Identification and modelling major geochemical processes in calcareous fens



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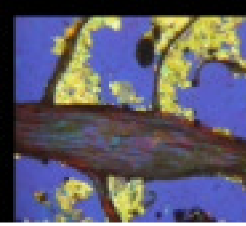
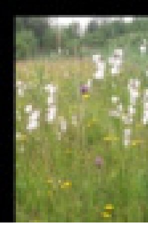
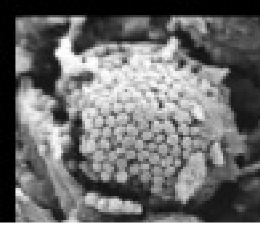
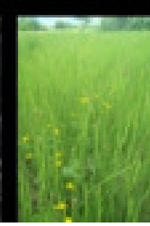
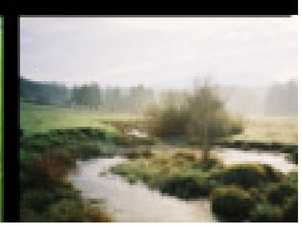

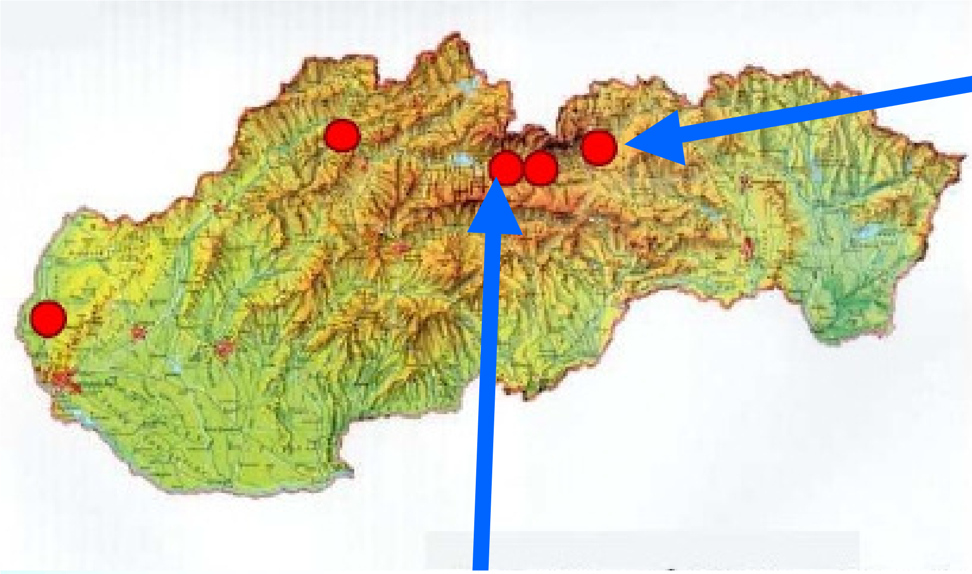


Belianske Lúky


Štrba


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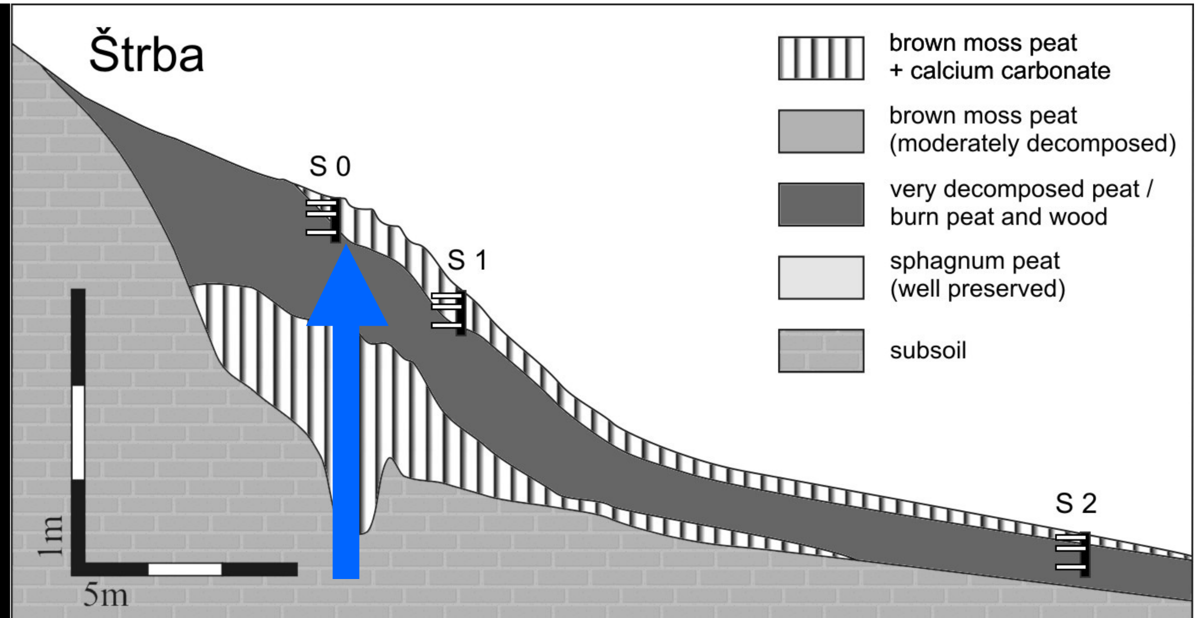
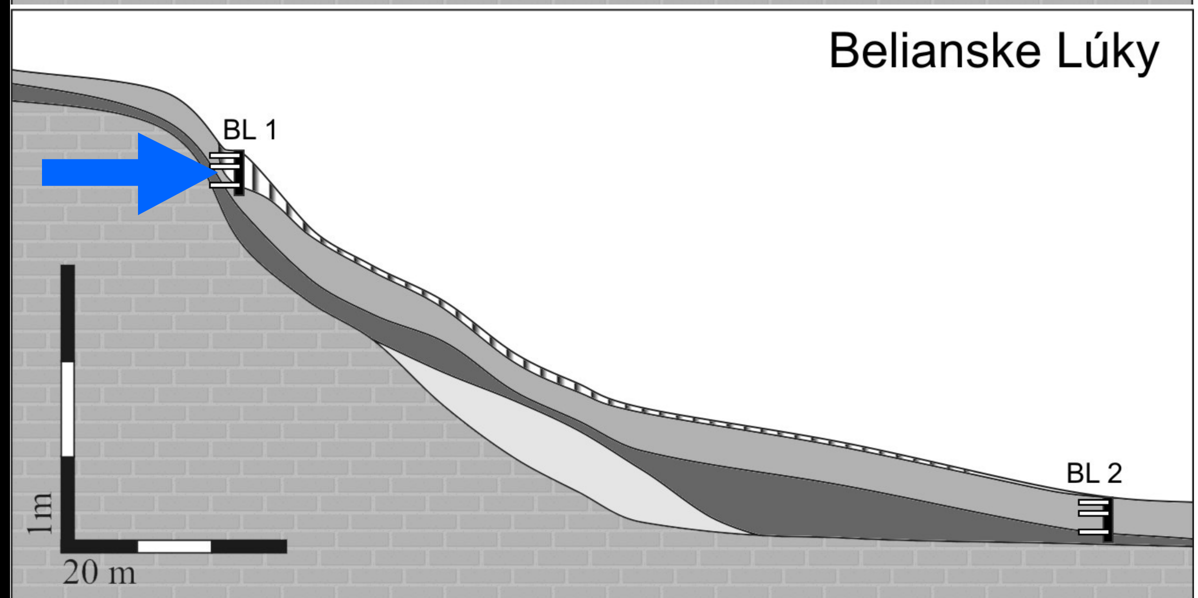
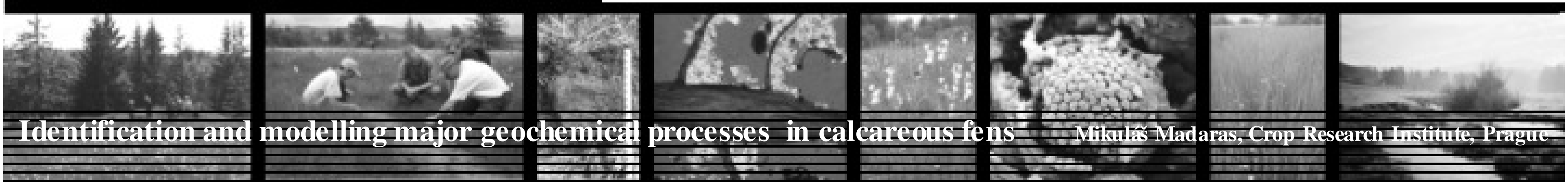
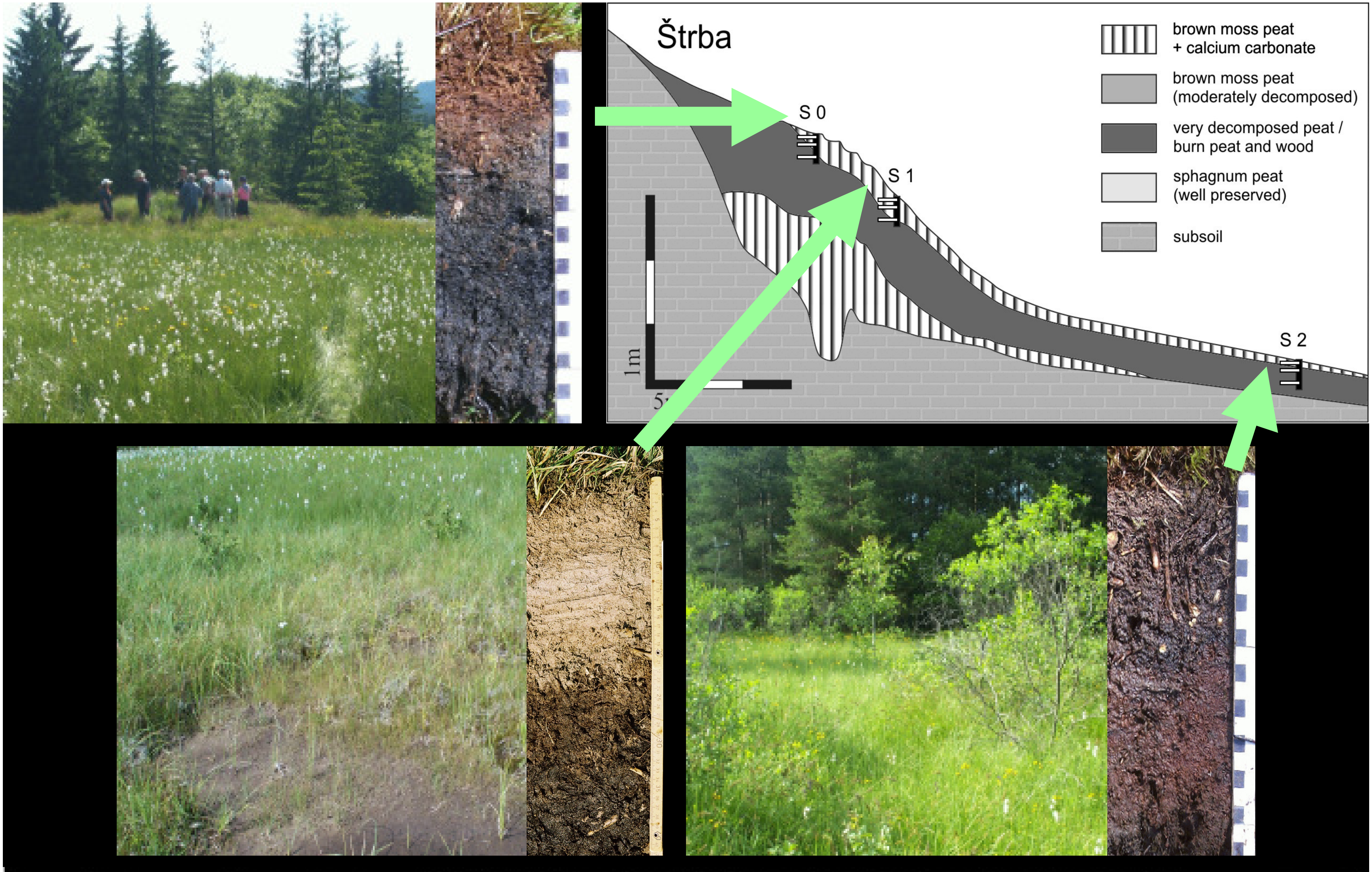
Different seepage type, common features:

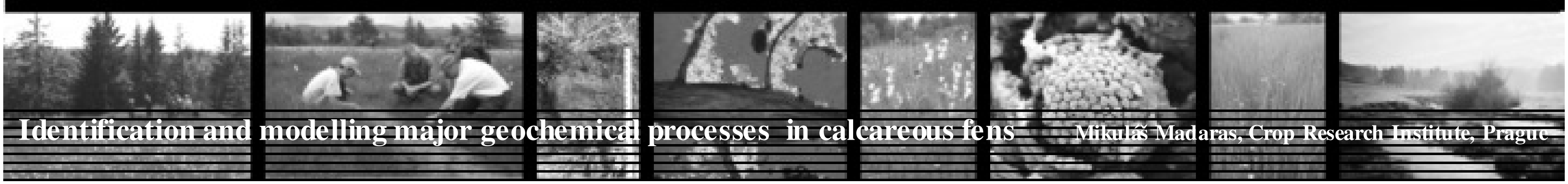
- seepage of calcareous groundwater (Ca^{2+}, HCO_3^-, Fe^{2+}, SO_4^{2-})
- topsoil carbonate precipitation
- sulphate reduction in near surface
- simillar vegetation types











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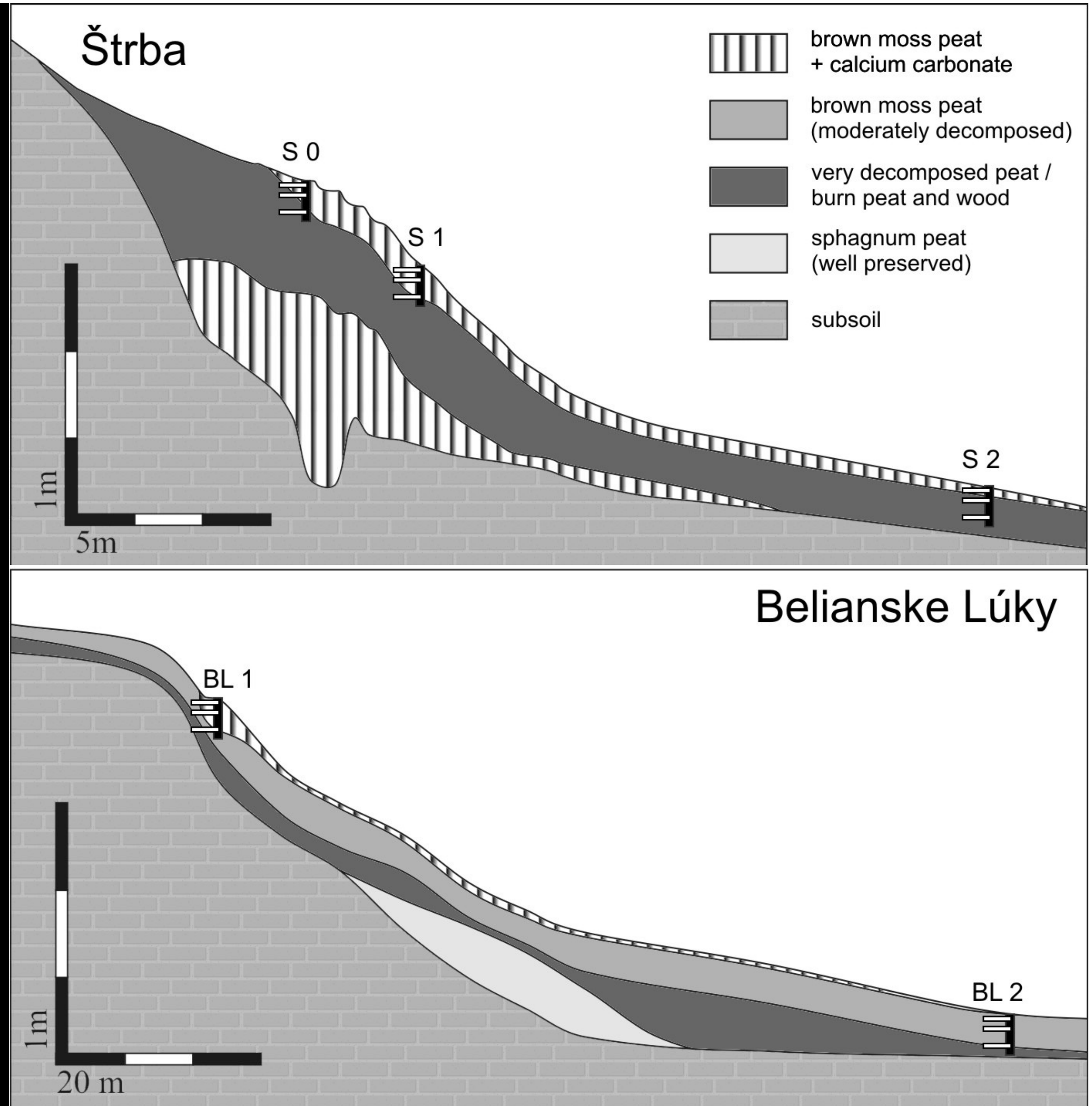
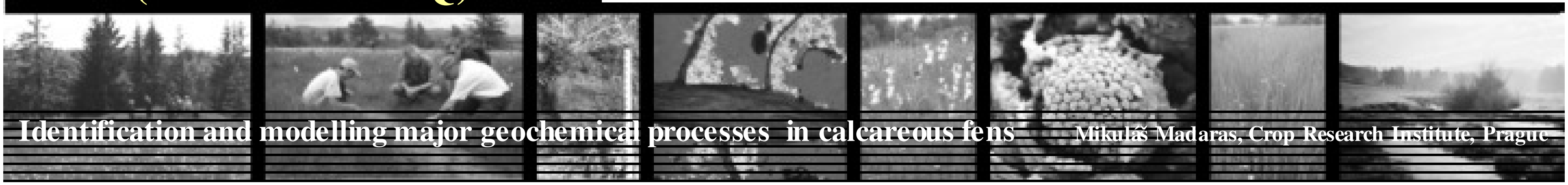
Methods of investigation:

- pore water analyses (water tubes, rhizon samplers)
- bulk peat chemical analyses
- in situ redox measurements
- SEM and thin section analysis
- RTG diffraction analysis

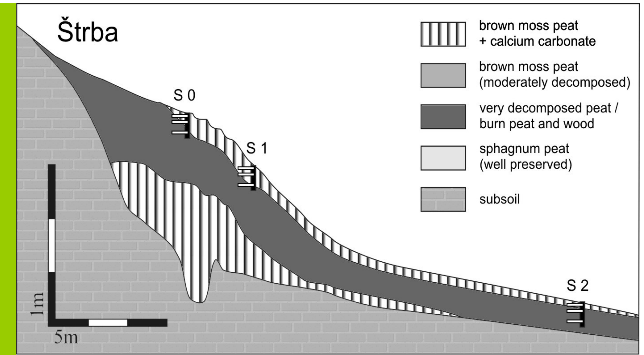
conceptual model of fen geochemistry

geochemical modelling (Visual MINTEQ)





Transformation of porewater geochemistry



Vertical towards topsoil:

- pH increasing
- Ca^{2+} and HCO_3^- slight increase, then sharp decrease

1. Anaerobic decay of organic matter
2. Degassing and subsequent $CaCO_3$ precipitation

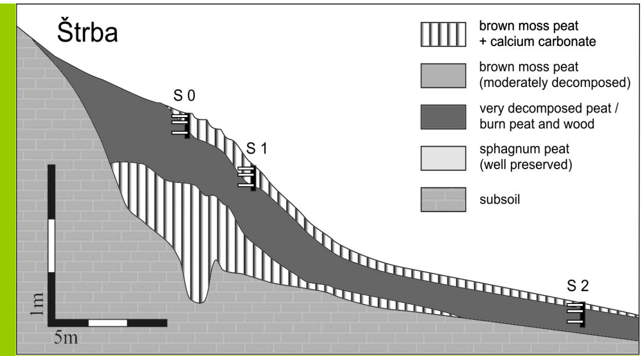
Horizontal towards low-end:

- pH, HCO_3^-, Ca^{2+} highest under „pool“ area
- Ca^{2+} afterwards slightly decreasing

A. Processes intensified by temperature increase in shallow pools

B. Decreasing mineralization due to carbonate precipitation and water dillution

Transformation of porewater geochemistry



Vertical towards topsoil:

- SO_4^{2-} decreasing (S0), may appear at top
- H_2S none at topsoil, behaves oppositelly in S0 and S1
- Fe under DL (S0, S1), peak in 25cm in S2

3. Anaerobic sulfate reduction
4. Topsoil S^{2-} reoxidation
5. Anaerobic Fe^{3+} reduction

Horizontal towards low-end:

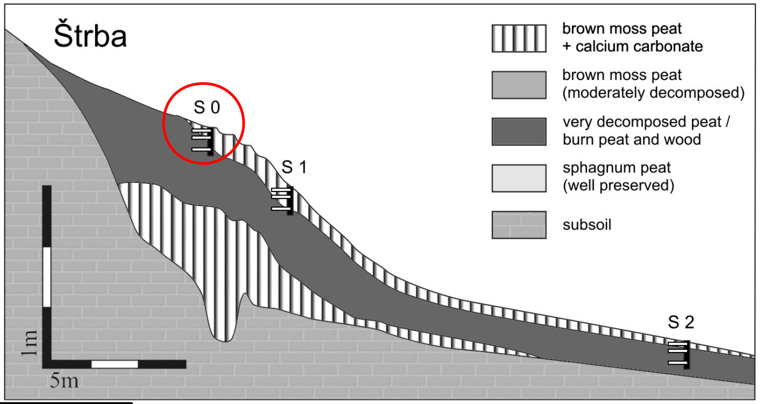
- SO_4^{2-} disappears
- H_2S max under pools, then disappears
- dissolved Fe appeares

C. S immobilization in upper part of the fen

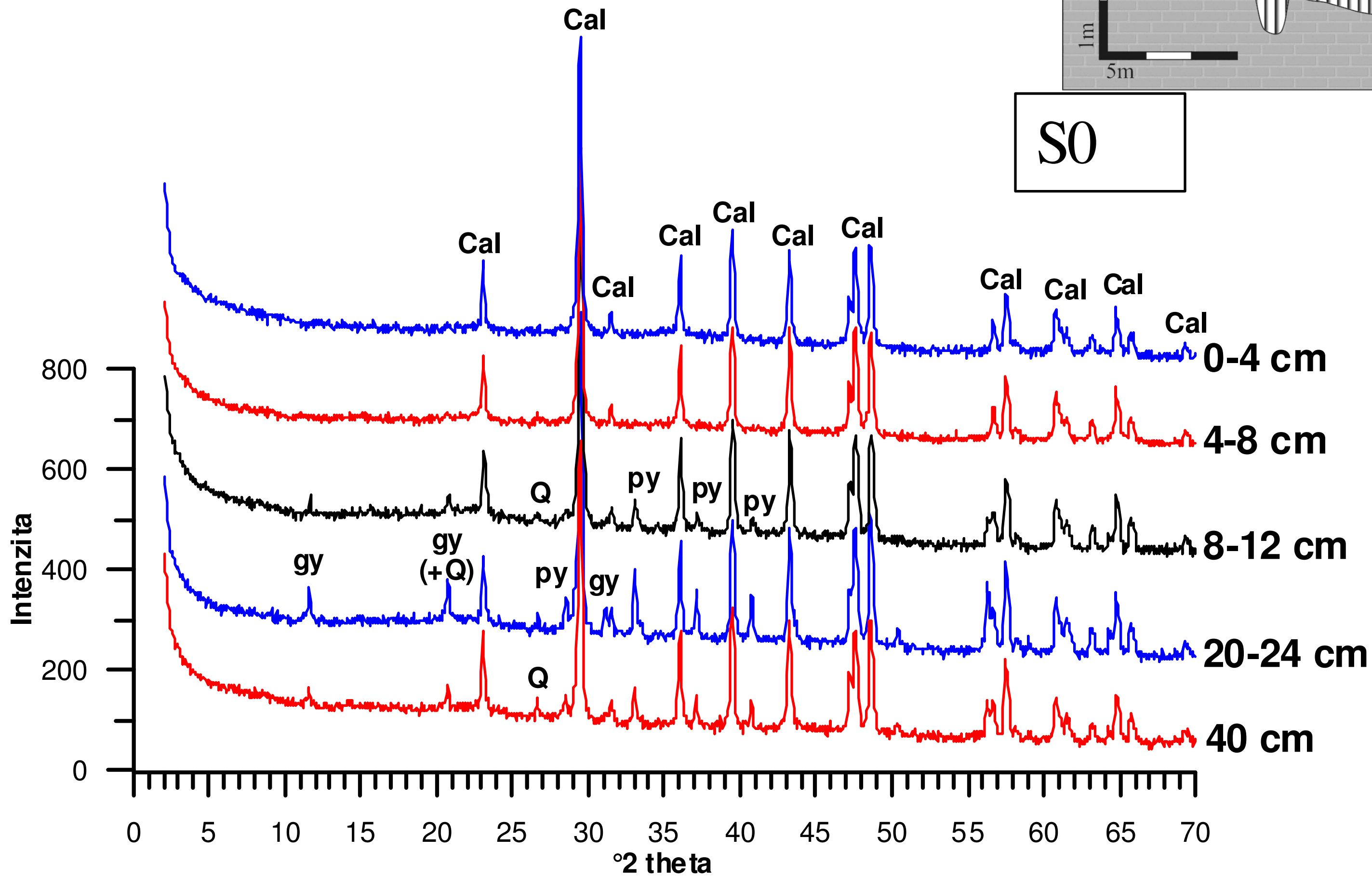
D. Consequent change of electron acceptor from SO_4^{2-} to Fe^{3+} in lower part

Which mineral phases are present ?

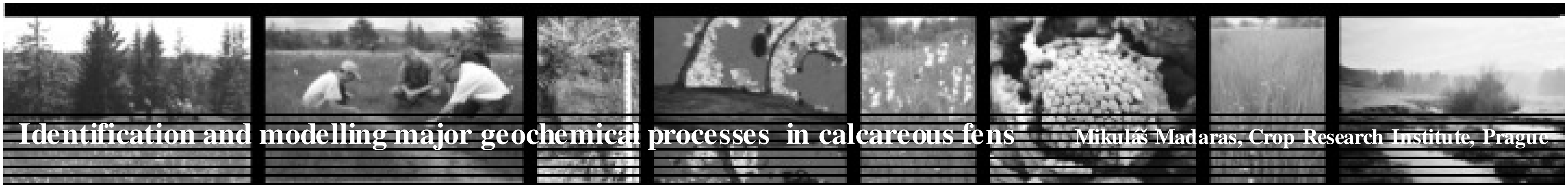
RTG diffraction patterns



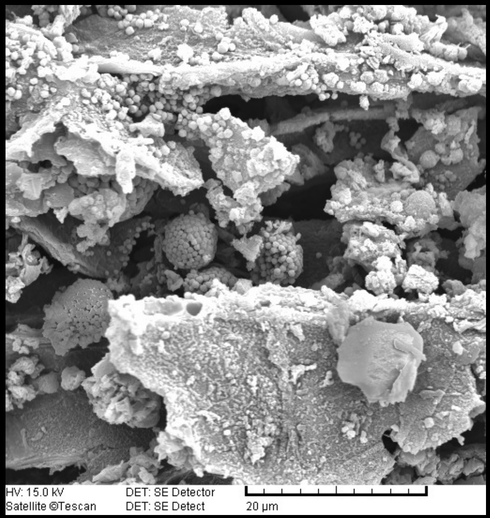
S0

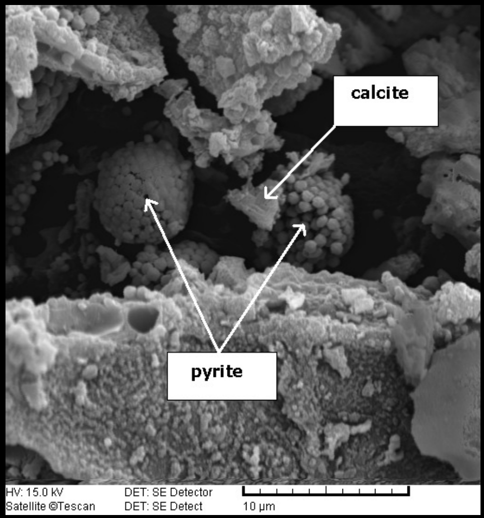


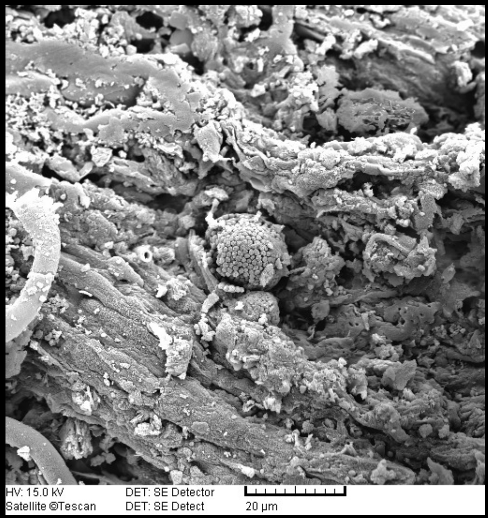
- $CaCO_3$
- FeS_2
- SiO_2
- $CaSO_4$



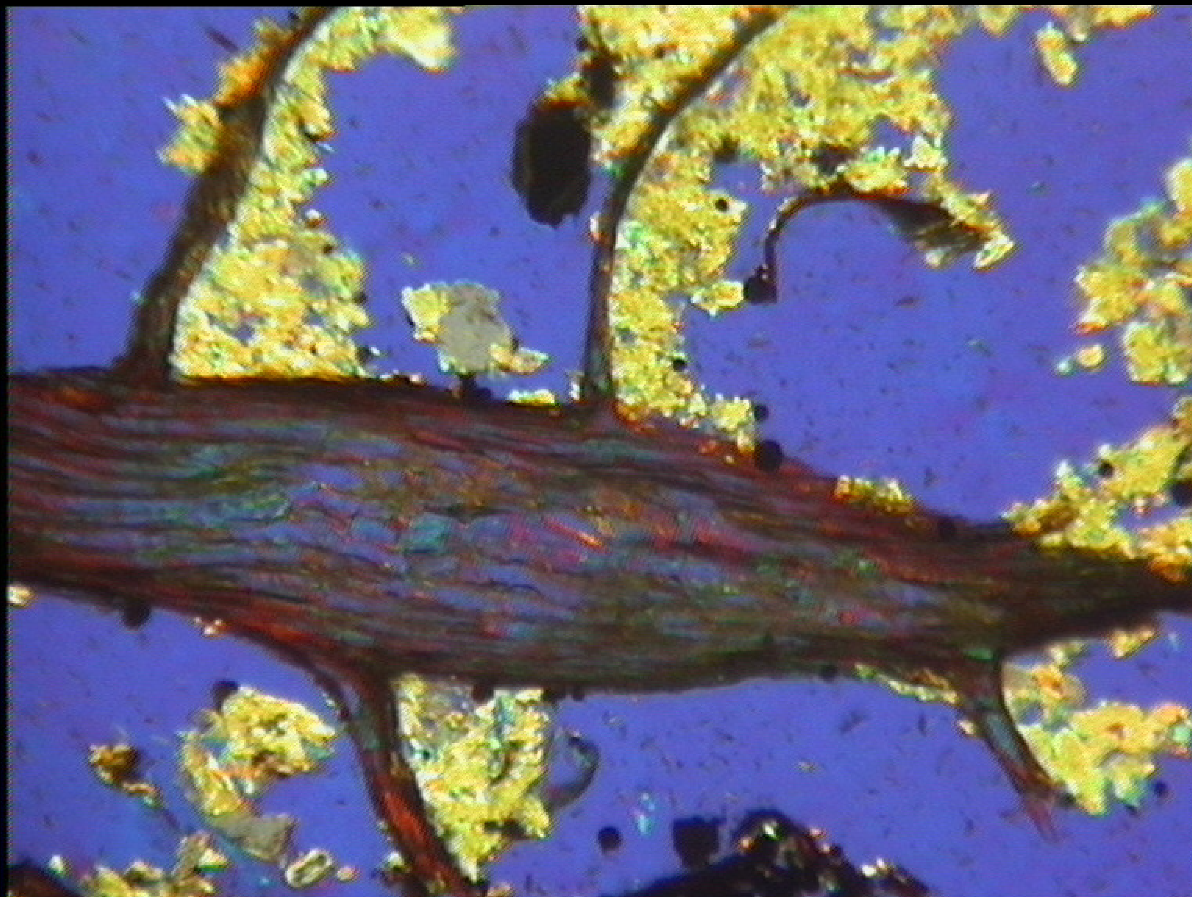
Scanning electron microscopy – pyrite framboid and calcite

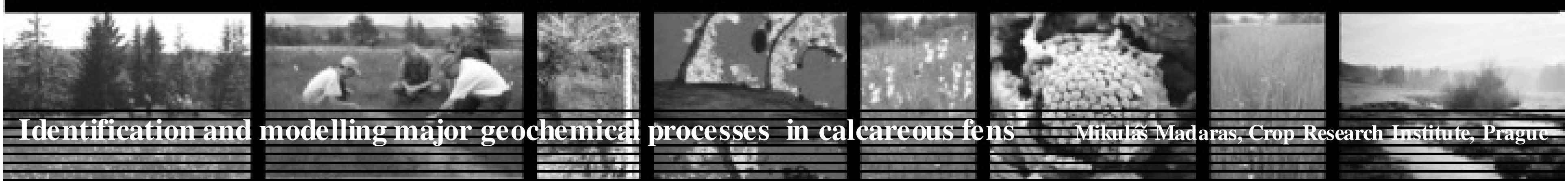






Thin section microscopy – fine-grained calcite and pyrite framboids



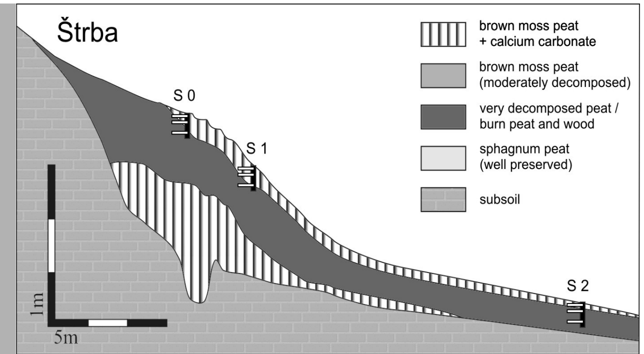


Gradients of peat composition

Vertical towards topsoil:

- topsoil carbonate and iron accumulation
- pyrite accumulation under water table

6. Pyrite / amorph. Fe interface at water table level
7. Carbonate precipitation and dissolution around the interface pyrite / Fe interface



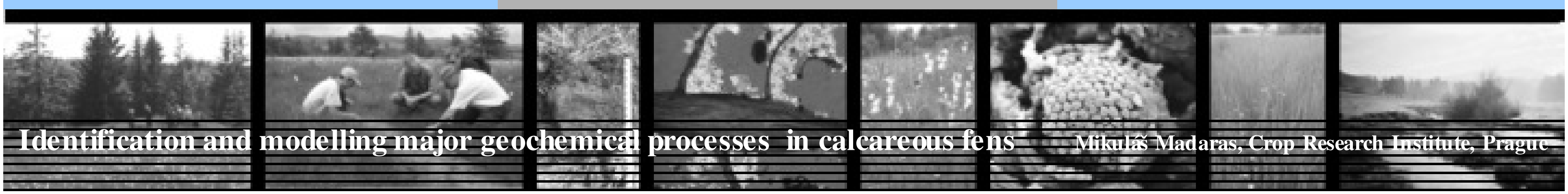
Horizontal

- Ca carbonate decreases
- Shift of pH buffering
- pyrite only in upper part of the fen
- amorphous Fe missing in the middle, S0 – topsoil peak, S2 – whole profile

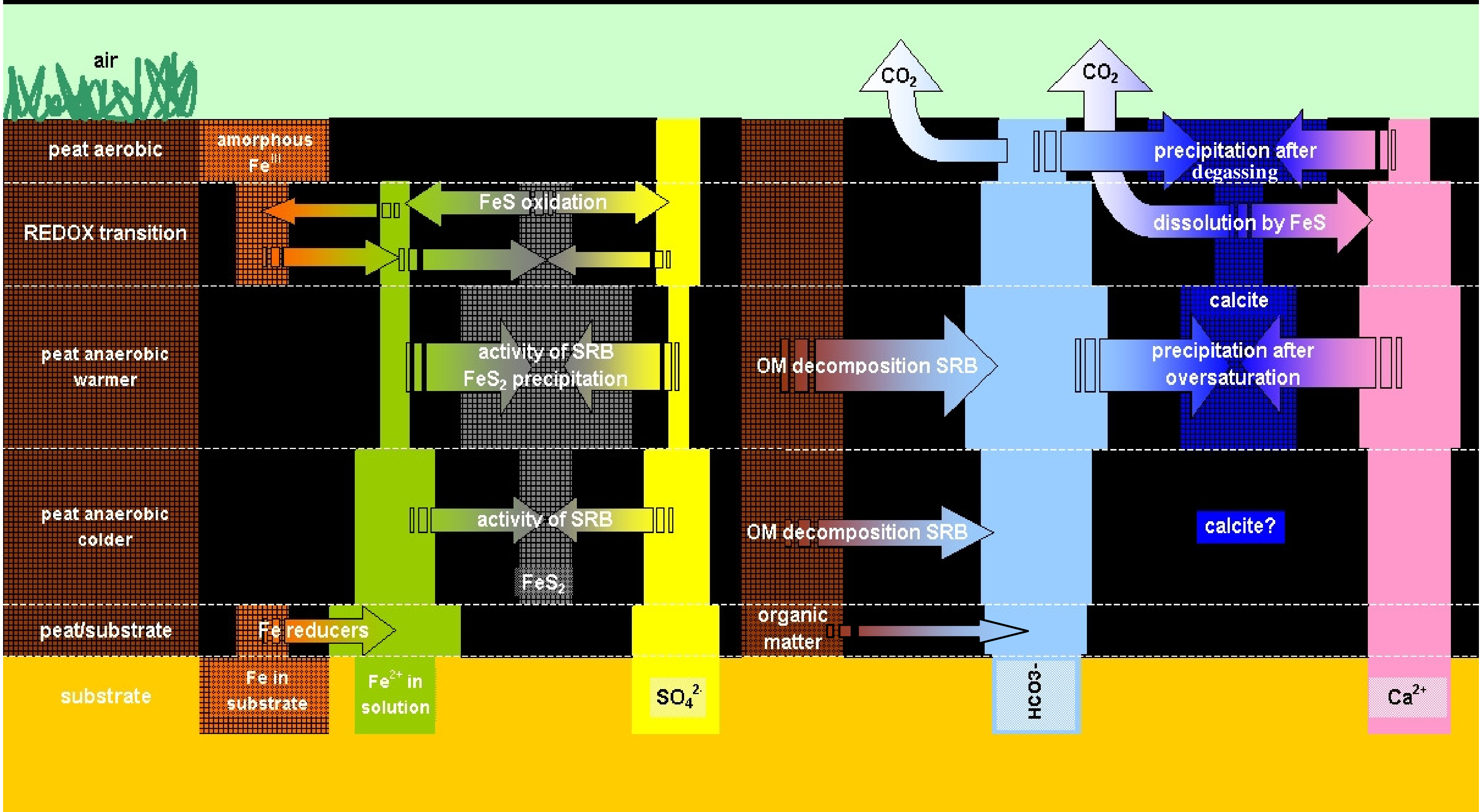
E. S fixation in FeS precipitates in upper part

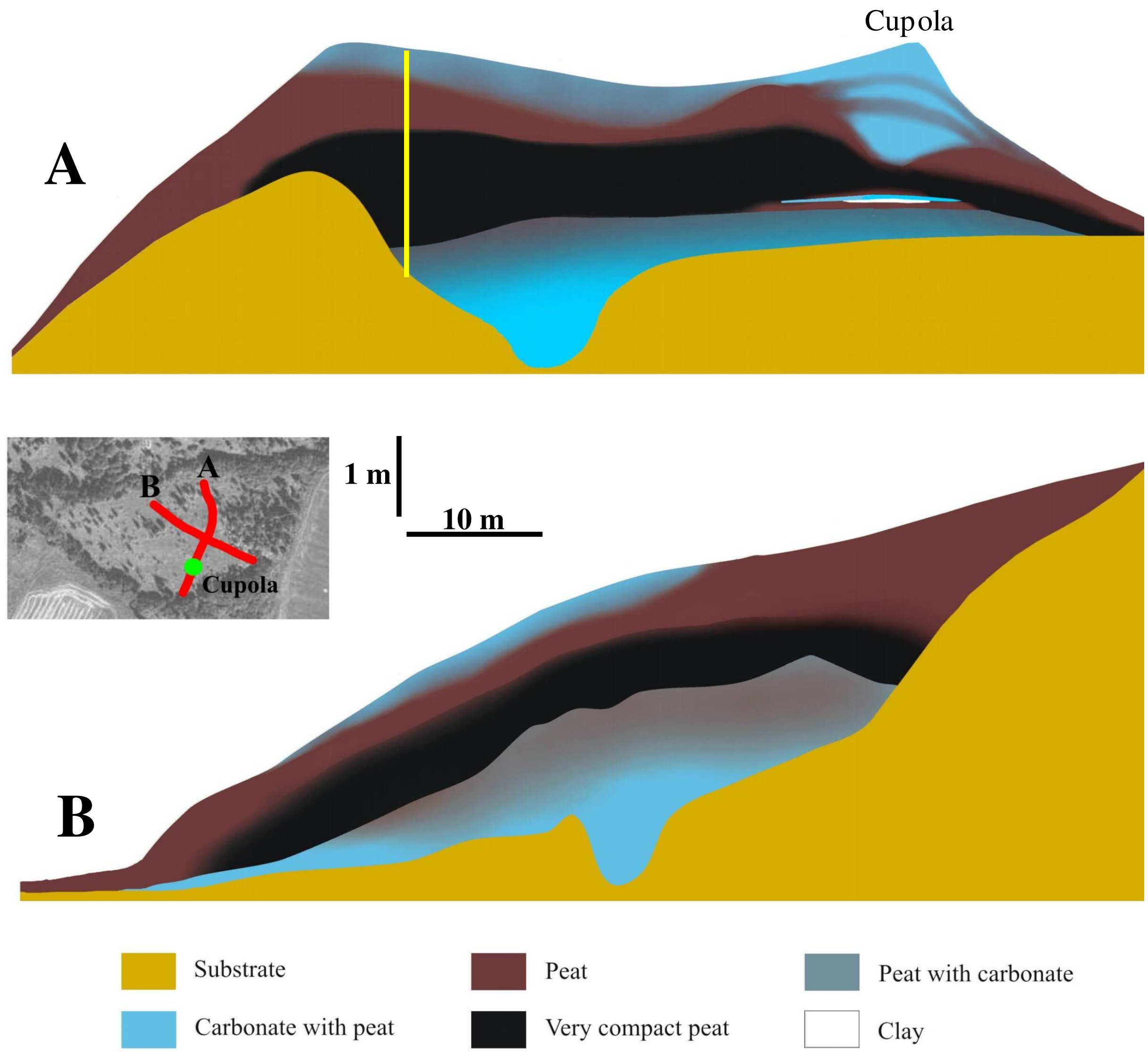
F. Iron fixation in S reducing environment

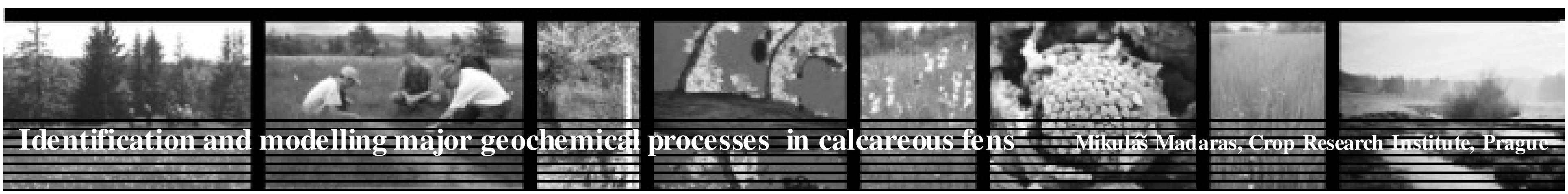
G. Shift in REDOX potential



Conceptual model of the fen chemistry




Cupola
A
B
A
B
Cupola
1 m
10 m
Substrate
Peat
Peat with carbonate
Carbonate with peat
Very compact peat
Clay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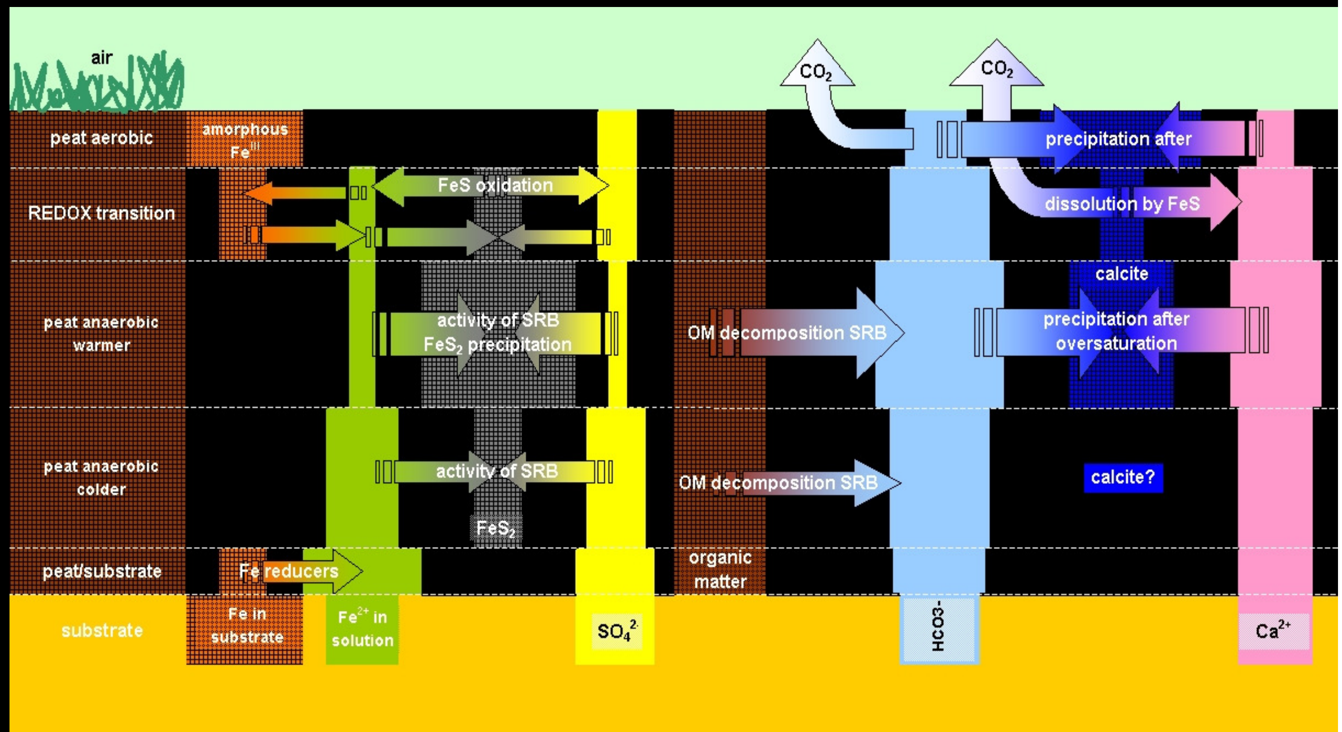
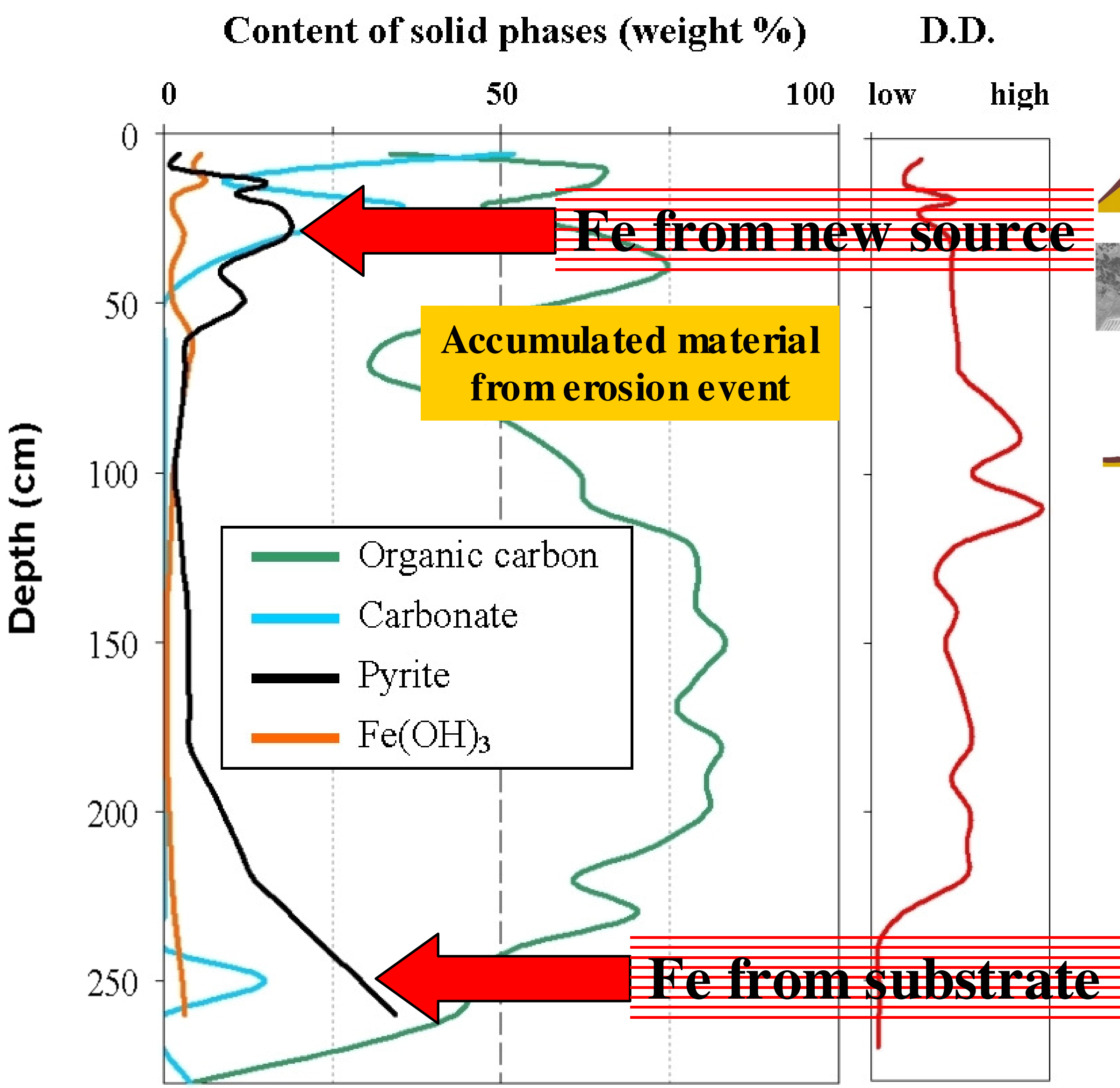
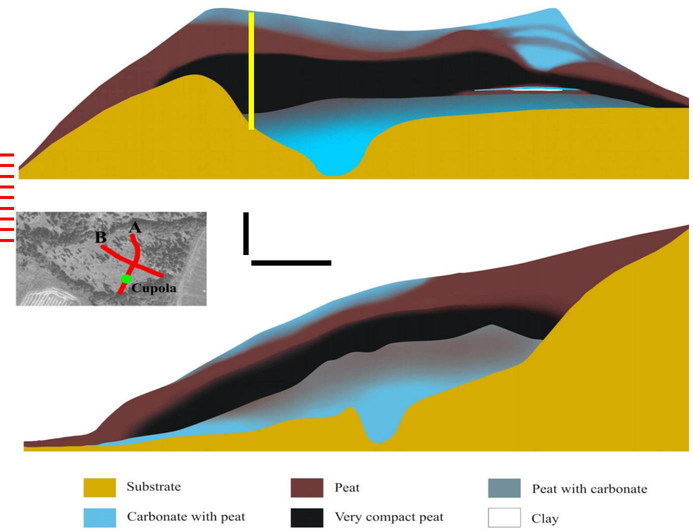
How can system change from $CaCO_3$ depositing to non-depositing and again to $CaCO_3$ depositing ?

1. Changes in the watershed (CO2 fluctuation)
2. Changes in S deposition („acid rains“)
3. Climatic-driven changes (fluctuating precipitation)
4. **Changes of Fe supply**







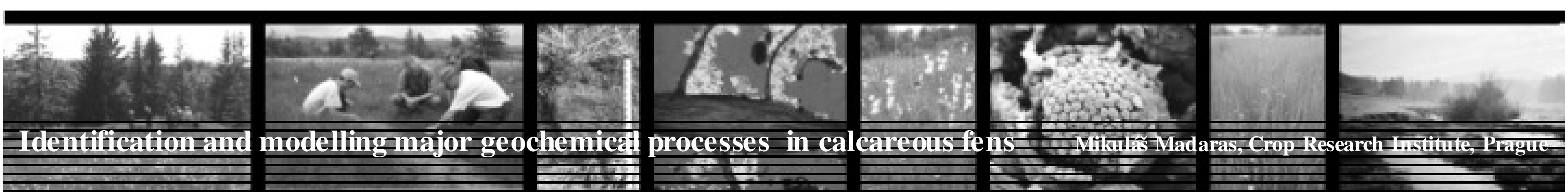
Effects of Fe^{III} addition:

Enhanced Fe reduction

⇒ FeS_2 precipitation,

⇒bicarbonate release

⇒ $CaCO_3$ precipitation



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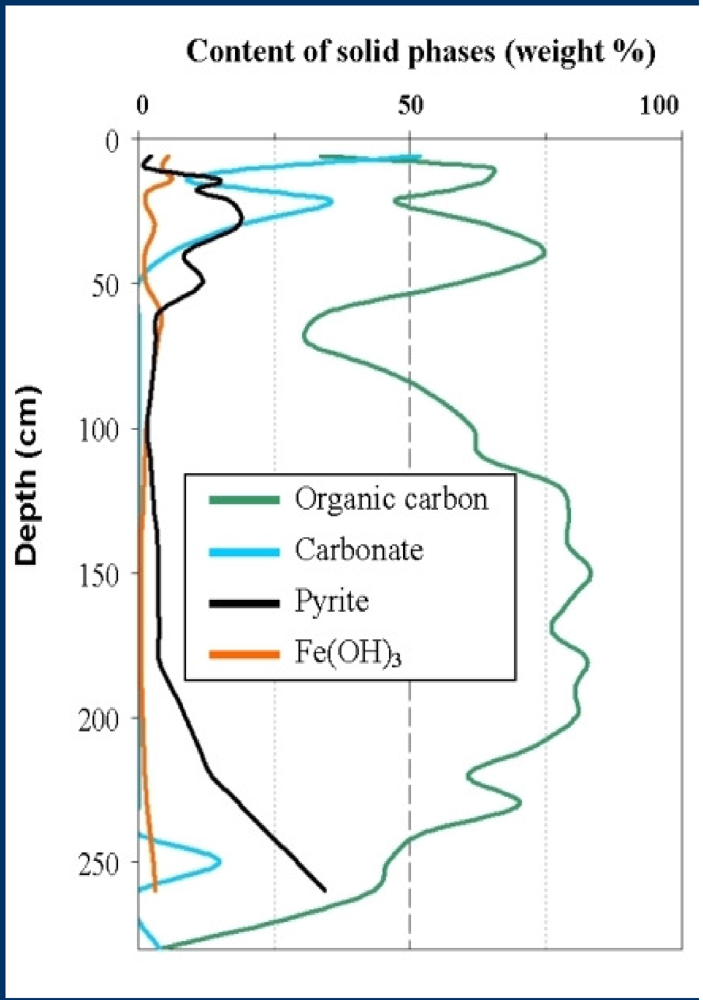
$CaCO_3$ topsoil precipitation – probably combined effects of change in land use (deforestation):



⇒ More water infiltrating in recharge area

⇒ More $CaCO_3$ leached from recharge area due to increased soil CO_2

⇒ New source of Fe (eroded soil) for pyrite

But where comes SO_4^{2-} from and when?

SO_4^{2-} still present or only last 40 years ?

Modelling an aeration of the profile S0

What did we model:

Decrease of water level

⇒Aeration of the reduced horizons

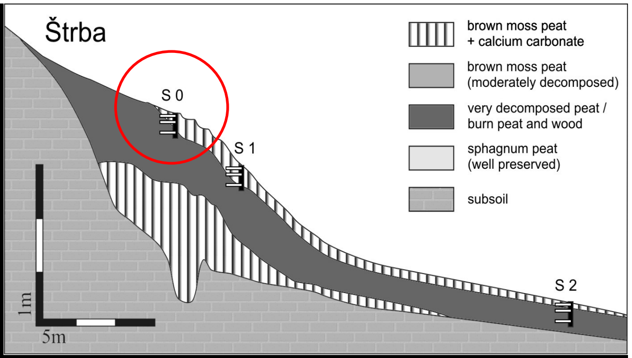
⇒Oxidation of the reduced compounds (FeS_2)

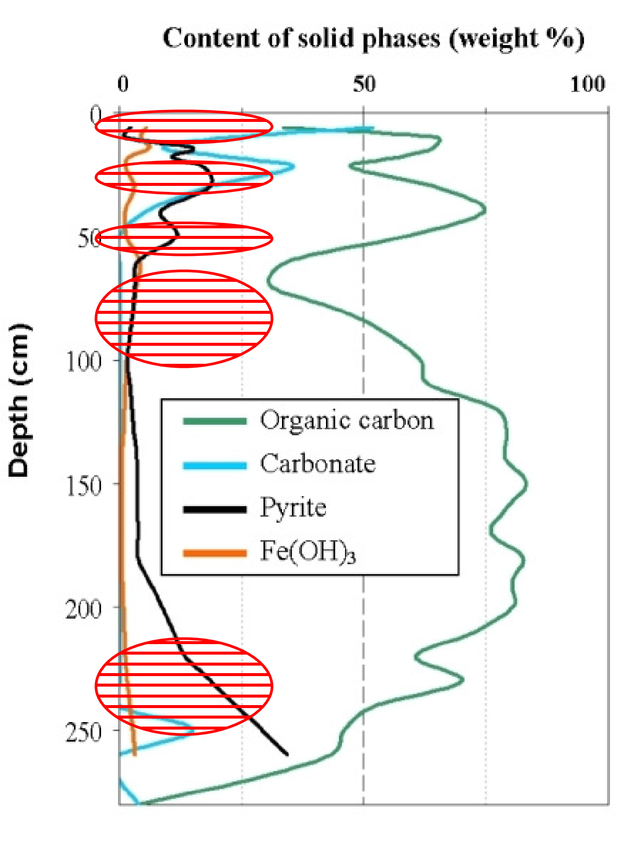
⇒Release of acidity (H_2SO_4)

⇒Acidity buffered by $CaCO_3$

model simplification:

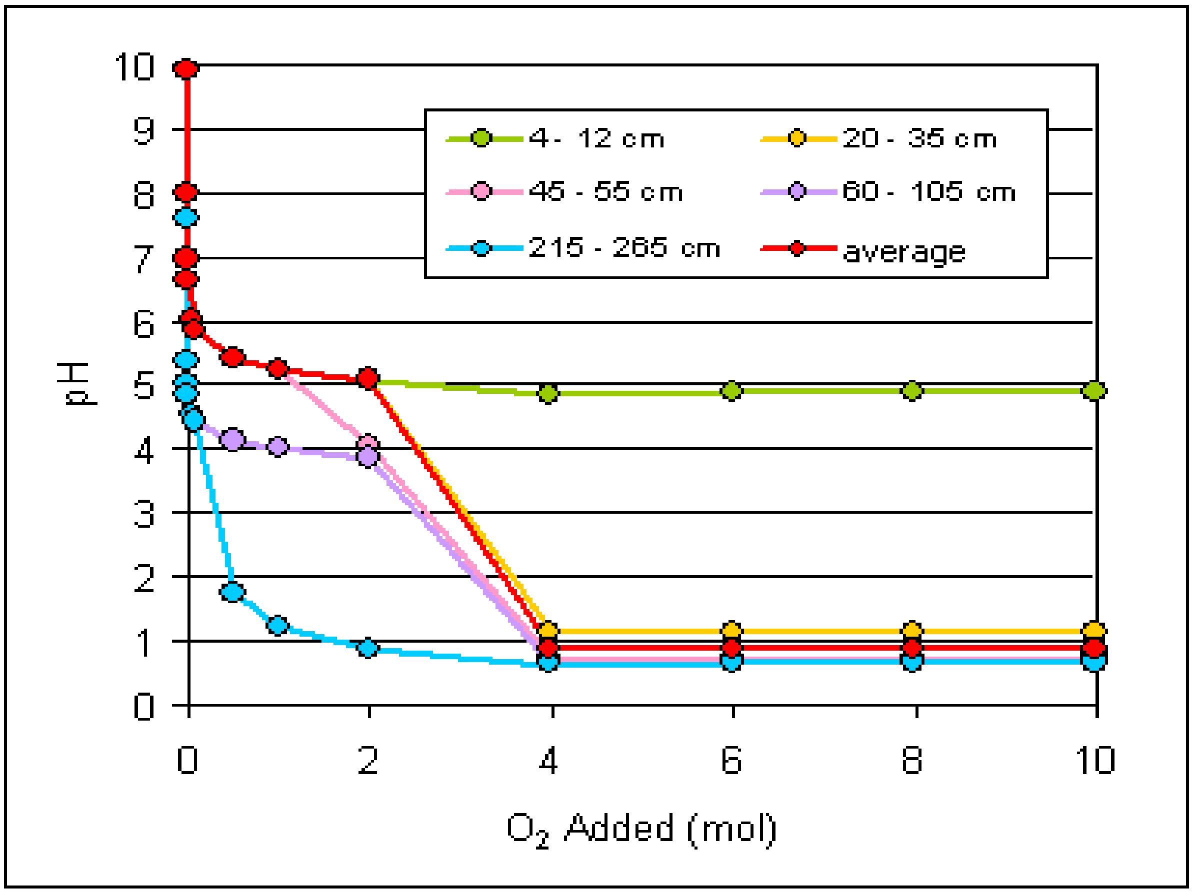
equilibration of mineral phases with O_2

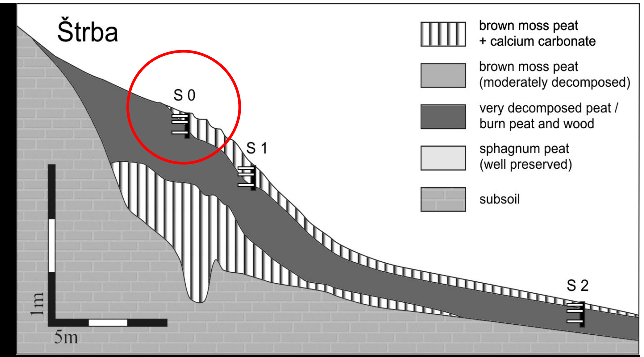




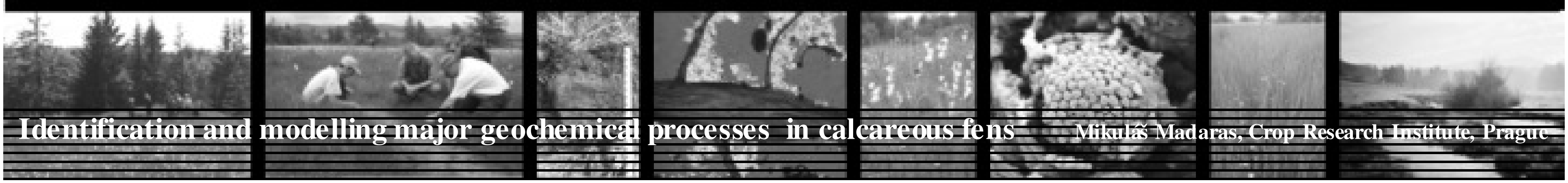
Modelling an aeration of the profile S0

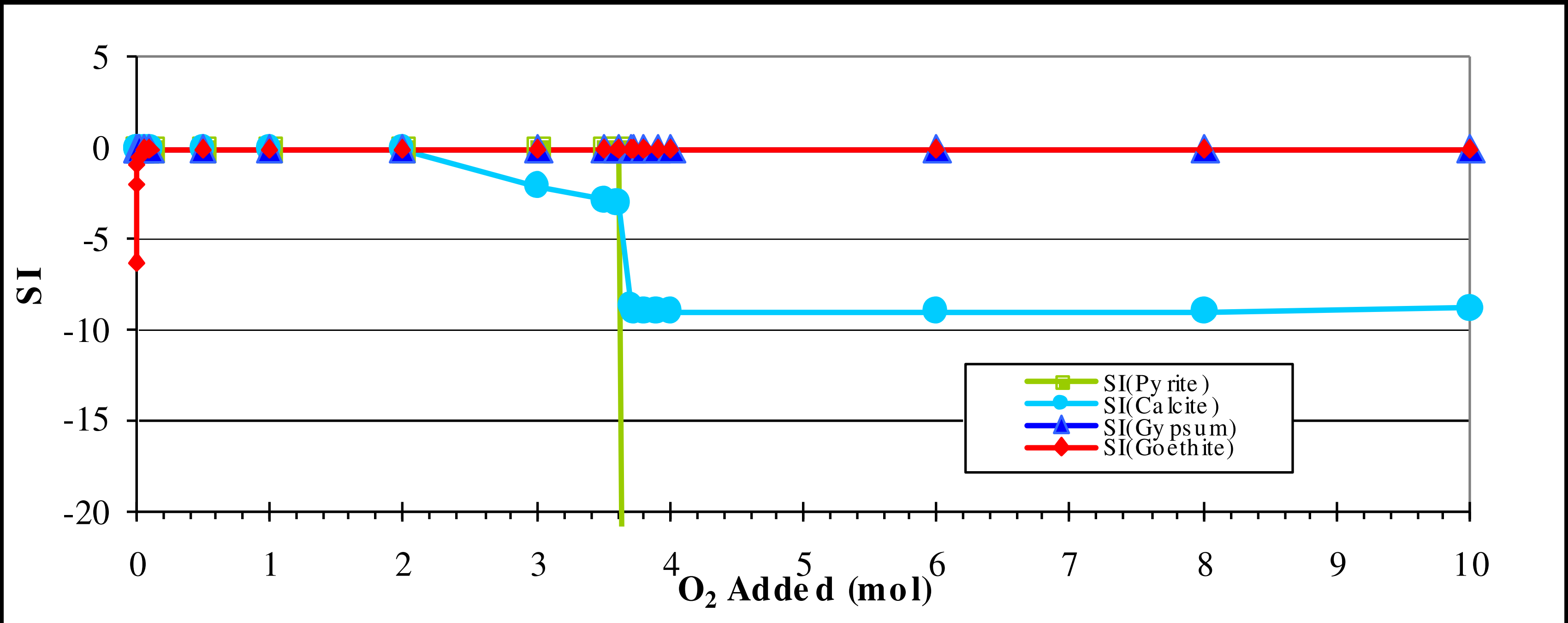
Results





Oxidation of the peat leads to severe acidification
(pH drop below 2)





The site S0 after drop of water level under 60 cm:

pH 2, Fe oxides, $CaSO_4$ (gypsum), high salinity.

Conclusions

1. Observed gradients of peat chemistry can be interpreted by several simple chemical processes

2. The material containing pyrite is sensitive to oxidation and acidification, which cannot be locally balanced by carbonates

3. Preservation of the water regime is crucial