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Geochemistry of the Scărişoara ice block chronosequence

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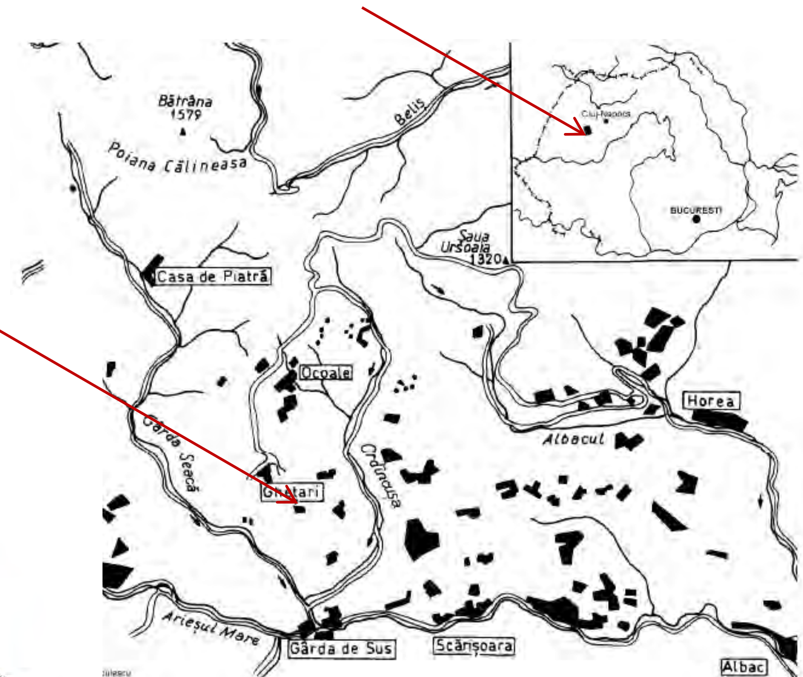
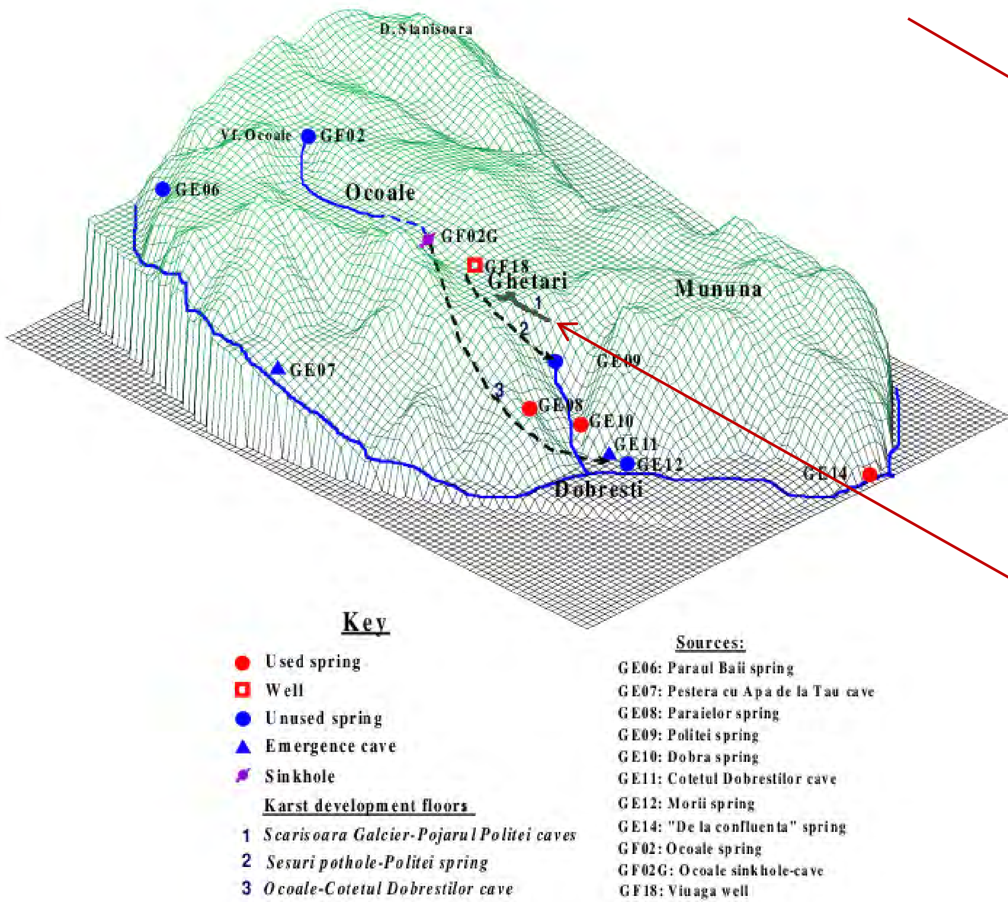
Scărişoara Ice Cave

Scarişoara Ice Cave is located in Bihor Mountains, Western Carpathians, in the North West part of Romania. The cave is situated at an altitude of 1,165 m above sea level, and holds one of the largest (100,000 m³) and oldest (>10,000-years old) perennial cave ice blocks in the world.

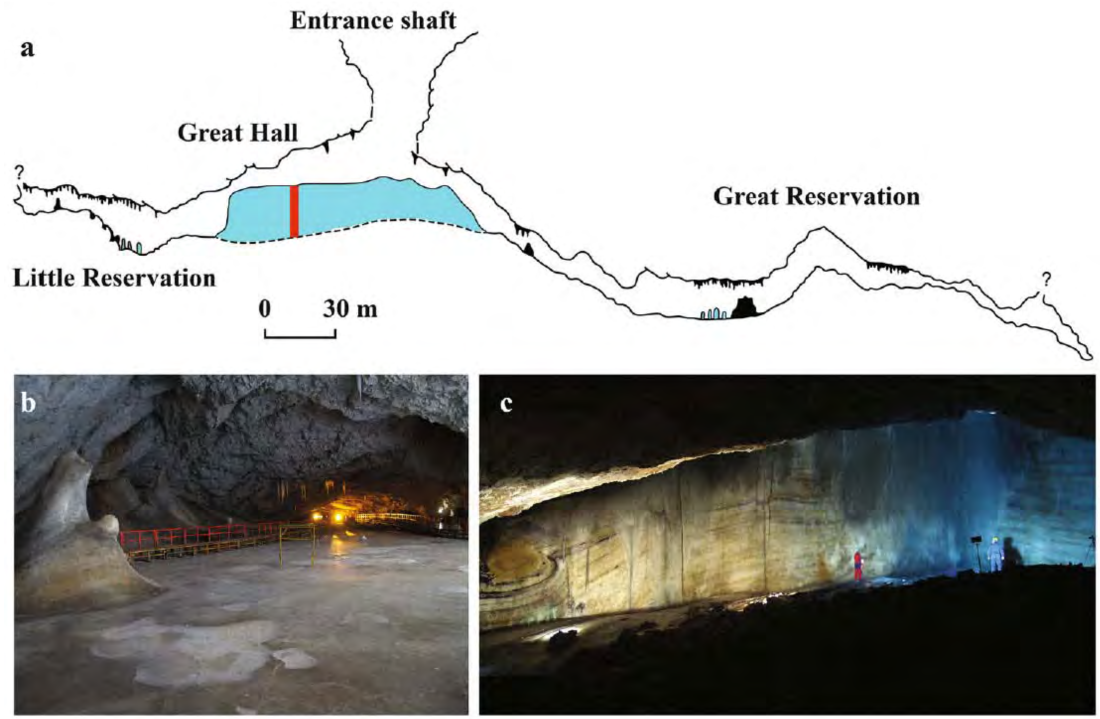




The cave belongs to a complex karst system, which has evolved, successively, over three distinct floors.

Method. Sampling and ^{14}C radiocarbon dating

Sampling was carried out by vertical drilling in the Great Hall area up to 25.33 m depth in the perennial ice block. The sampling was carried out under aseptic conditions, by flaming the auger for 5 seconds after spraying it with laboratory grade alcohol. The ice surface around the drilling hole was also flamed between each step to avoid contamination. 97 ice core fragments of variable lengths (10-60 cm) were recovered and transferred to sterile plastic bags in the presence of an open flame.



Scărișoara Ice Cave. (a) Cross-section of the cave. Red bar marks the position of the drilling site. (b) Surface of the ice block. (c) Side view of the ice block with visible layering. (Perşoiu *et al.*, 2017)

Visible organic matter containing ice samples (~1g) were collected from each core sample for ^{14}C dating using sterilized metallic tweezers.

Method. Chemical analysis

22 ice core samples were selected for microbial and chemical characterization. Melted ice from selected samples was filtered on 0.22-µm sterile MF-membranes (Merck Millipore, Germany) and stored at 4°C in 50-mL plastic conical tubes. The complete chemical analysis of all samples was conducted in the Hydrogeochemistry Laboratory (Speleochem) of the "Emil Racoviţă" Institute of Speleology, Bucharest.

Spectrophotometry for SO4. LAMBDA 25 UV/Vis Spectrophotometer, PerkinElmer.

Utilized analytical techniques:

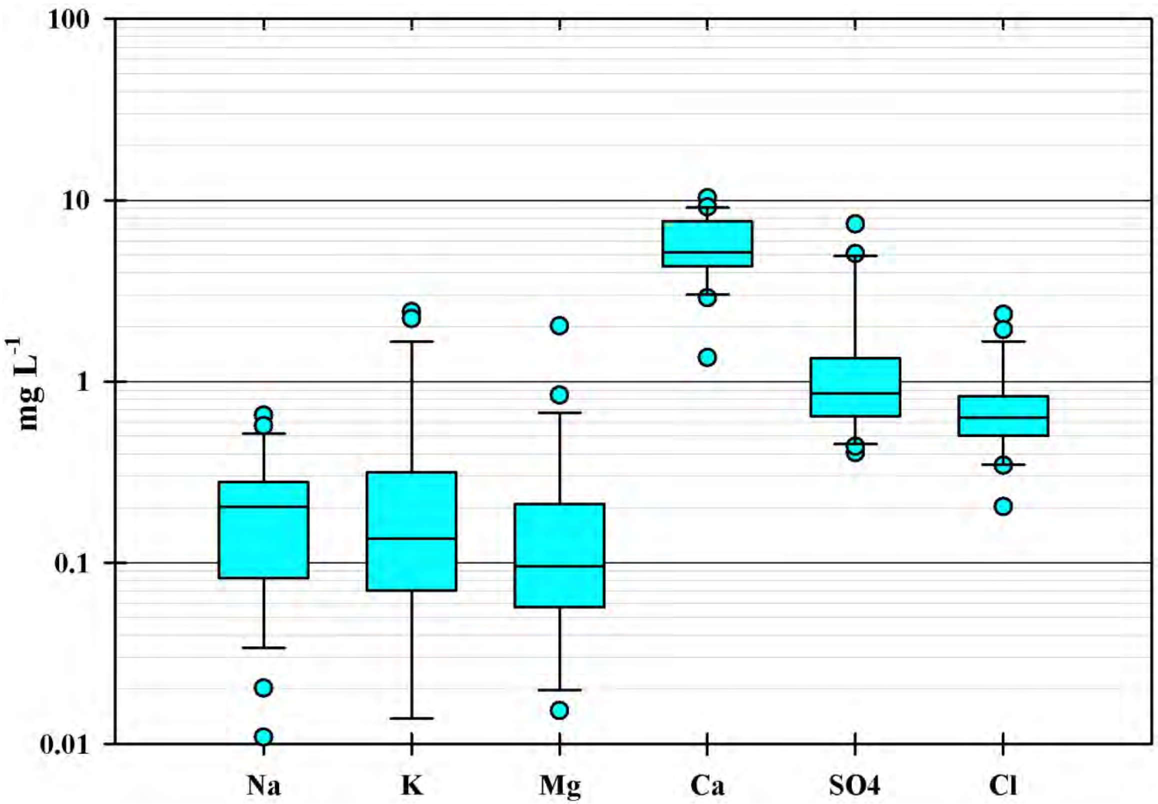
Catalytic Combustion for Dissolved Total Carbon (DTC) / Dissolved Inorganic Carbon (DIC) / Dissolved organic carbon (DOC). FORMACS^{HT} Total Organic Carbon Analyzer, Skalar Analytical B.V.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) for all major and trace components. NexION 300S ICP-MS, PerkinElmer.

Major components. Distribution

The ice deposit in Scărisoara cave is chemically similar to other perennial ice blocks preserved in caves (Kern *et al.*, 2011, Clausen *et al.*, 2006, Citterio *et al.*, 2004).

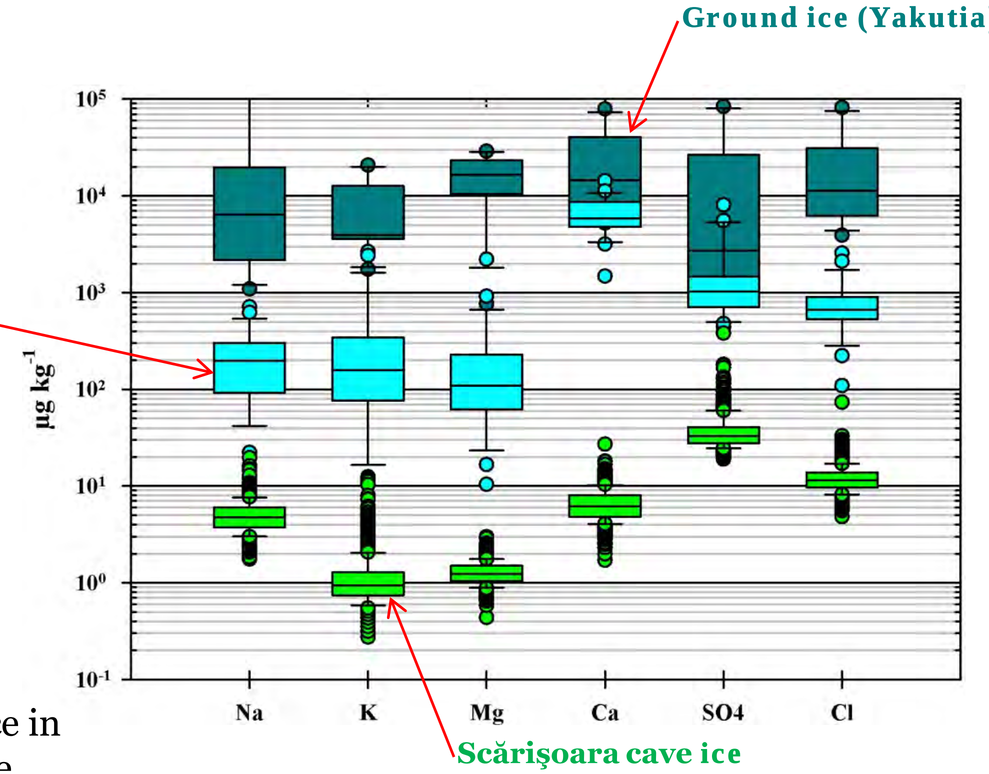
Calcium, obviously, dominates among the major components.

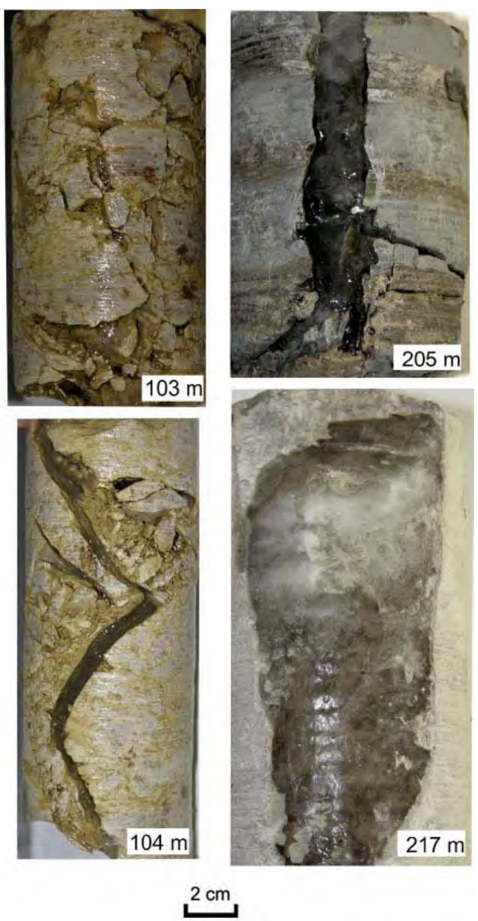


Major components. Comparisons

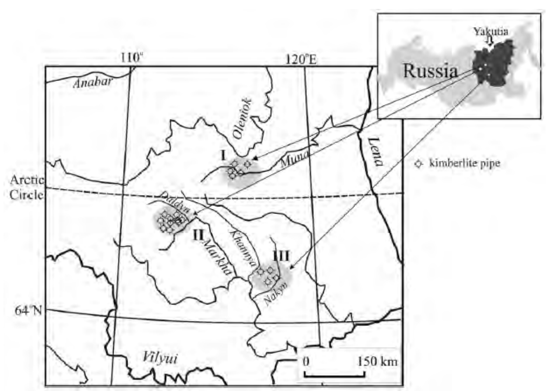
A comparison between the Scărisoara cave ice chemical composition, and:

– **Ice core GISP2 Greenland**: it originates exclusively in meteoric water freezing;





– **Ground ice, Yakutia/Russia**: ice in close contact with the adjacent rock (Alexeev *et al.*, 2016)



The generation of the Scărişoara ice deposit

The ice block development is governed by the annual freezing/melting cycles.

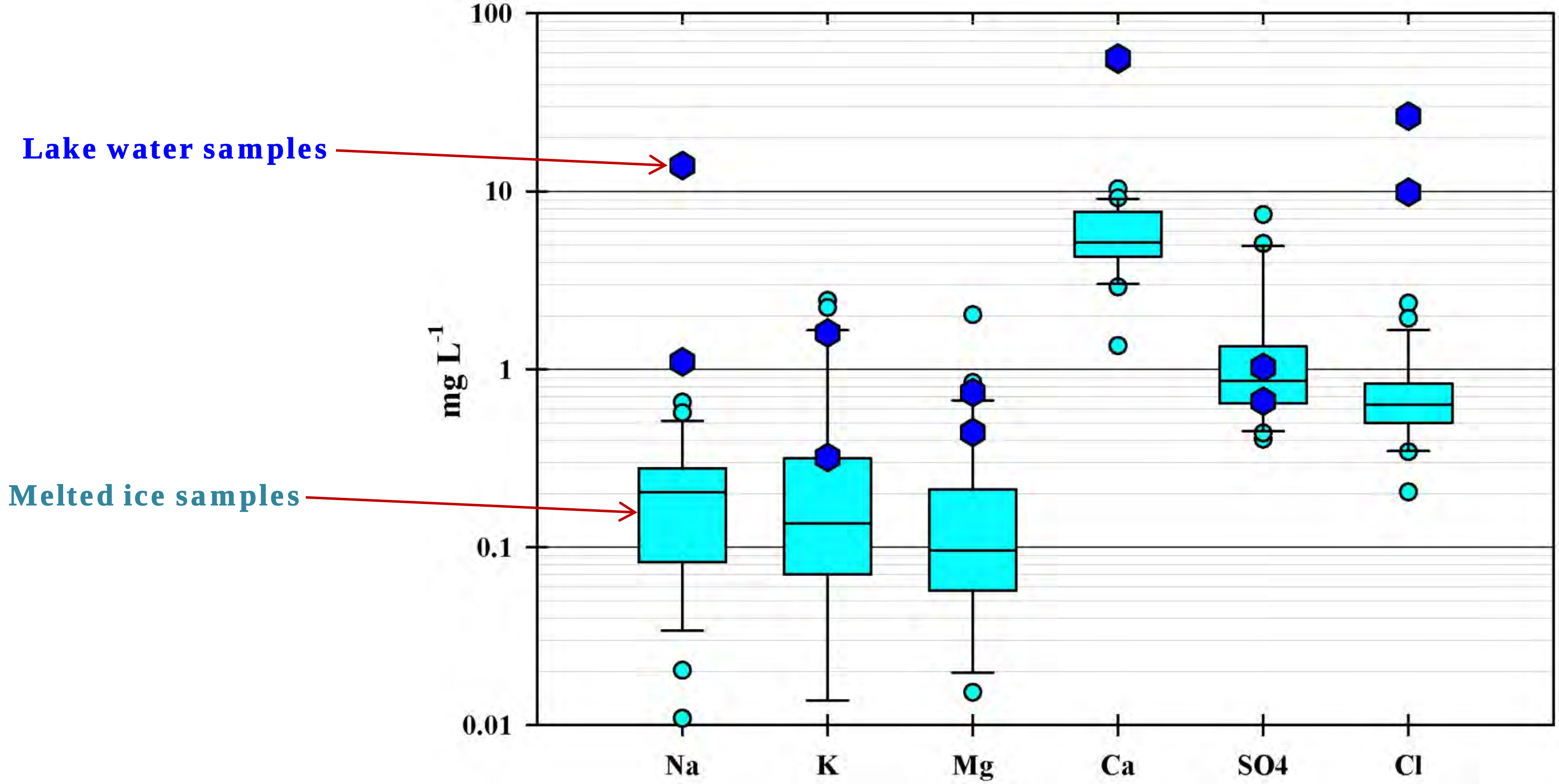
During the cold season,
- – meteoric water;
- – drip water;
- – evapocondensation-derived water (?)

contribute to the development of the Scărişoara ice block.

During the warm season, the shallow upper section of the block melts, and that meltwater accumulates in a lake which subsequently, during the cold season, freezes again.

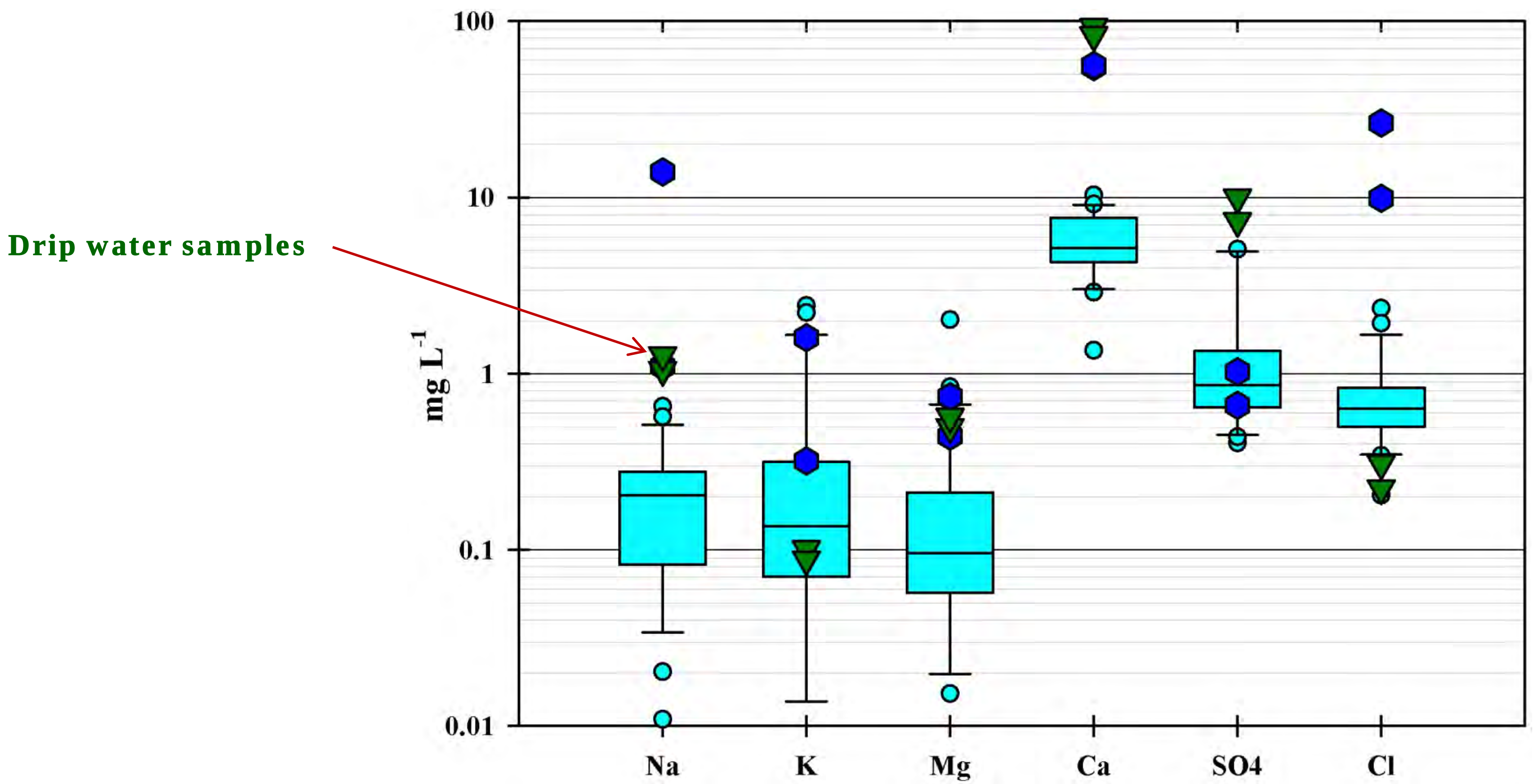
The generation of the Scărişoara ice deposit. Lake water

In the water of the lake developed on the ice block during the warm season (2016), most major components occur in larger concentrations, as compared to those found in the ice. The only exception is the SO_4 anion.
The distribution of the concentrations measured in the ice refers to the entire core, covering the complete age-succession.



The generation of the Scărişoara ice deposit. Drip water

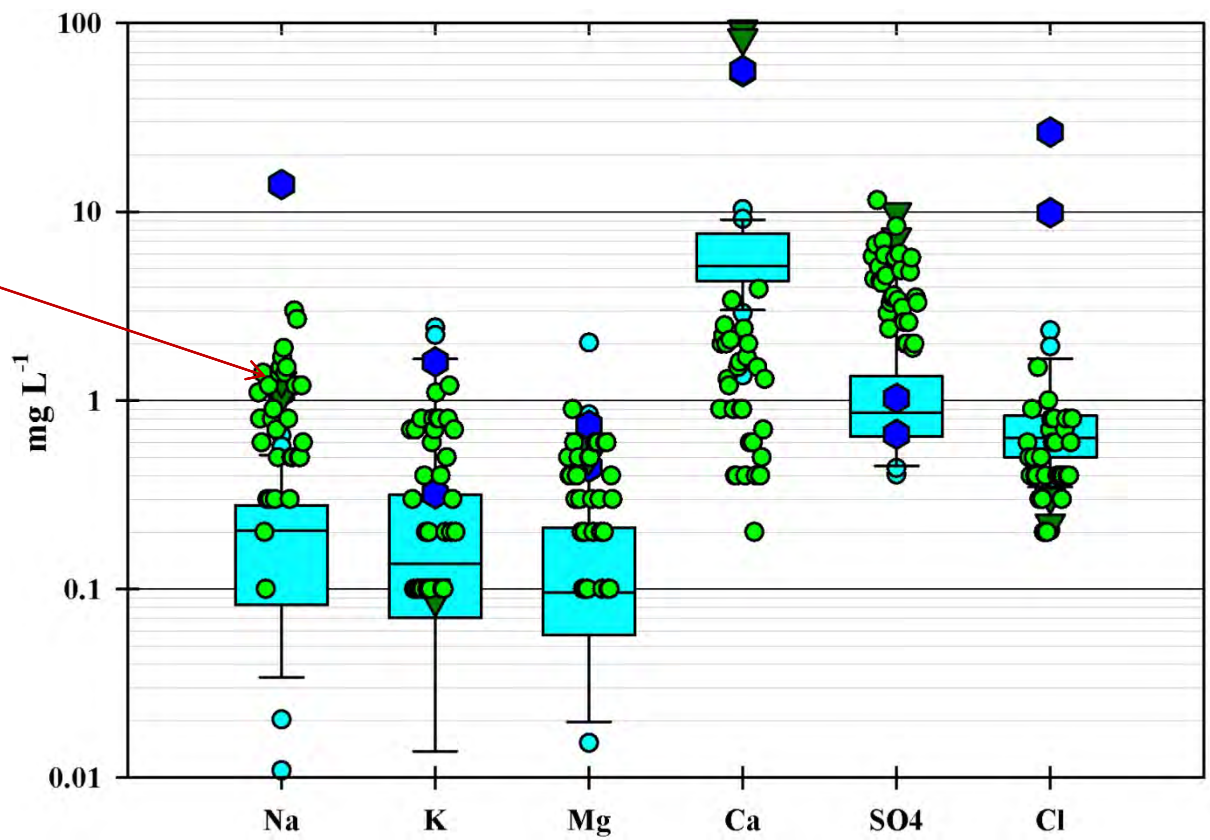
The present-day drip water is significantly more concentrated in Ca, Na, Mg and SO_4, as compared to the corresponding element-concentrations determined in the ice core. Alternatively, the K and Cl (as chloride) concentrations in the drip water are lower than the corresponding average concentrations in the ice core.



The generation of the Scărişoara ice deposit. Rain water

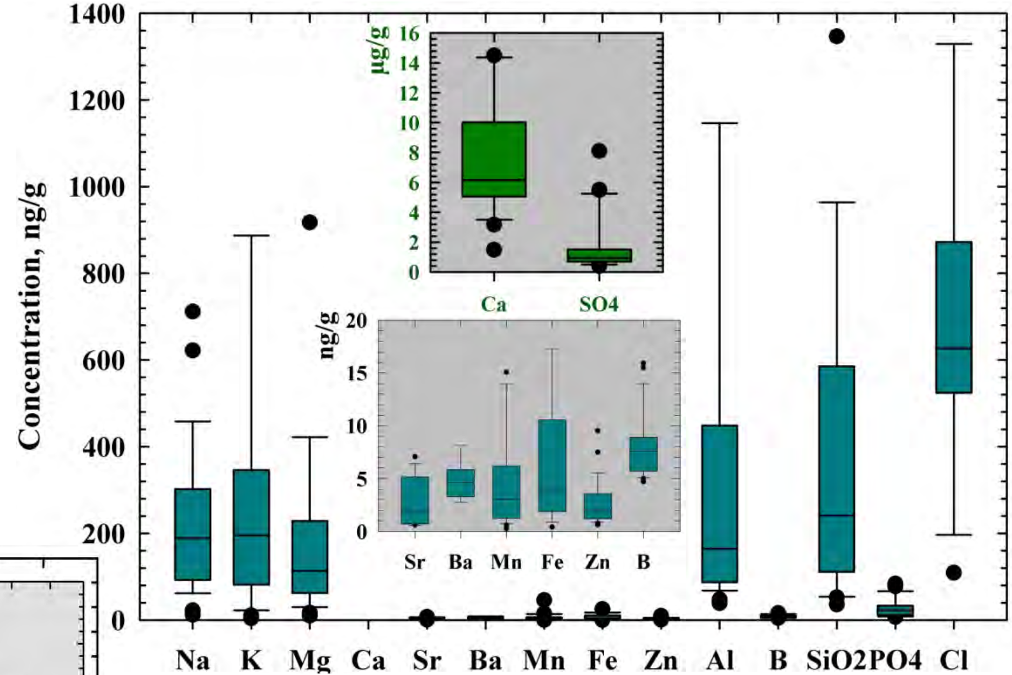
As compared to the ice core, present-day meteoric water (determinations performed in the year 2001 – Apuseni Project) displays similar concentrations of chloride, slightly larger concentrations of Na, K, Mg and SO_4, while Ca occur in far smaller concentrations.

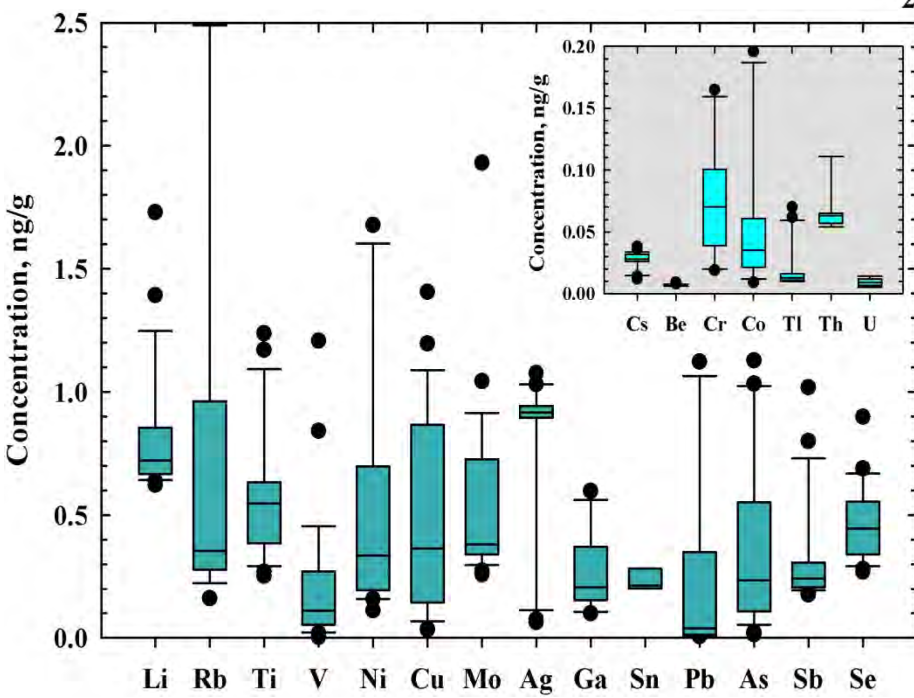
Meteoric water samples



Minor and trace constituents

Aluminum and silicon, which habitually are minor constituents in natural waters, occur in the ice core in large concentrations, similar to those of Na, K, Mg or Cl.
Sr, Ba, Mn or Fe in the ice core were probably uptaken ensuing to the limestone substratum dissolution by the drip water.

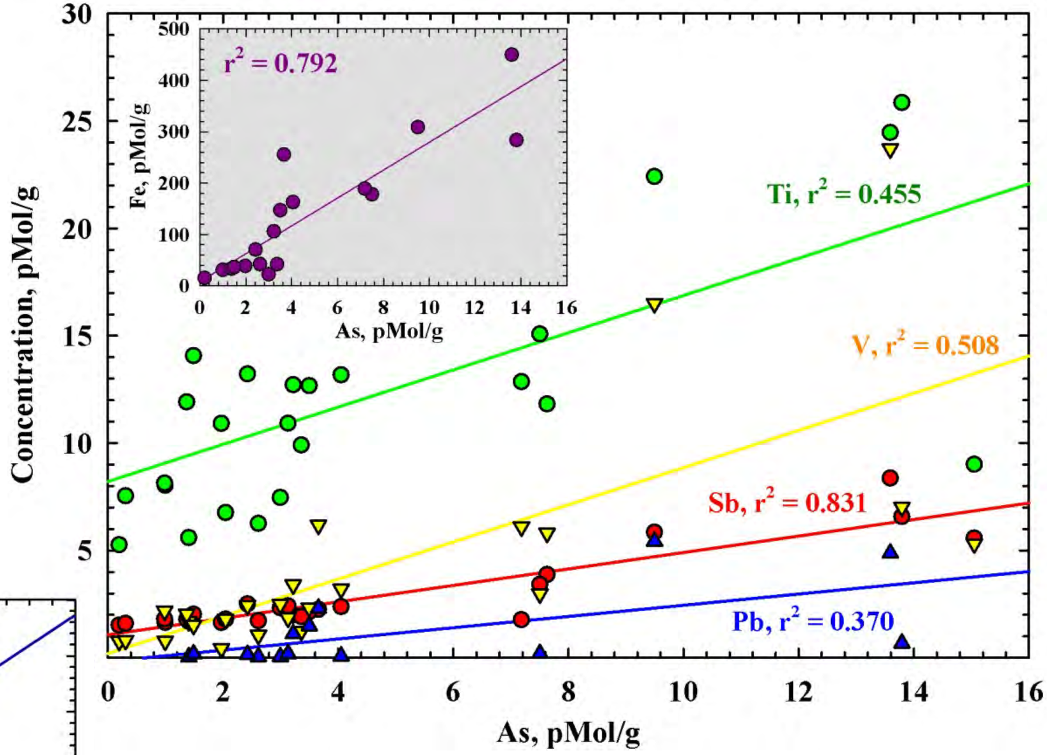


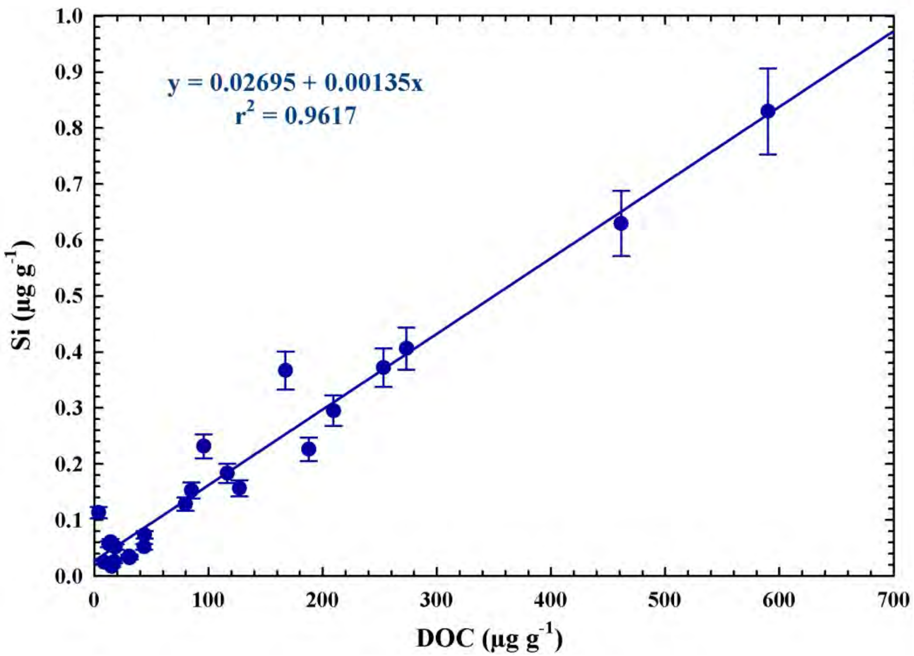


For most trace elements detected in the ice core, it is difficult to trace their origin. A possible source might be the rock substratum dissolution, but dust/aerosol particles conveyed by meteoric water are a similarly plausible source.

Minor and trace constituents

A series of correlations could be outlined between the concentrations of various constituents detected in the ice core. For instance, the arsen concentrations are correlated with those of antimony and iron, a circumstance which suggests a common origin.



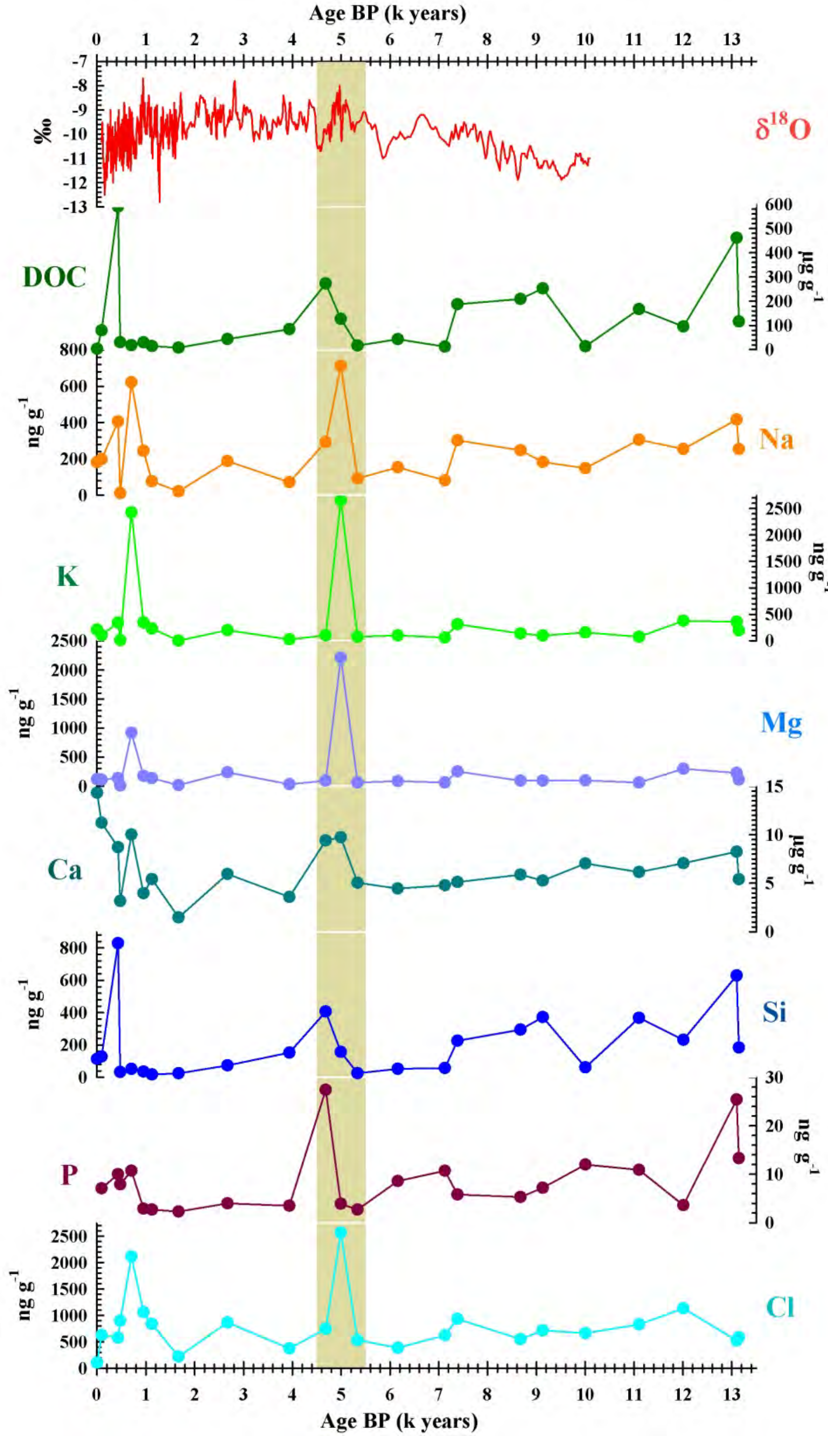


The concentrations of Si and of Dissolved Organic Carbon are tightly correlated. This indicates that silicon detected in the ice originates mainly in vegetal debris trapped in the ice block.

Cronosequence. Major components

The concentration of various chemical constituents detected in the Scărişoara ice core fluctuated in time. It is difficult to explain some of these fluctuations, for instance those occurred over the last 2000 years: they might be caused either by climate changes, or by geochemical impacts; moreover, the small number of analyzed samples corresponding to that epoch does not favor rigorous interpretations.

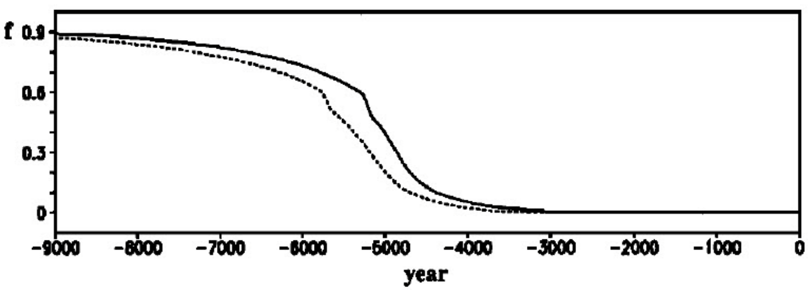
In contrast, the conspicuous concentration peak displayed by the major chemical components for the time-interval 4400-5600 years Before Present (BP) is undoubtedly due to a sudden climate change. Isotopic measurements published by Perşoiu *et al*. (2017) indicate that a warmer and drier climate was installed then. And correspondingly, in terms of water chemistry, a reduction of the liquid fraction supply would results in higher concentrations of the dissolved components.



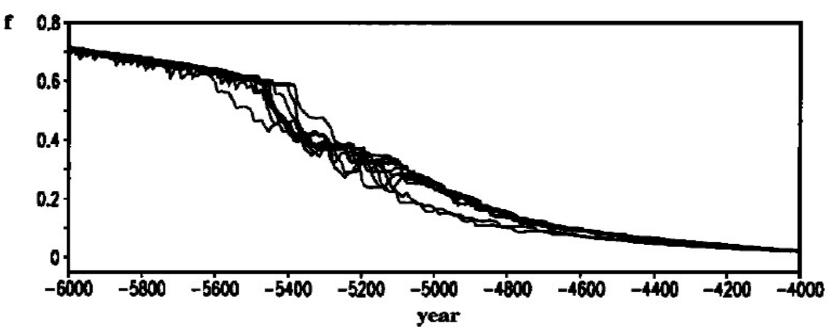
Cronosequence. Major components

The climate change occurred 5000 ago has been highlighted by several proxies. Worth noticing are especially the isotopic measurements conducted on speleothems from Soreq cave, in Israel (Bar-Matthews *et al.*, 1999).

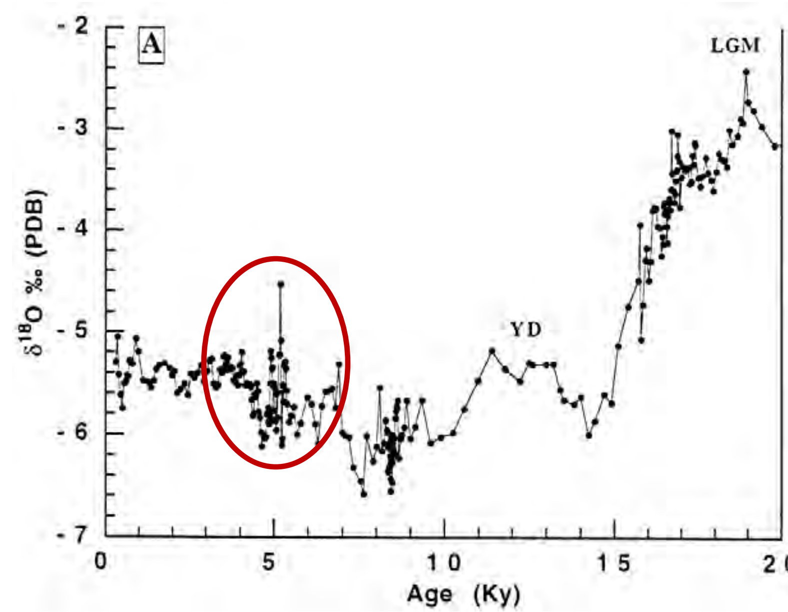
The change undoubtedly mirrors the fact that the southern part of the Mediterranean realm became dominated by a warm and dry climate - a consequence of which was Sahara turning into a desert.

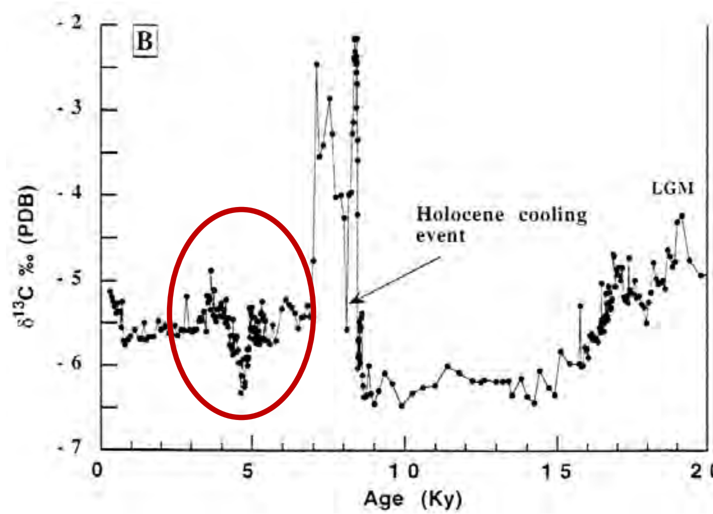


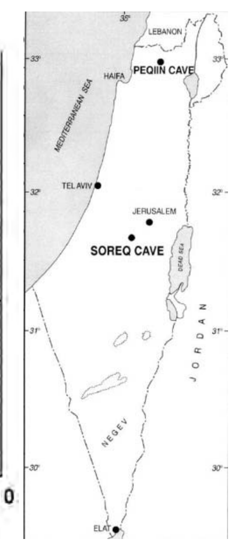
Fraction of vegetation cover in the Sahara region simulated by using the atmosphere-vegetation model (Claussen *et al.*, 1999).



Fraction of vegetation cover in the Sahara as obtained from an ensemble of 10 simulations with the fully coupled model (Claussen *et al.*, 1999).

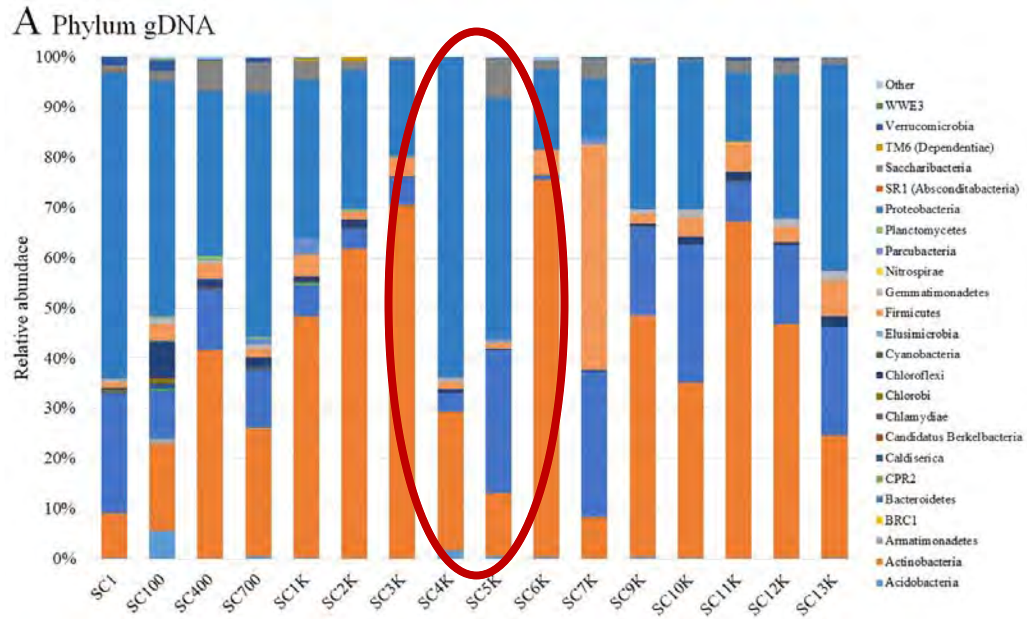




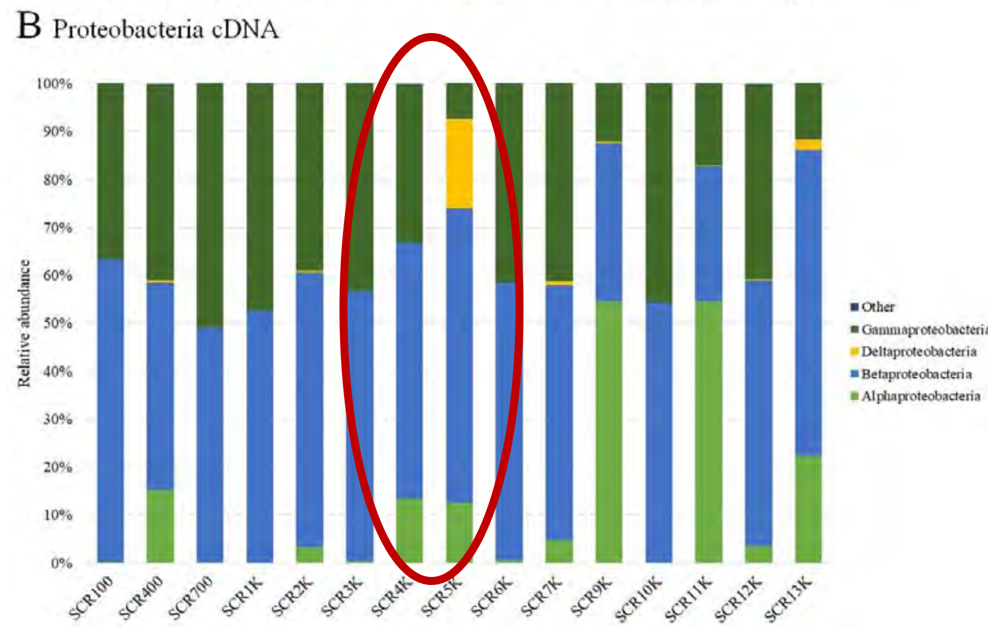


Cronosequence. Microbiology

The same climate changes are also mirrored by the bacterial community structure variability (Paun *et al.*, 2019).



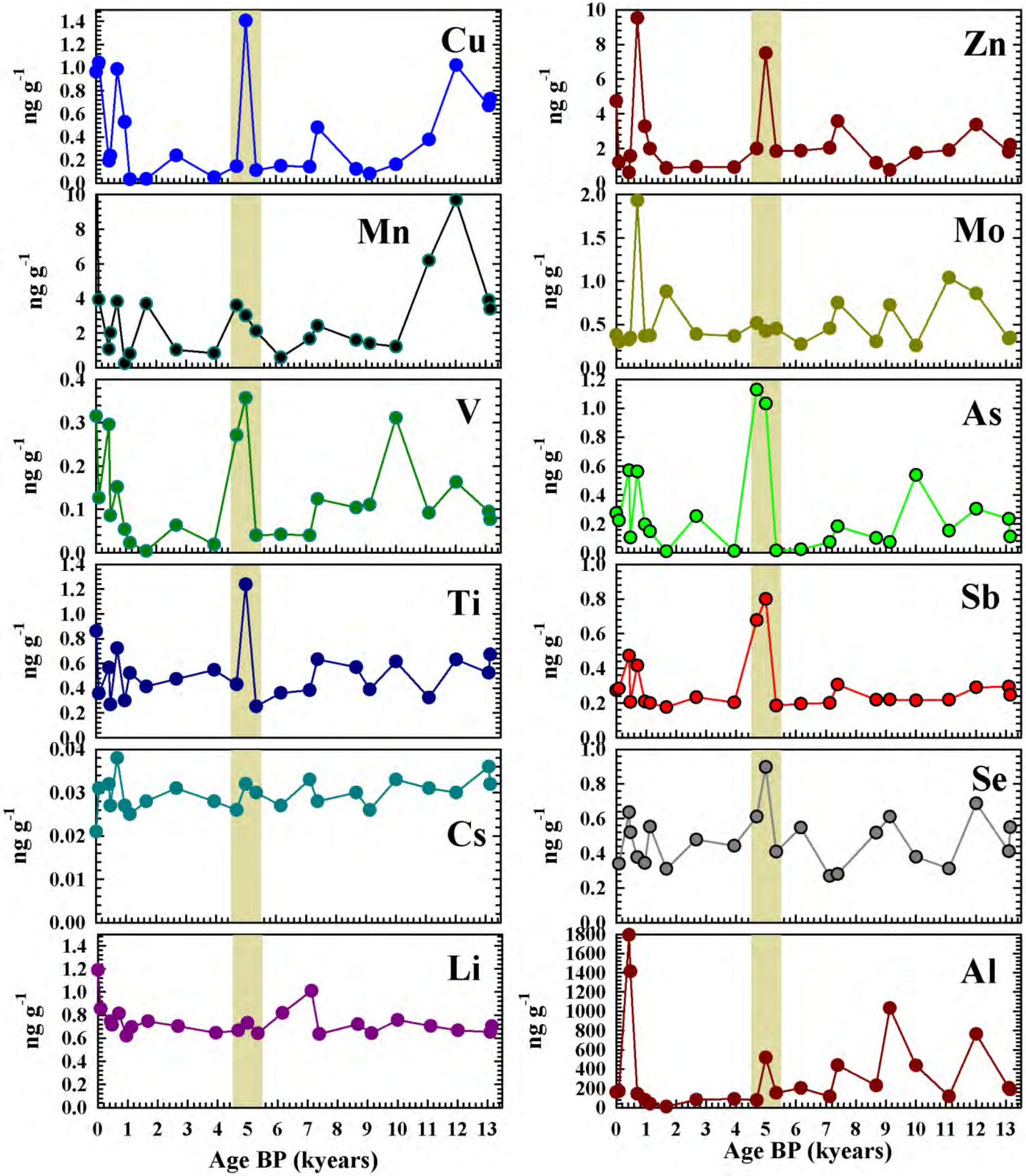
Relative abundance of bacterial taxa in 13,000 years old cave ice chronosequence at Phylum level for total bacteria (gDNA).



Relative abundance of bacterial taxa in 13,000 years old cave ice chronosequence at Phylum level for total bacteria (gDNA).

Cronosequence. Trace elements

A series of trace elements display the same time-evolution as the major components, while other trace elements do not.



Conclusions

- The chemical composition of the ice accumulation in Scărişoara cave differs significantly from that of polar ice sheets, or of continental glaciers.

- The ice in Scărişoara is generated, to a large extent, by meteoric water (rain/snow), with additional contributions provided by drip water, which conveys a much more significant mineral load, and probably by water resulted from the evapocondensation process.

- Information provided by the ice chemical composition can be utilized as a valuable proxy for detecting paleo-climate changes. Yet in contrast to isotopic measurements, the chemical-analytical data must be interpreted by taking into account the evolution and the dynamics of the hydrogeochemical processes which operate when ice forms.

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