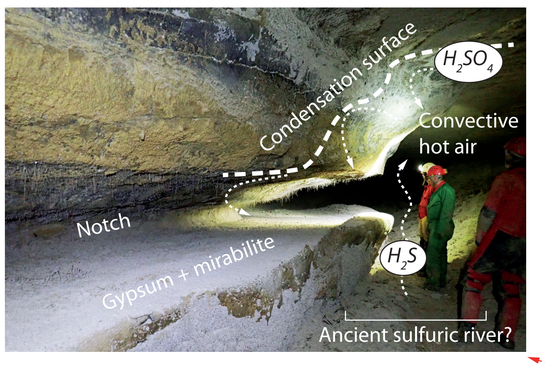


Cross section of the Arbailles Massif (modified from Viaud, 1991)

- Albian-Ceno.: conglomerates
- Up. Aptian/Albian: black schistose marls
- Aptian: Urgonian limestones
- Lo. Aptian: Ste Suzanne marls
- Kimmeridgian: limestones Oxfordian: Hosta Marls
- Lias/Dogger: marls and limestones
- Up. Triassic/Lo. Lias: limestones and dolomites
- Up. Triassic: gypsum-rich marls
- Supposed hypogenic caves and thermo-mineral springs

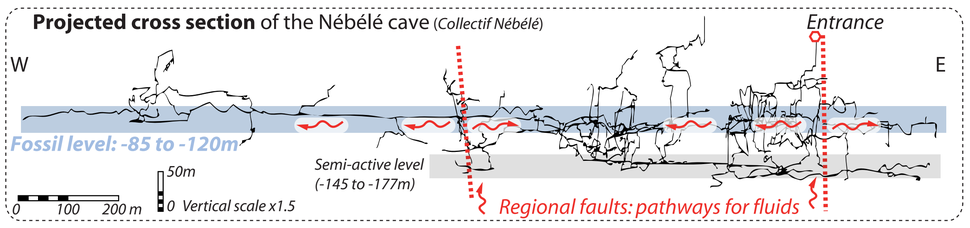
Example of the Nébélé Cave

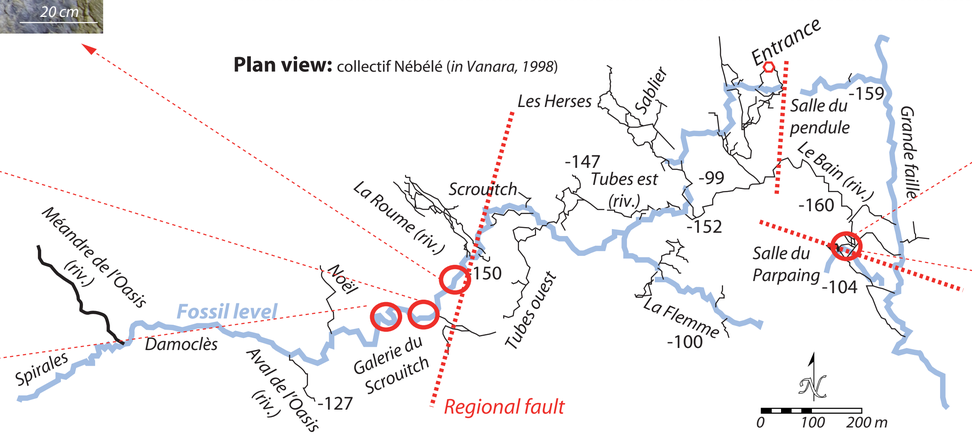
Notch and corrosion table



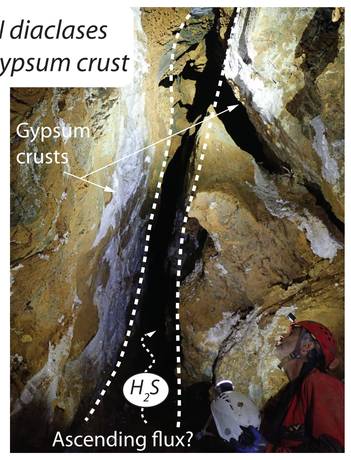
Replacement pocket

Typical morphologies and mineral markers of SAS observed along a fossil level (-85 to -120m)



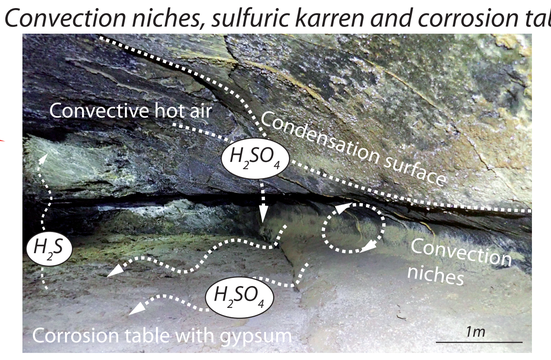


N120-80N diaclases coated by gypsum crust



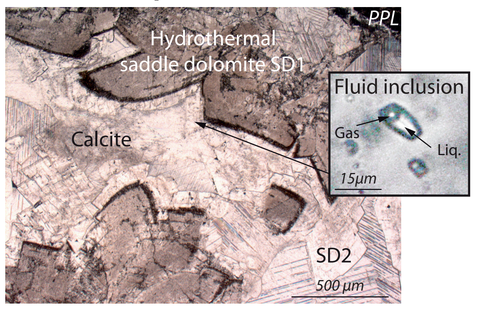
Mirabilite flower ($Na_2SO_4\text{-}10H_2O$)

Convection niches, sulfuric karren and corrosion table

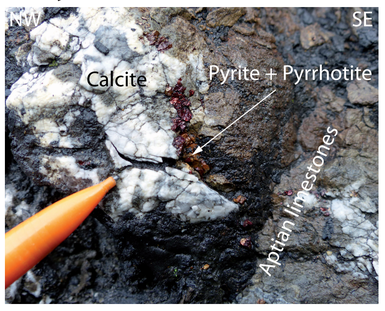


Potential sources of sulfur in the sedimentary basin

H_2S-rich hydrothermal carbonate veins in Aptian limestones

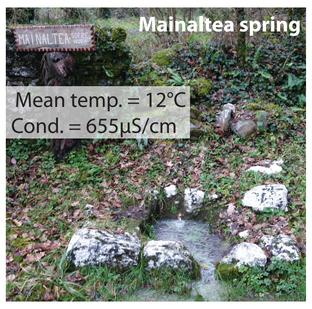


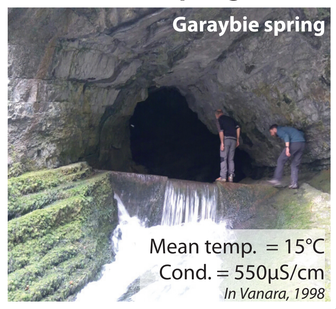
Pyrite in veins



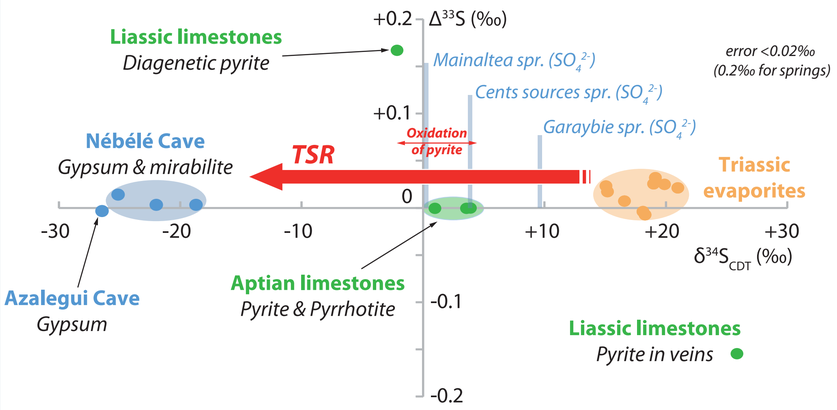
Diagenetic pyrite

Sulfate/sulfur-rich thermo-mineral springs





4- Sulfur isotopes: origin and processes



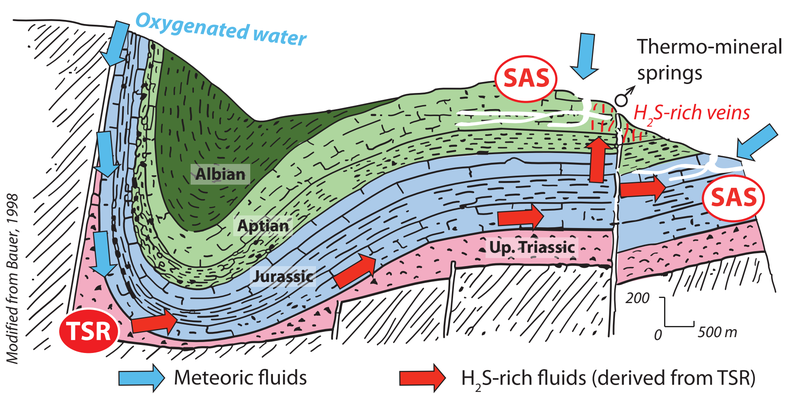
Cave sulfates are not linked to evaporite leaching or pyrite oxidation:
- such processes do not involve significant $\delta^{34}S$ fractionation
- very few pyrites in sediments

→ High $\delta^{34}S$ fractionation between Triassic evaporites and cave sulfates
-> Evidence of TSR and H_2S-rich fluid migration

5- Conclusions: 1st hypothesis and Perspectives

Preliminary conceptual model

(i) **TSR of Triassic evaporites** starting during Cretaceous extension
(ii) **Migration of H_2S-rich fluids** towards basin margins (timing?)
(iii) Mixing between deep fluids and oxygen source -> **SAS**



Modified from Bauer, 1998

Perspectives

Methods	Lessons
S isotopes on gypsum & water	S species & origin
O isotopes on gypsum & water	Conditions during SAS
C isotopes on water & veins	Organic matter involved in TSR
Fluid inclusions in veins	P/T of fluids & S species
U/Th on gypsum	Absolute dating of SAS

6- Collaborations

P. & S. Degouve (GSHP Tarbes)
M. Douat (ARSIP, ICE Himalayas)
Collectif Nébélé
P. Sorriaux & CDS09/SCHS
CDS64
Data base Karsteau