ISOTOPIC AND ELEMENTAL CHEMOSTRATIGRAPHY

Assoc. Prof. George Kontakiotis

Branches of Stratigraphy

Stratigraphy is the study of layered rocks

- Rock Based – Lithostratigraphy
- Fossil Based – Biostratigraphy
- Polarity - Magnetostratigraphy
- Time Based – Chronostratigraphy
- Chemistry Based - Chemostratigraphy

How does chemostratigraphy differ from biostratigraphy?

- **Chemostratigraphy** differs from biostratigraphy in that it uses variations in chemical signatures within sedimentary rock layers to establish stratigraphic relationships, whereas **biostratigraphy** relies on the distribution of fossils.
- Chemostratigraphy focuses on isotopic and elemental data, while biostratigraphy uses fossil assemblages to date and correlate strata.

What is chemostratigraphy?

- Chemostratigraphy is a branch of stratigraphy that uses the chemical composition of rocks to correlate them across different locations and time periods.

- Particularly, it is the study of chemical variations within the sedimentary sequences, either based on the elemental or isotopic compositions of the rock to determine stratigraphic relationships. It is a very powerful stratigraphic tool which is applied in combination with bio- and magneto-stratigraphy. It also provides a useful tool for paleoenvironmental reconstructions, unconventional resource exploration and development.

What is chemostratigraphy?

- The characterization of "fingerprinting" and correlation of sedimentary sequences using inorganic geochemical data. This characterization enables the identification of chemostratigraphic units on the basis of elemental concentrations, ratios or systematic trends.

Basic Premise

- Chemostratigraphy is based on the principle that rocks of the same age have similar chemical signatures, because they were formed or deposited under similar conditions. By measuring and comparing the concentrations of certain elements or isotopes in the rocks, the researcher can establish a relative or absolute chronology of different kind of events (e.g., related to the ocean chemistry, climate, biosphere, tectonic activity), and correlate them with global or regional changes.

The importance of sedimentary inorganic geochemistry

- Inorganic geochemistry of sediments is highly variable and sensitive to subtle changes in source composition, facies, weathering or diagenesis. Therefore, apparently uniform successions may show primary differences in the chemistry of constituent minerals, particularly in accessory phases.

- The keys to a successful chemostratigraphic study is to understand the association of elemental chemistry and geology.

The importance of sedimentary inorganic geochemistry

- Geochemical proxies used for stratigraphy were originally developed and utilized as proxies for paleoenvironmental change. Many of these chemical proxies turned out to record – to different degrees – global and/or regional changes in paleoclimate and paleoceanography reflecting mostly climate and depositional variations, tectonic setting, provenance reservoir characteristics.

- These changes left their signature in marine or terrestrial sedimentary records. Due to the geologically short mixing time of the ocean-atmosphere system, which is in the order of thousands of years, some signatures of global environmental change stored in the atmosphere and/or seawater will be minored in a variety of proxies that can be used as accurate stratigraphic marker.

How do you measure the chemical composition of rocks?

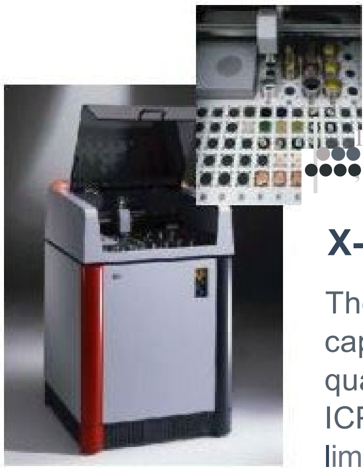
To measure the chemical composition of rocks, you need to collect samples from different locations and depths, and analyze them in a laboratory using various techniques, such as:

- Mass spectrometry measures the mass and abundance of atoms or molecules in a sample, and can determine the isotopic ratios of elements.
- X-ray fluorescence measures the emission of X-rays by atoms in a sample, and can determine the elemental composition of rocks.
- Inductively coupled plasma measures the emission of light by atoms or ions in a sample, and can determine the elemental or isotopic composition of rocks.

Analytical Techniques

Inductively coupled plasma spectrometry

Remains the most effective all round tool for analysis, but in recent years several other viable options have appeared



X-Ray Fluorescence

These instruments are now capable of producing high quality data comparable to ICP, but with sample quality limitations

Bench-top X-Ray Fluorescence

Small compact instruments that are now capable of producing good data in remote locations

Laser Induced Breakdown spectroscopy

Small compact instruments that are now capable of producing good data in remote locations

How do you interpret the chemical data of rocks?

To interpret the chemical data of rocks, you need to compare them with reference values or curves that represent the global or regional variations of the chemical parameters over time.

These values or curves are derived from well-dated and well-studied rock sections, such as marine sediments, volcanic rocks, or ice cores.

By matching the patterns of your data with the reference values or curves, you can assign ages to your rocks, and correlate them with other rock sections or events.

Branches of Chemostratigraphy

- ## Elemental Chemostratigraphy
  - The application of major- and trace-element geochemistry for the characterization and subdivision of sedimentary sequences into geochemically distinct units and correlation of strata in sedimentary basins
  - Element rock composition: The element composition of sedimentary rocks is governed by their mineralogy which reflect the history of the sedimentary rocks.
- ## Isotopic Chemostratigraphy
  - Oxygen chemostratigraphy uses the ratio of oxygen isotopes (O-16 and O-18) to infer changes in temperature, ice volume, and salinity of the oceans.
  - Carbon chemostratigraphy utilizes the ratio of carbon isotopes (C-12 and C-13) to infer changes in the carbon cycle, organic productivity, and atmospheric oxygen levels.
  - Strontium chemostratigraphy utilizes the ratio of strontium isotopes (Sr-86 and Sr-87) to infer changes in continental weathering, volcanic activity, and seawater composition.

Oxygen Isotopes as stratigraphic tool

The two oxygen isotopes used in chemostratigraphy are ^{16}O and ^{18}O. Over 99% of the oxygen on Earth is ^{16}O, with most of the remainder being ^{18}O.

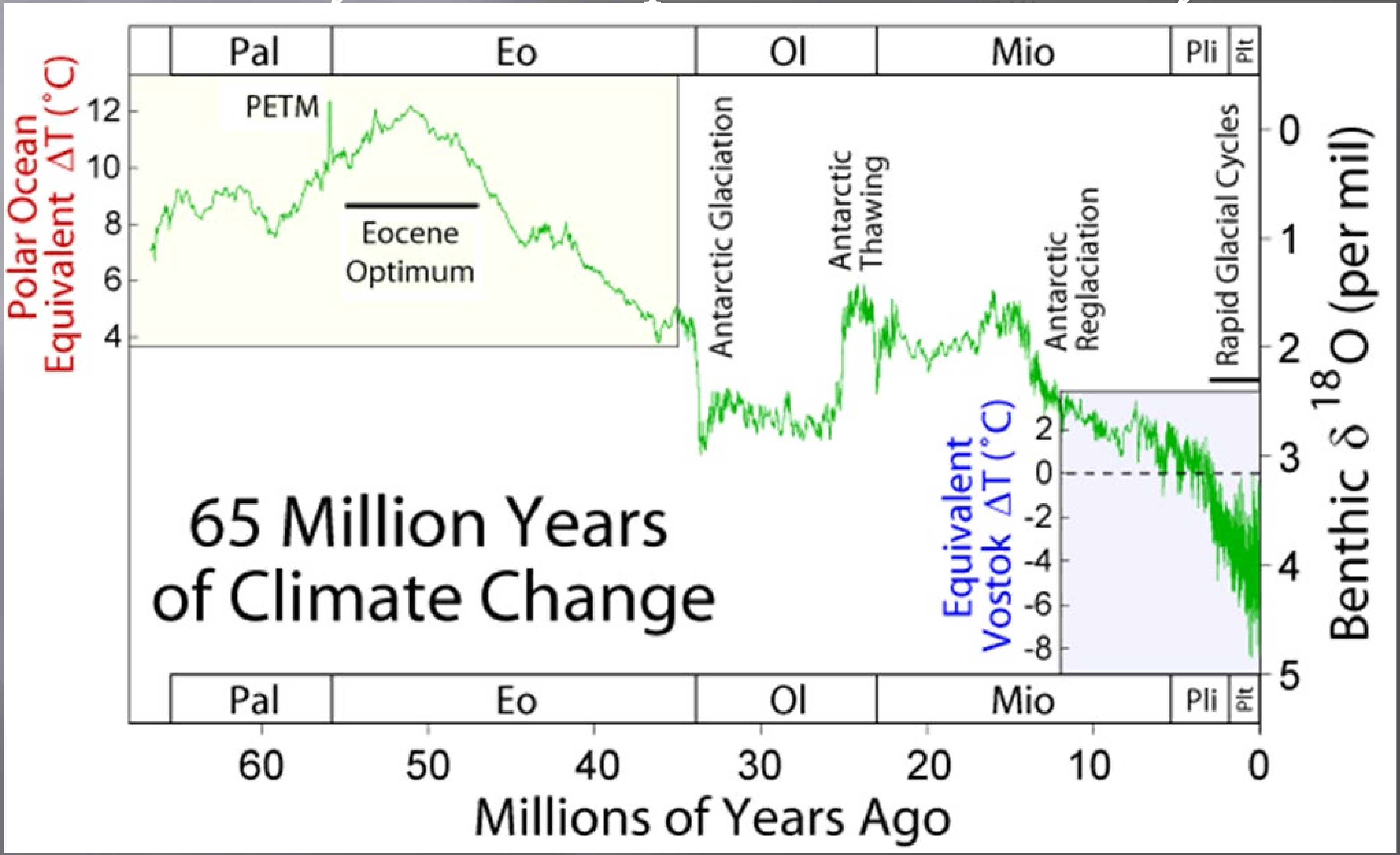
Since there is significantly less ^{18}O on Earth, we can compare subtle fluctuations in ^{18}O relative to ^{16}O to get a sense of what climatic processes were happening at some point or region over a certain amount of time.

$$\underset{\text{(in ‰)}}{\delta^{18}O} = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \times 1000$$

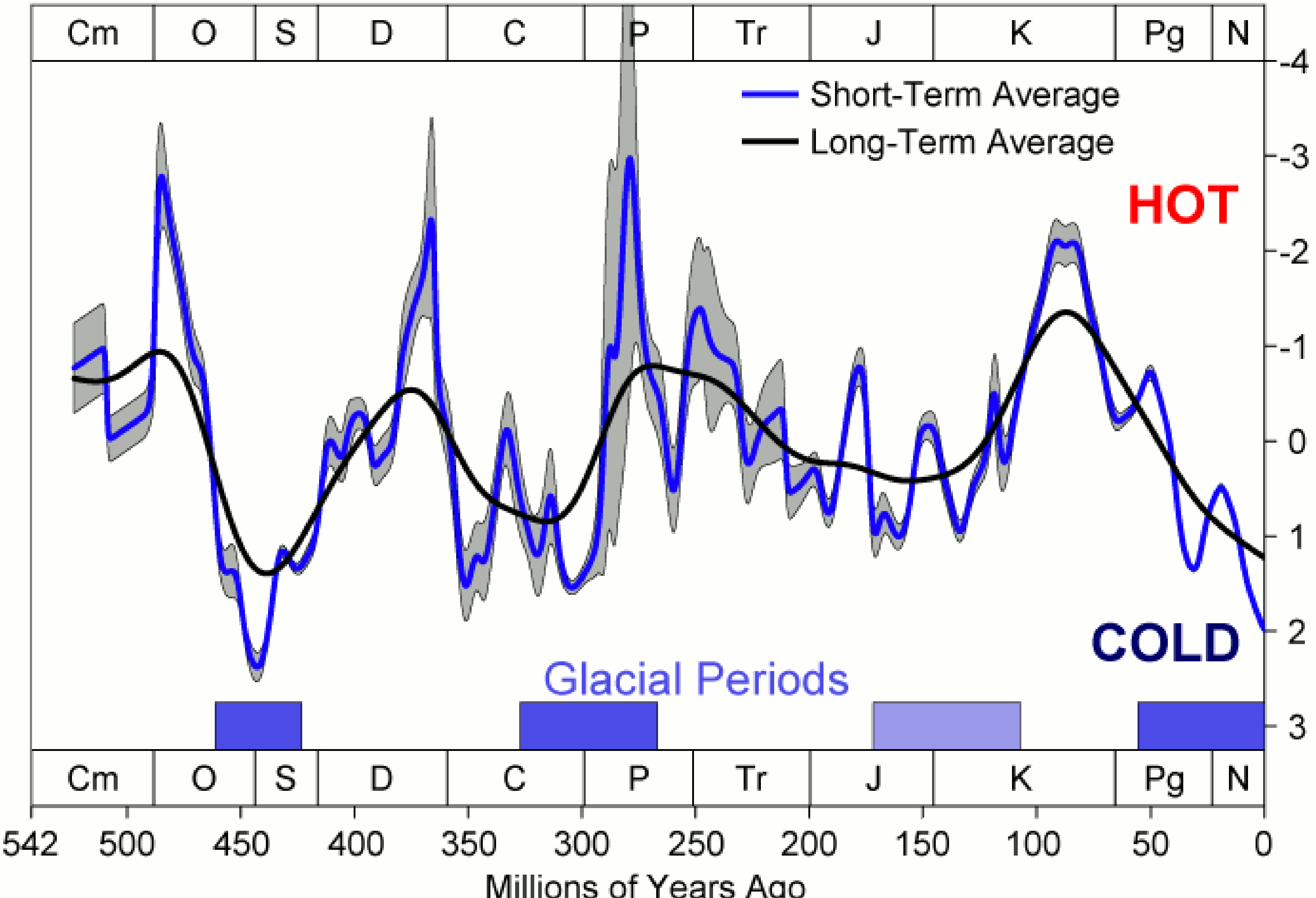
$^{18}O/^{16}O$ values are reported relative to international laboratory standards (V-PDB, VSMOW). The results are expressed in the per mil notation. Oxygen isotopes are measured in the shells of marine organisms, because the isotope record occurs primarily in ocean water.

Isotopic Chemostratigraphy

- The most powerful method used in chemostratigraphy is stable isotope geochemistry and is mostly used for paleoclimatic analyses



Phanerozoic Climate Change

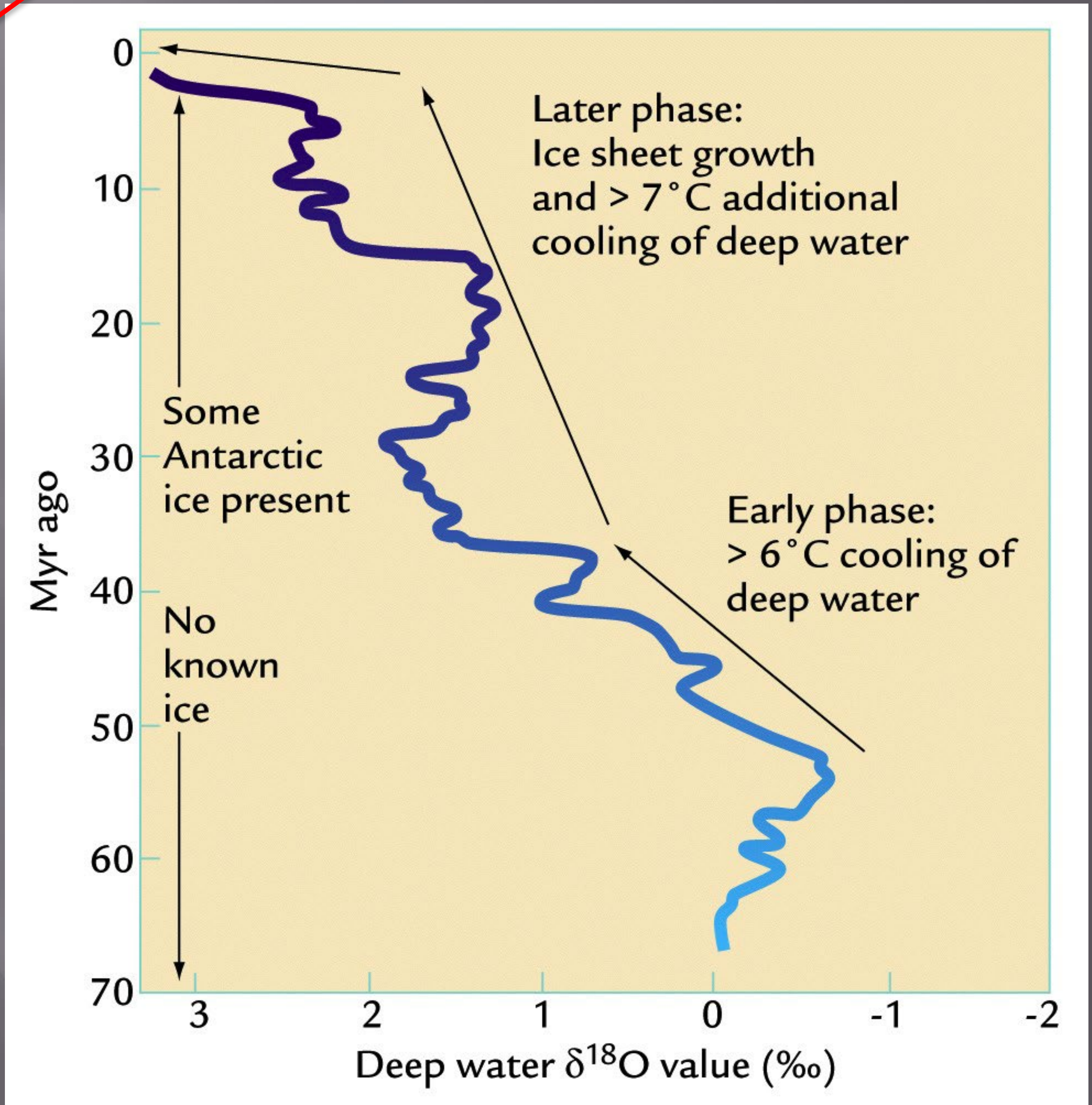


Long-term δ¹⁸O trend in the deep ocean as measured from the calcite shells of foraminifera

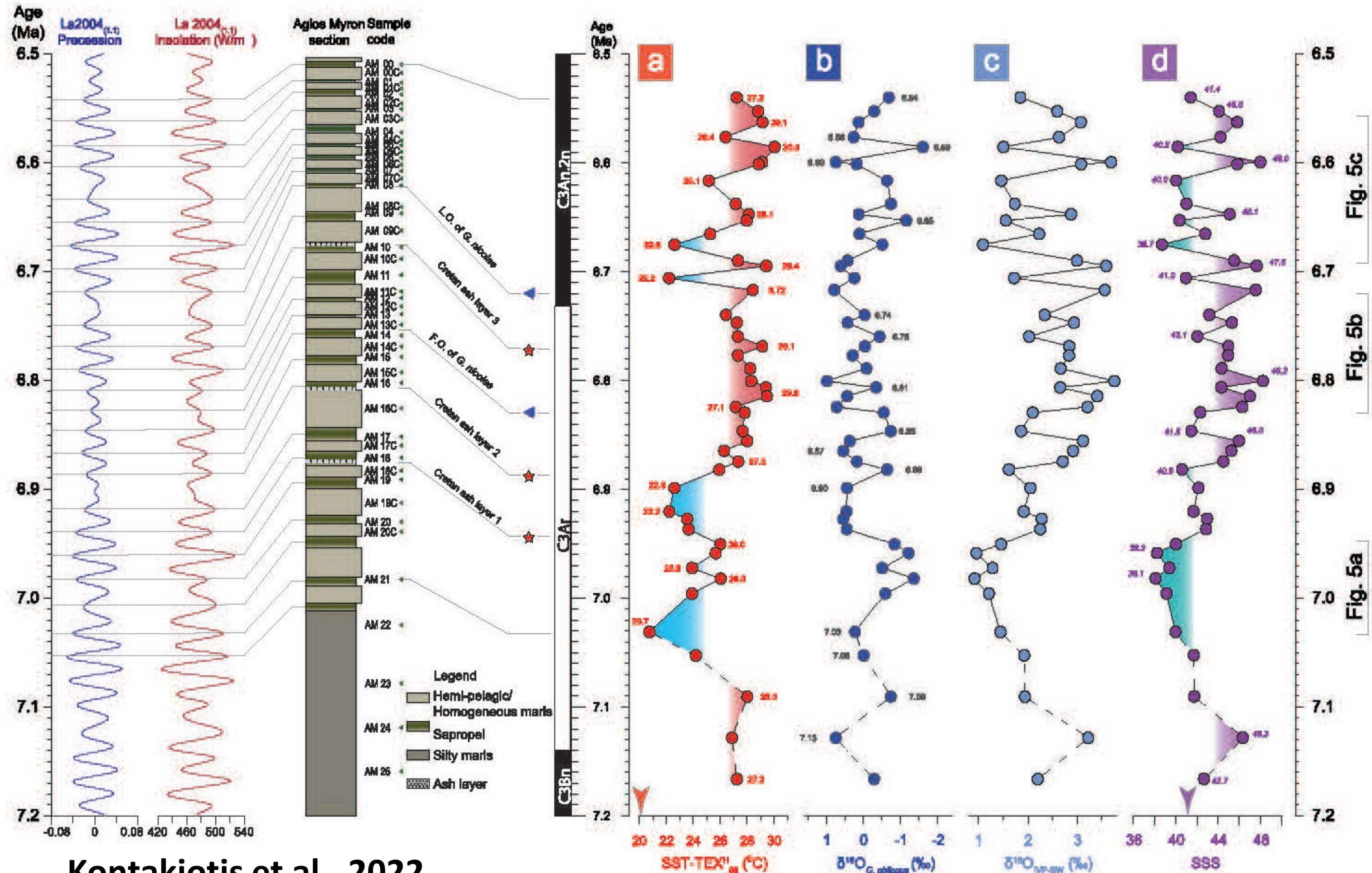
Two factors:

(1) Changes in deep-ocean **temperatures**

(2) Growth of **ice sheets** on land (^{16}O enriched)



More chemostratigraphic environmental constraints… Mediterranean Messinian salinity variations



Kontakiotis et al., 2022

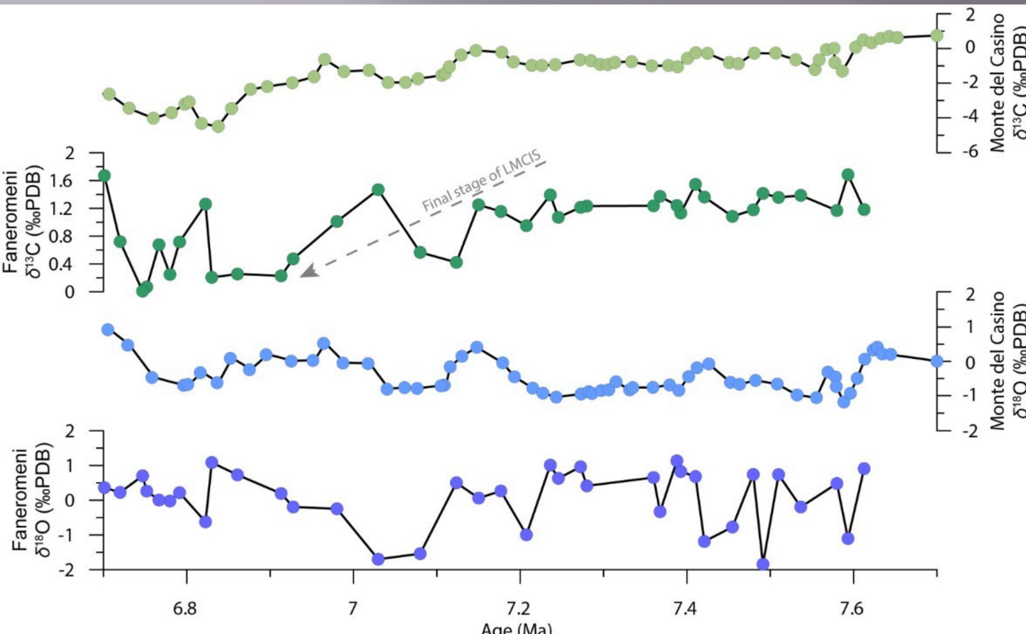
Carbon Isotopes as stratigraphic tool

- Of the two stable carbon isotopes, the abundance of ^{12}C is given as 98.89%, while ^{13}C forms the remaining 1.11%.

- Mass differences of the two C-isotopes lead to strong fractionation during photosynthetic incorporation of carbon into organic matter, while inorganic carbonate precipitates formed in the aquatic environment are less affected by fractionation processes.

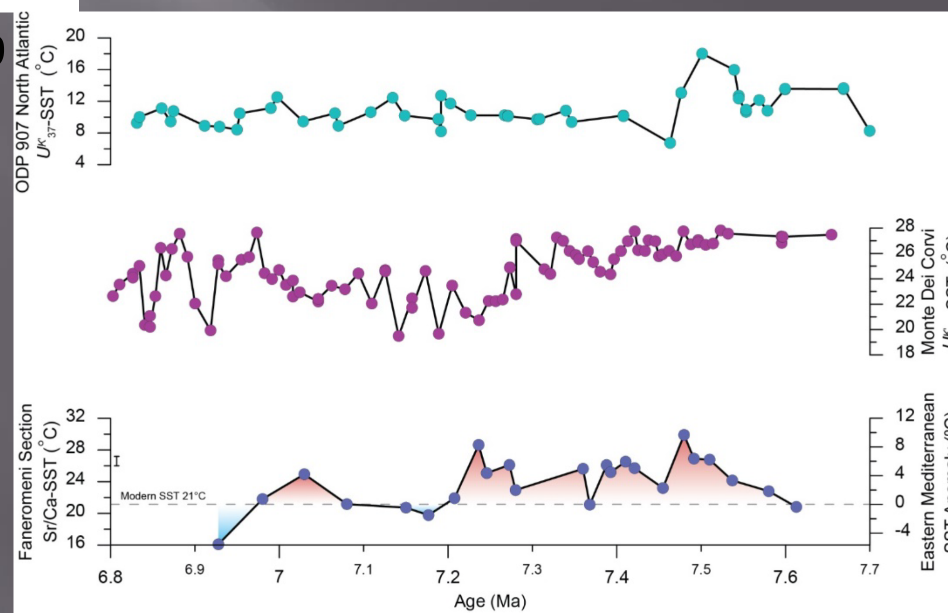
- The knowledge of the C isotope record is very important not only in stratigraphic correlation but also because of its potential to help understand the development of Earth's climate, evolution of its biota and CO_2 levels in the atmosphere.

More chemostratigraphic environmental constraints… Messinian cooling event and LMCIS



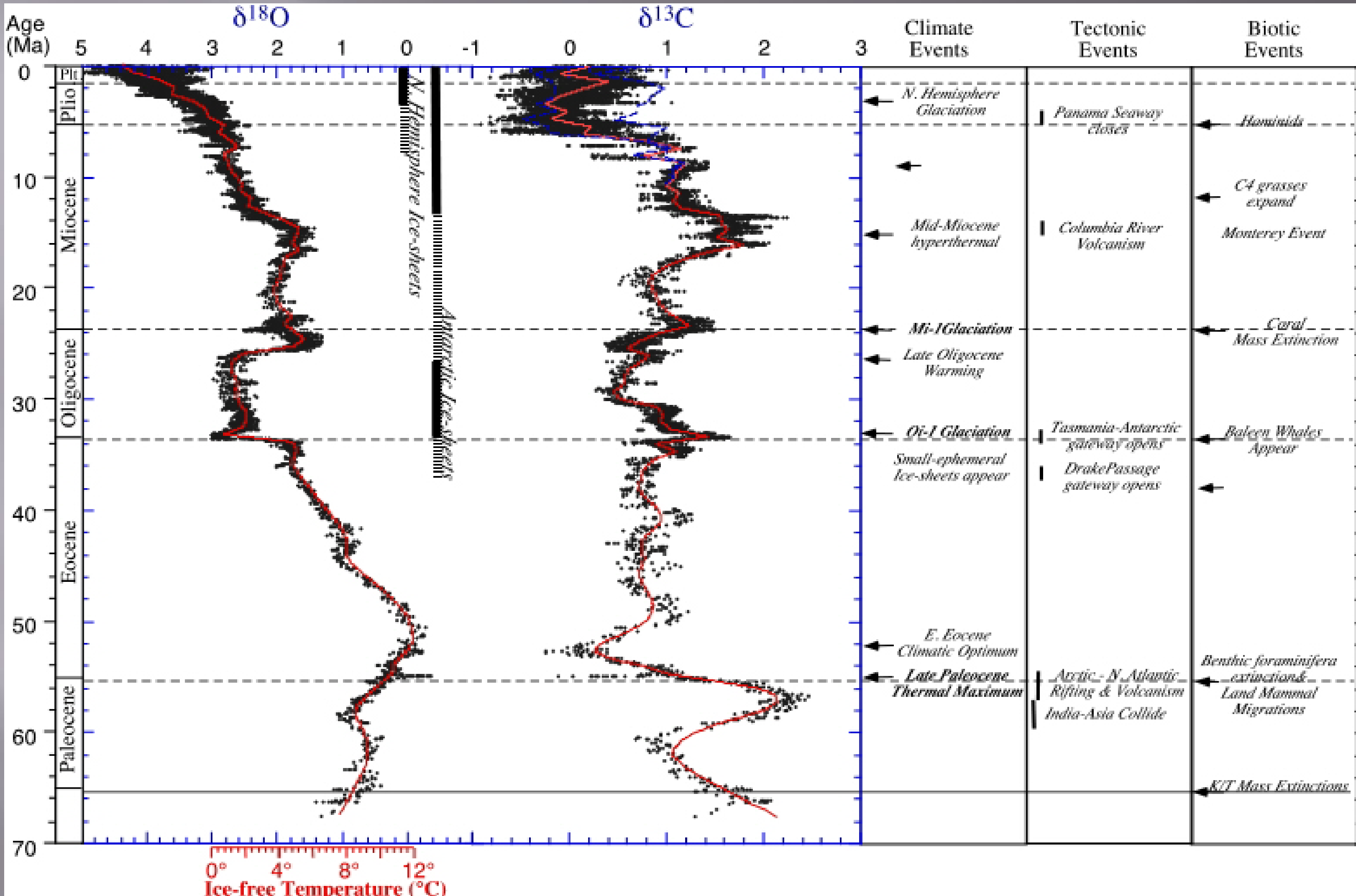
Lower $\delta^{13}C$ => Late Miocene Carbon Isotope Shift (LMCIS)

Kontakiotis et al., 2019



Heavier $\delta^{18}O$ isotopes => cooling

Lower SSTs => cooling

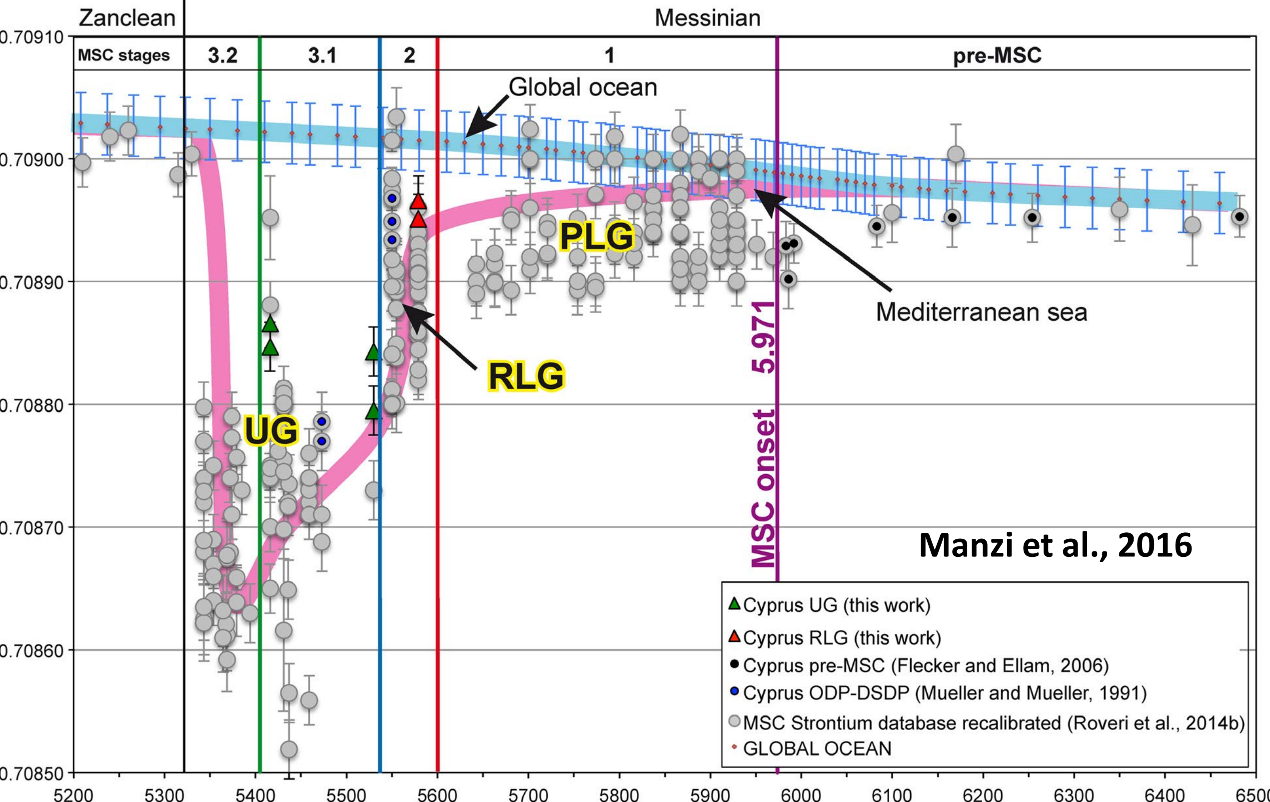


Carbon isotopes show overall storage of organic carbon in organic matter (**if globally more carbon is stored in organic carbon, the record of carbonates moves to heavier values**). Note the very short-term changes to extremely low values at about 55.5 million years ago (in the latest Paleocene), the time of the LPTM (PETM).

Sr-Isotope Stratigraphy

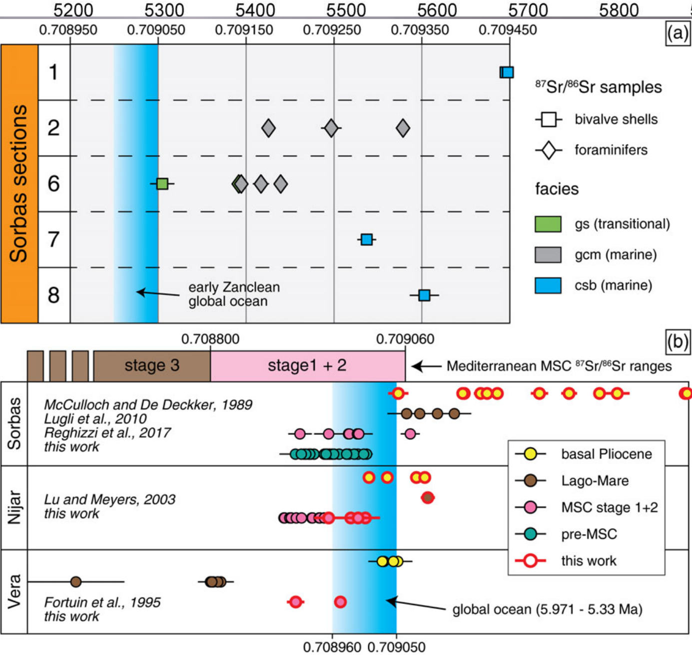
- Sr has a long ocean residence time of 2.4106 years, and therefore Sr isotope geochemistry has been of limited use for high-resolution stratigraphy (104-105 years).

- The Phanerozoic Sr-isotope composition is characterized by long-term fluctuations marked by major turning points in the Sr-isotope curve which can be used as stratigraphic marker levels. For example, the turning point in the Mesozoic $^{86}Sr/^{87}Sr$ in the Late Jurassic, the rapid change in Sr-isotope values around the Aptian, and at the Ordovician-Silurian boundary.



Manzi et al., 2016

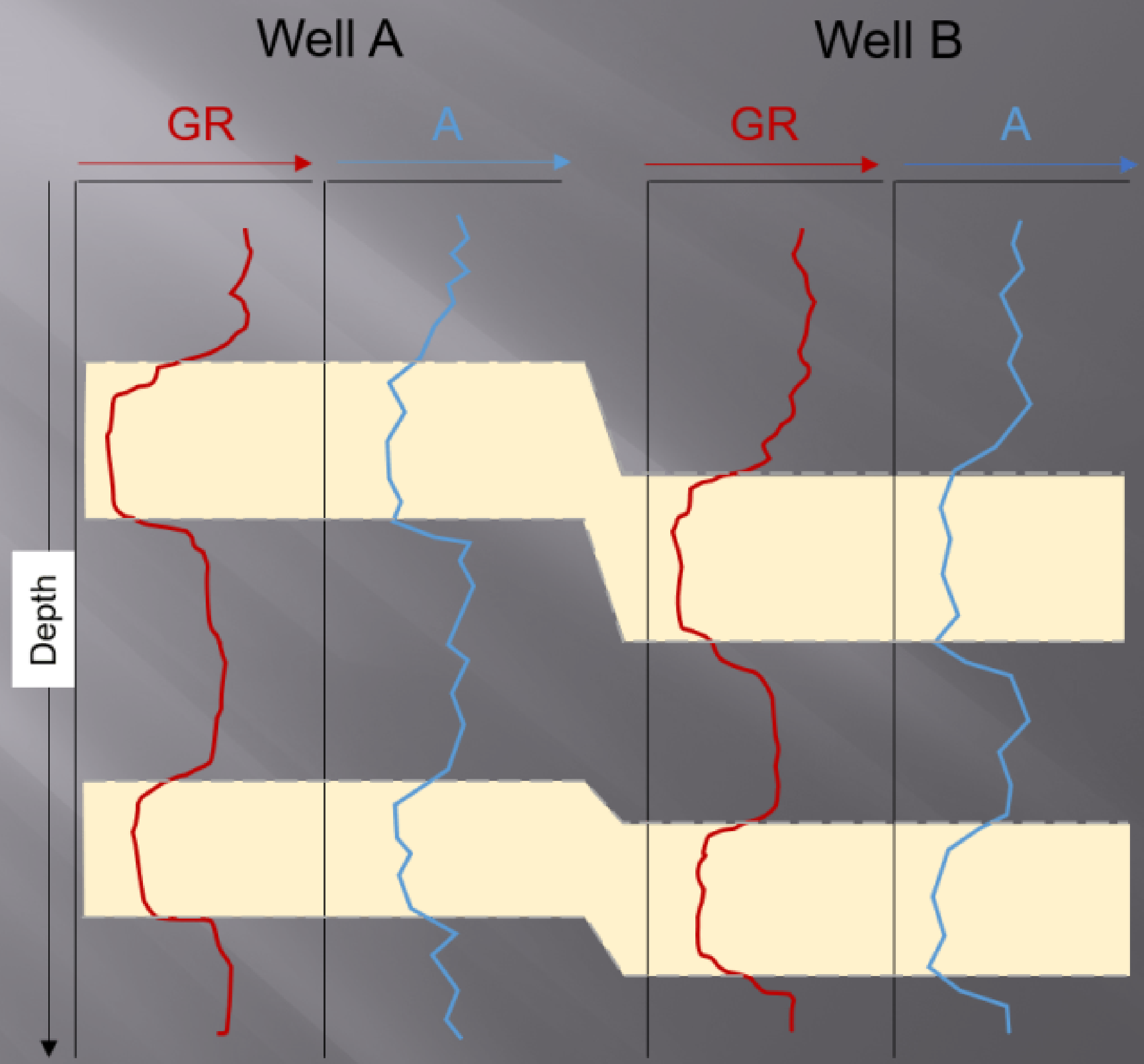
Sr isotope curve



Roveri et al., 2018

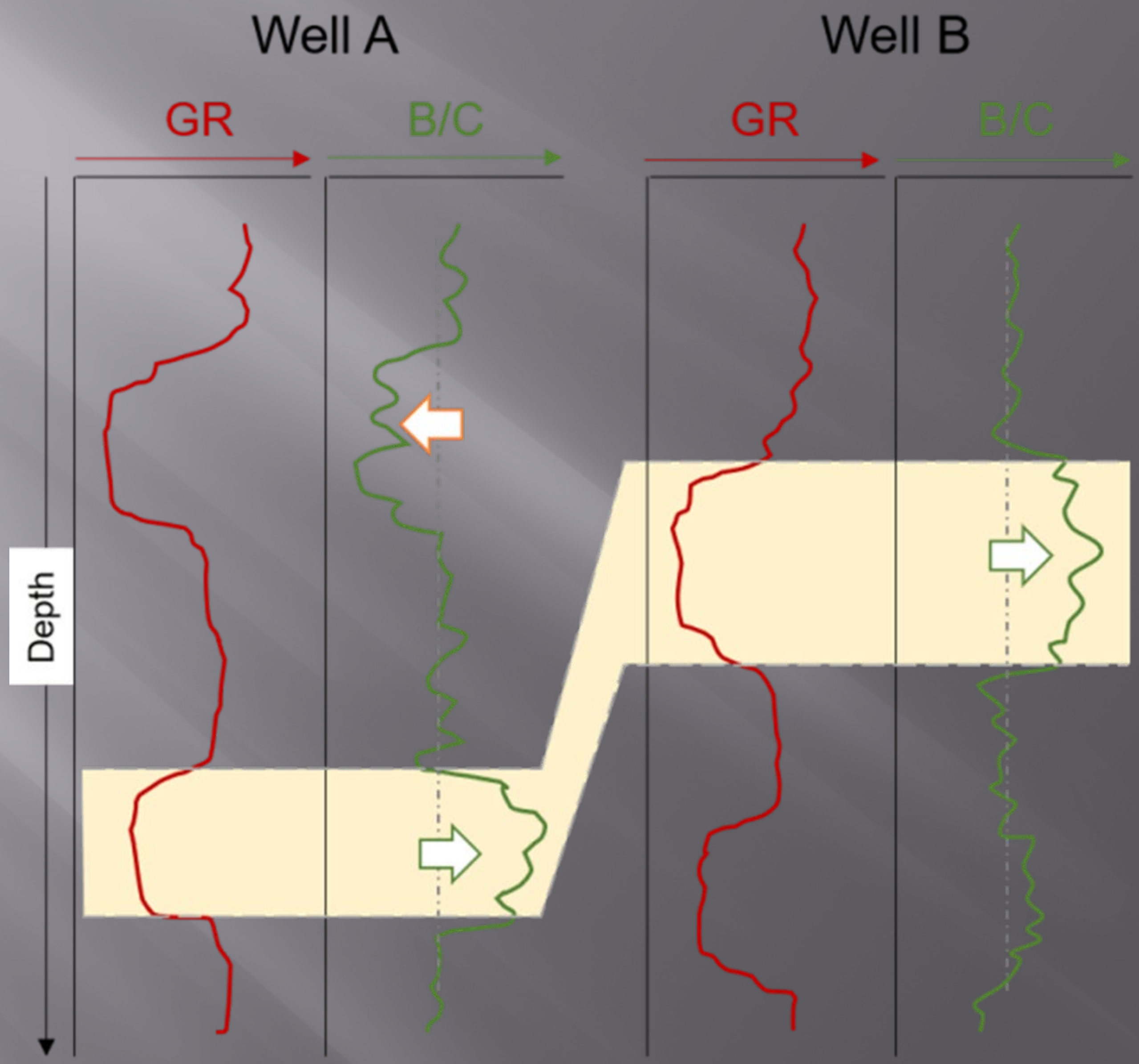
The Mediterranean Sr curve is strongly differentiated from the global ocean curve and presents distinct values within the MSC stages, indicative of the paleoenvironment

Example: well-to-well correlation



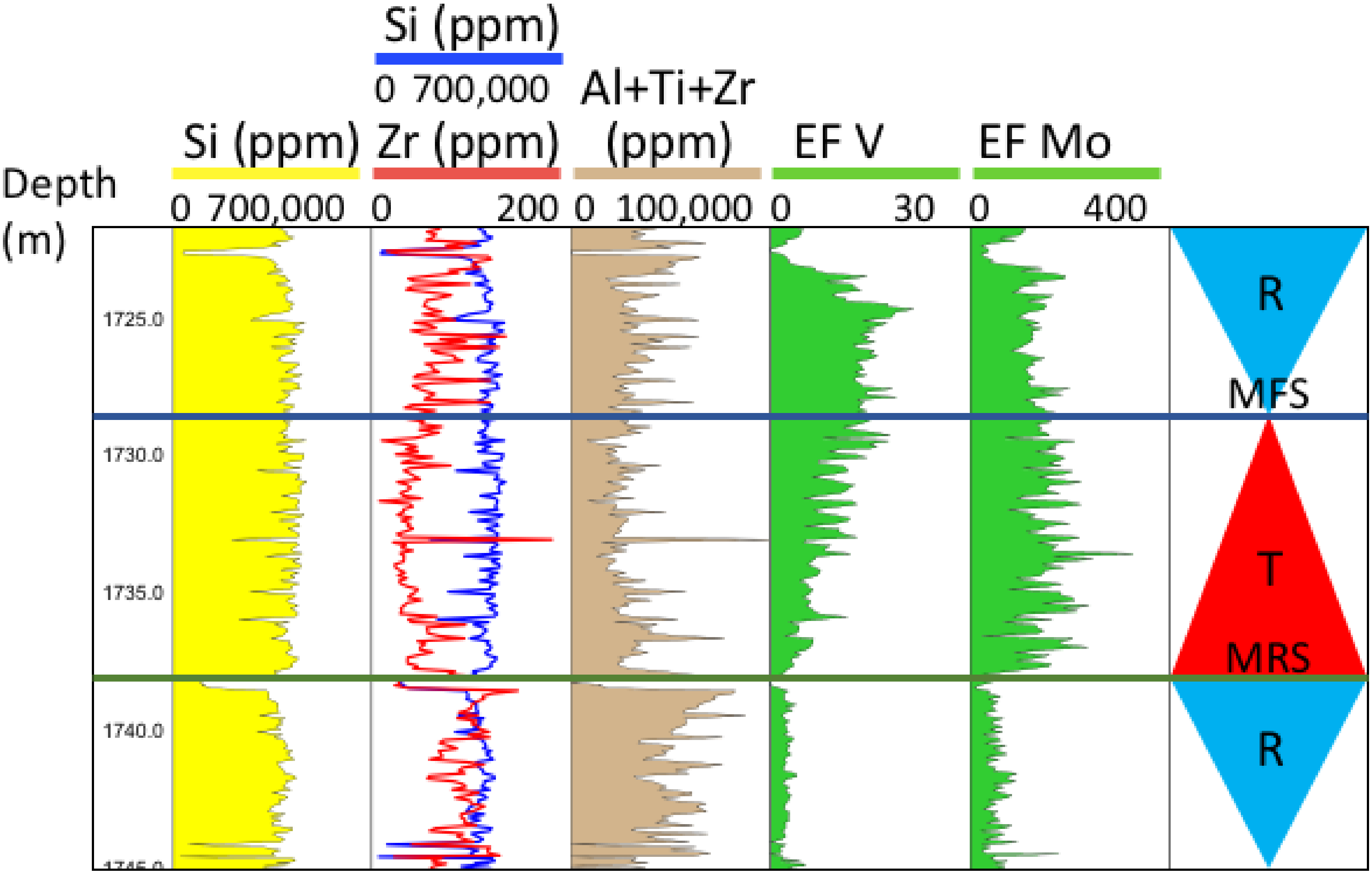
Correlation between well A and well B based on GR and lithology depending element (A).

Example: well-to-well correlation



Correlation between well A and well B based on lithology independent element/element ratio (B/C).

Example: sequence stratigraphic development



The chemostratigraphic expression of transgression (T), regression (R), maximum flooding surfaces (MFS), and maximum regressive surfaces (MRS)

Potential Advantages

Chemostratigraphy has several advantages over other classical methods of stratigraphy, such as:

- its ability to be applied to any type of rock, providing high-resolution and continuous records of the geological and environmental history, even when the rocks are not well-preserved or well-exposed.
- It can be integrated with other methods of stratigraphy, like biostratigraphy, lithostratigraphy, magnetostratigraphy or cyclostratigraphy, to enhance the accuracy and trustworthiness of the correlations.

Potential Advantages

- Chemostratigraphy is not restricted by lithology or sample type. It can be applied to samples of any lithology in clastic, carbonate and unconventional reservoirs (including but not restricted to claystones, sandstones, volcaniclastics, coals, carbonates and evaporites), any age found in any location and deposited in any environment, and equally as well in core, outcrop and well cutting samples, including turbine- drilled cutting samples.
- Analyses can also be performed on a small amount of sample, where sample volumes are limited, particularly in well cuttings, so initial preparation involves ”picking” the desired lithology and washing to remove drilling fluid contamination.

Potential Limitations

- The requirement of specialized equipment and expertise to measure and analyze the chemical composition of rocks, which can be costly and time-consuming.
- It can be affected by diagenesis, metamorphism, or contamination, leading to alterations of the original chemical signatures.
- It can be influenced by local or regional factors, such as the source of the rocks, the depositional environment, or the tectonic setting, potentially creating variations or anomalies in the chemical data.

What are some of the events in Earth's history that chemostratigraphy has been able to explain?

One example is the causes of mass extinctions. For instance, biostratigraphy identified the huge Cretaceous-Paleogene boundary extinction based on the fossil content, but chemostratigraphy greatly contributed to our understanding of its causes (asteroid impact versus volcanism), through the identification of heavy-metal enrichments and isotopic shifts in the boundary beds.

What are some of the events in Earth's history that chemostratigraphy has been able to explain?

Another example is the recognition of extreme, near-global glaciations ("Snowball Earth") in the Neoproterozoic was aided by carbon isotope chemostratigraphy. Likewise, the discovery that the Earth lacked an ozone layer in the Archean, and the identification of its formation in the early Paleoproterozoic, was based mostly on sulphur isotope chemostratigraphy.

What might past geologic events in the chemostratigraphic record be able to tell us about the future?

Rocks are influenced by the environment in which they originated. Any environment can be defined as a set of physical, chemical, and biological conditions. These conditions are all inter-related through the interactions of lithosphere-hydrosphere-atmosphere-biosphere, to which the chemical elements and their isotopes are all sensitive.

Through documentation of geochemistry of these archives, we can trace past environmental variations, (e.g., ocean temperature, ice volume) and extrapolate them into the future, enabling the distinction of natural cycles from anthropogenic impacts.

Applications of Chemostratigraphy

Chemostratigraphy has been used to address several geological problems, such as:

- ✓ fixation of the age,
- ✓ accurate correlation of rocks located in geographically distal regions,
- ✓ identification of climate changes, and
- ✓ hydrocarbon exploration.

However, it is noted that the potential applications are much broader.

Applications of Chemostratigraphy

They also include:

- ✓ identification of exact locations of artifacts of ancient cultures through geochemical fingerprinting,
- ✓ understanding the ancient climatic changes, and
- ✓ the reliable identification of ancient catastrophic events, such as meteorite impacts, major volcanic eruptions, ocean chemistry turnover, and extreme glaciations.

Applications of Chemostratigraphy

Chemostratigraphy is a fascinating and rapidly-evolving field of geoscience. It will continue to shed light into the deep geological past and allow us to reconstruct, in unmatched detail, sudden, catastrophic events.