

UNIVERSITY OF PADUA  
DEPARTMENT OF GEOSCIENCES



Master's Degree Course in Geology and Technical Geology

MASTER'S DEGREE THESIS

**Changes in biological productivity in the lower part of the PCS  
sediment core (Lower Pleistocene, Calabria, Southern Italy)**

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## 1.Introduction

In this paper, we reconstruct the ancient marine information of the Plio-Pleistocene Mediterranean by analyzing carbon isotope and oxygen isotope from cores in Crosia, a small town in Cosenza Province at the southern tip of Italy. I used isotopic change curves combined with previous research records to analyze the genesis of sapropel and sand, and changes in paleomarine productivity.

Experimental samples are marine sediments from Luca Capraro et al., at ca.90m in Crosia. In this experiment, a more intensive sampling interval was used, with samples taken every 10 cm in the 50 to 76.4m section of the core, for a total of 264 samples. We conducted experiments at the Department of Earth Sciences of the University of Padua to screen the benthic foraminifera *Uvigerina peregrina* in the samples and obtain them  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  to obtain high-resolution curves. Analyze the variation of bottom water biological productivity according to the changes of isotope curves, and explain the reasons for the changes of isotopes in the sand layer and sapropel intervals.

## 2. geological stratigraphy

### 2.1 Croisia geological background

The study area is located in the northern part of the Croisia, Cosenza province, southern Italy, which is about 200 meters above sea level, with slopes facing the sea and a gentle coast without cliffs.



Figure 2.1.1 The red circle in the picture is the study area, located in Cosenza province, southern Italy. Image taken from Baidu.

Geologically, it is located at north of Calabrian Arc. As shown in the figure 2.1.2, Calabrian Arc is made up of three parts, Sila massif, Serre and Aspromonte massif. Our study area is in Sila massif's north-eastern slope. Calabrian Arc is basically composed by crystalline rocks, with meta-ophiolitic units from Tethyan ocean crust and metamorphic rocks in the upper part, but in our study area, the upper part of Sila massif is a nappe composed Mesozoic sediments (Reghellin, 2011)

From the outcropping of Calabria, it can be inferred that a thin, metamorphic unit of the Calabrian basement deformed during Late Eocene and then overthrust Tethyan carbonate platform areas in the Apennine Chain, covering the top layer of the rock formation. Outcropping in northern Calabria shows many opposite verging tectonic units in the middle level. At the bottom, is the fundamental crustal that continuity with the foreland area (Van Dijk, 2000). Geologically, a shear zone splits it into two parts with the Apennine Chain, which does not belong to the Apennine Chain, but to the African block.

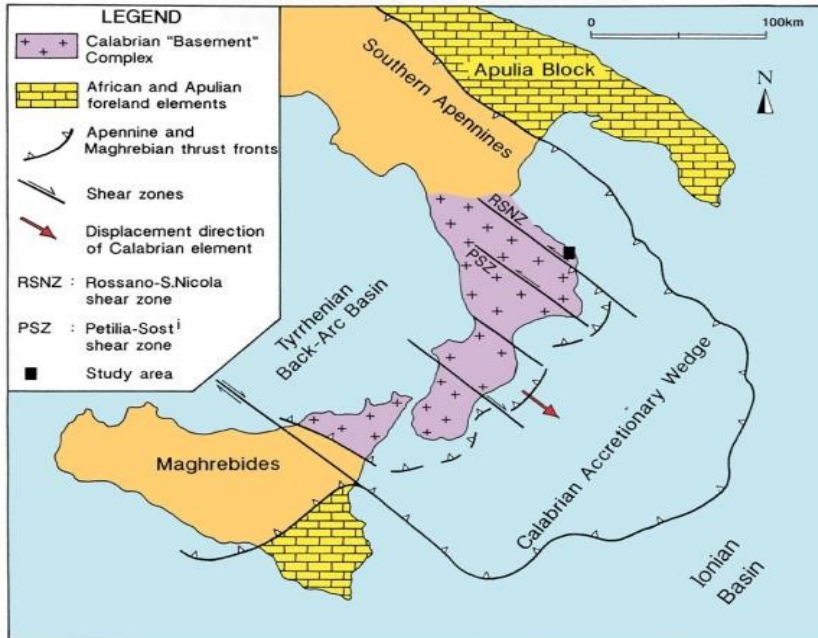


Figure 2.1.2 Structural map of Southern Italy (Massari et al., 2002) and the location of the study area (black square)

The Crosia-Calopezzati area is located between the late Neogene Crotone Basin and the coeval Crati Basin, both basins located in the upper part of the Calabrian accretionary wedge. During the Pleistocene, it experienced uplift and depression due to tectonics and eustasy, thus recording more continuous Pleistocene marine sediments. In summary, during the Upper Pleistocene, the region experienced transgression and regression several times due to tectonics, but eventually dominated by drowning events, and sediments manifested as transgressive units (Ogniben, 1962). This fact is also confirmed by Panizza's analysis of the region foraminiferal assemblages (Panizza, 1967). As a result, the original Highstand System Tract in the basin was truncated and began to be filled with nearly 250 meters of marine sediment, dominated by pelitic facies lithologies (Bigazzi and Carobene, 2004; Gozzer, 2011). During the Middle to Late Pleistocene, the region began to gradually release pressure, and the plates gradually rose and rotated, gradually exposing the sea, leaving marine terraces. In the late Pleistocene, the plates entered the contractional phase.

Segalla described the stratigraphy succession of the region from bottom to top in 2007 based on field evidence:

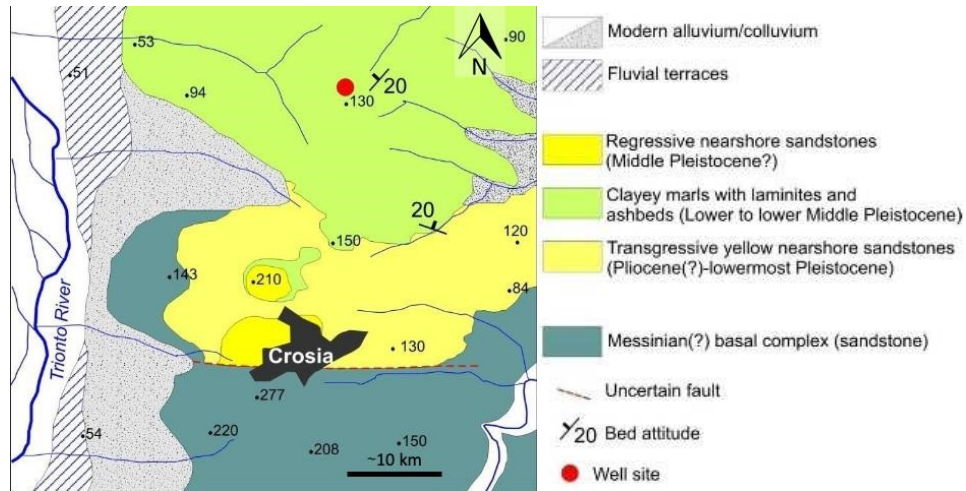


Figure 2.1.3 Simplified geological map of the Crosia sector (not to scale), showing the main identified unit and PCS drilling locations (Gozzer, 2011).

- Messinian basal complex
- Transgressive yellowish sandstones (Pliocene-Lower Pleistocene)
- Clayey marls containing laminites and ash layers (Lower-Middle Pleistocene)
- Regressive sandstones (Middle Pleistocene)
- Marine terraces (Middle-Late Pleistocene)

## 2.2 Crosia stratigraphy and chronology

At the 18th International Geological Congress, the agreement defined the Pliocene-Pleistocene boundary as 'at the horizon of the first indications of climatic deterioration in the Italian Neogene succession.' (King and Oakley 1949). Initially, this boundary was identified as characterized by cold-water mollusk *Arctica islandica* and the cold-water foraminifer *Hyalinea balthica* (Sibrava, 1978), but Arias denied this view, arguing that these two creatures appeared before the boundary line. After three decades of investigation, the Pliocene/Pleistocene boundary was finally placed by the International Commission on Stratigraphy (ICS) as a Global Stratotype Section and Point (GSSP) at the Vrica section. The astronomically tuned age of this boundary is 1.806 Ma (Lourens et al., 1996a). In the discussion of this article, we still use this standard.

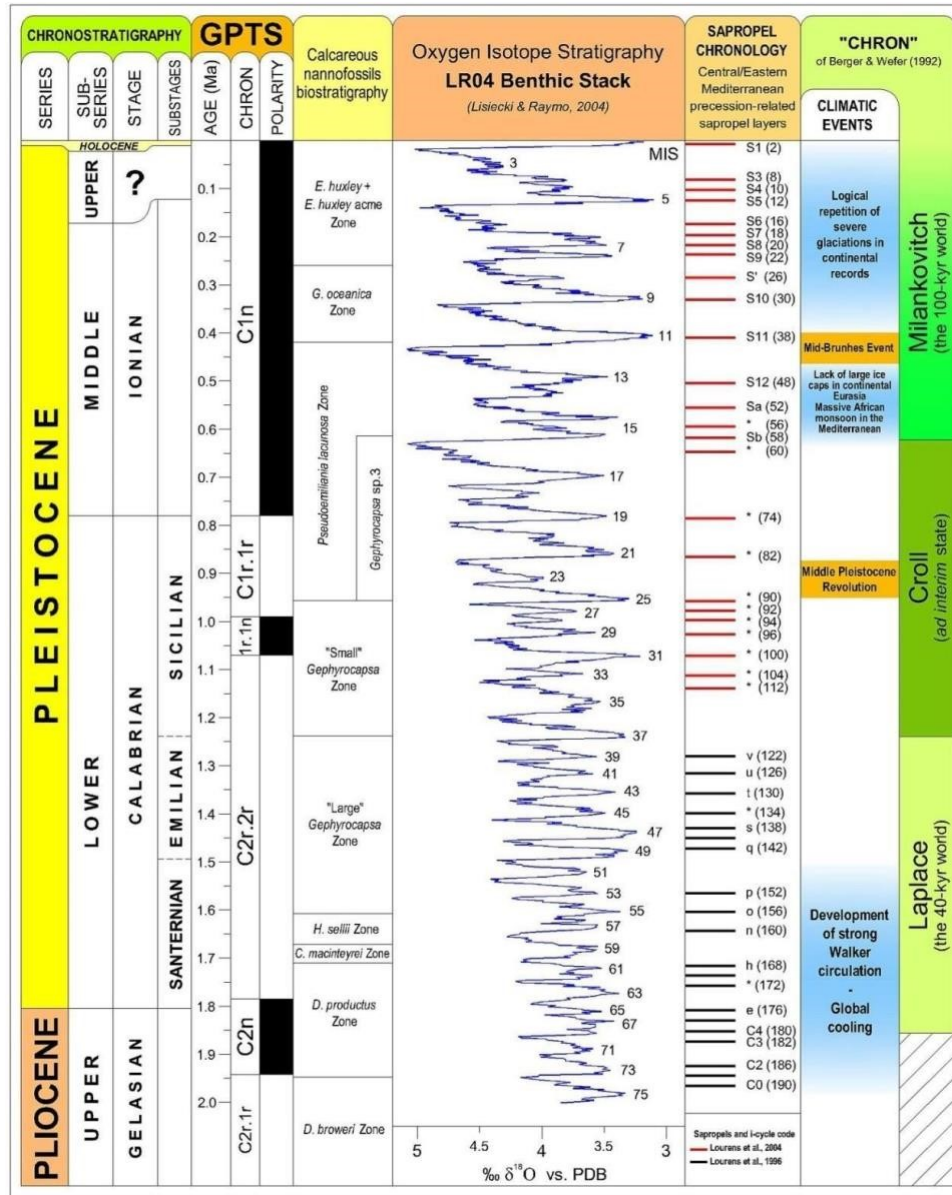


Figure 2.2.1 Chronostratigraphy of the Plio-Pleistocene (Various Authors 1990-2005).

For the discussion of the age of samples, we need to combine the Mediterranean standard sapropel stratigraphy, volcanic ash record and biostratigraphy.

In our reference section, the Vrichetta section, the sediment is predominantly clayey marls. Researchers have identified four different layers (Carobene, 2003), and we can obtain some age limitations by analyzing these four layers. As shown in Figure 2.2.2, they are, from top to bottom, Ledro, Ermes, Alessandro, Cristina.



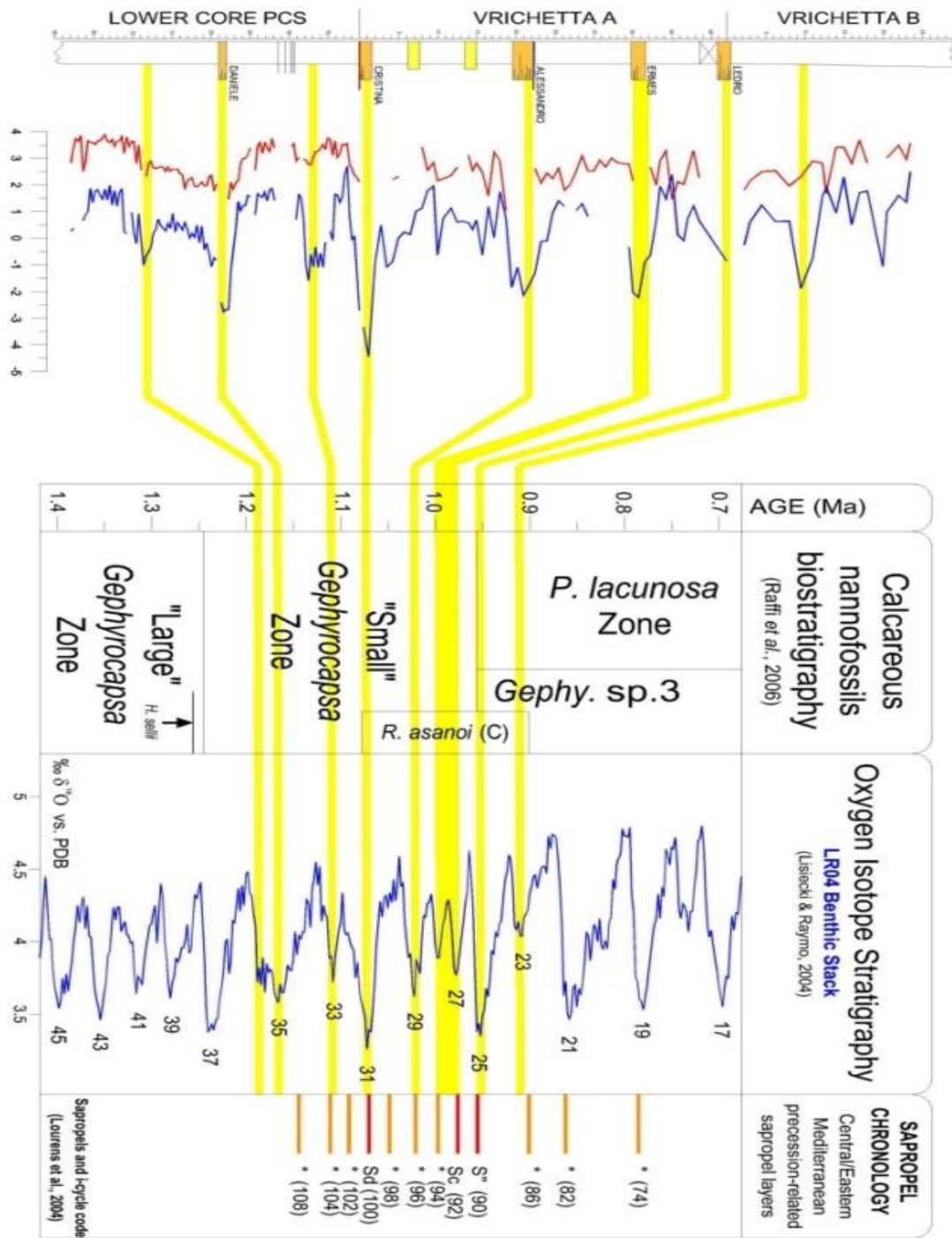


Figure 2.2.2 Proposed correlation between Crosia 18O record and standard references, as well as simplified biostratigraphy information(Reghellin, 2010).

Among them, the bottom of the "Cristina" layer also has a volcanic ash about 5 cm, which shows a change from orange to red. The "Alessandro" layer is topped with a pink layer mixed with clayey sediment, about 10 cm. These evidence is sometimes associated with

pyroclastic horizons, which facilitate the identification and recognition of individual laminates and provide a useful tool for correlations at the basin scale ( Lourens, 2004).

In terms of biostratigraphy, the data was mainly collected at pelitic intervals, while the coarser units are often characterized by the absence or scarcity of signal due to their rearrangement and/or scrambling. By combining the Calcareous nannofossils data collected by previous researchers with the Calcareous nannofossils biostratigraphy shown in Figure 2.2.2, the age of the Clayey Portion can be limited to a rough range.

The "large" Gephyrocapsa zone was found in the base of the lower core PCS, we cannot determine its bottom age, but we can determine that it is capped at 1.25 Ma. One layer above that appeared Lowest Gephyrocapsa sp.3, which is a "Small" Gephyrocapsa Zone (Rio et al., 1990), which includes the pelitic unit deposited during the last phase of marine transgression. Up to the top, the richest and most recorded biostratigraphic data were identified. At the same time, the explosion of Gephyrocapsa sp.3 and the base of Pseudoemiliana lacunosa Zone appeared, and their boundary with the Small" Gephyrocapsa Zone was about MIS 25 (ca.0.96Ma). On this layer, R. asanoi also appeared. The base of the "Pseudoemiliana lacunosa Zone" is often characterized by purely pelitic facies, and in the section of the town next to Crosia, it is identified the first advent of the regressive facies. (Gozzer, 2011). Biostratigraphy provides us with a good dating limit, which limits the dating of our samples to a relatively reliable framework. Combined with the comparison of glacial ages in Figure 2.2.2, we can limit the age of core PCS to MIS23 to MIS36, but the precise age at both ends cannot be determined.



Figure2.2.3 "Vrichetta" section shot in the field (Michieletto, 2019)

"Pozzo Crosia" (PCS core) was drilled on a gentle slope facing the sea, north of the Crosia town, with a total length of 87m. It is closer to hinterland than the "Vrichetta" section, so more stratigraphic information can be obtained in a smaller thickness while maintaining the representation of the underlying layer. The pelitic facies in the core represent the bottom layer in the profile, which can be seen as a reference layer to correlate with previous studies, such as the -25m depth of the Ledro layer representing the top of the "vrichetta" section. But there is currently insufficient biostratigraphic evidence to precisely prove the overlapping relationship between the "vrichetta" section and the PCS core.





Figure 2.2.4 **Left:** Caterpillar at work in the Crosia Village. **Right:** Sediments stored in dedicated polystyrene boxes, with the rightmost core in the box loose and unrepairable.

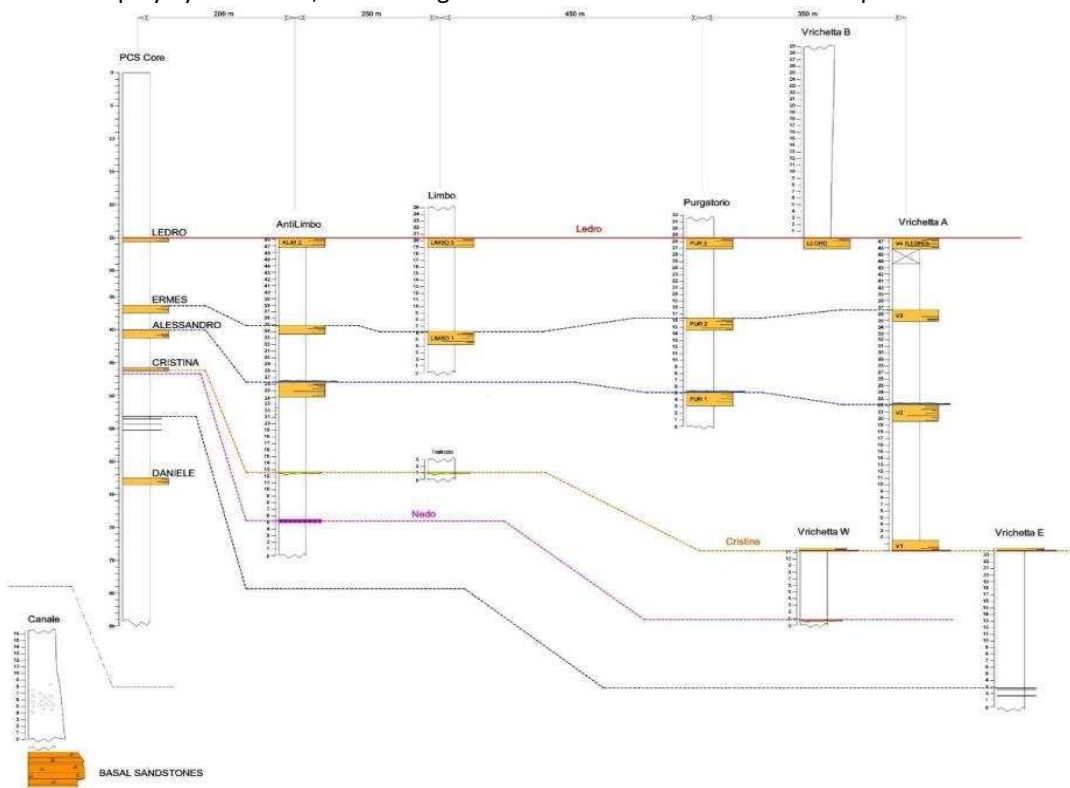


Figure 2.2.5 Correlation between the Crosia sector and Vrichetta section (modified from Segalla, 2007).

### 2.3 Current and monsoon

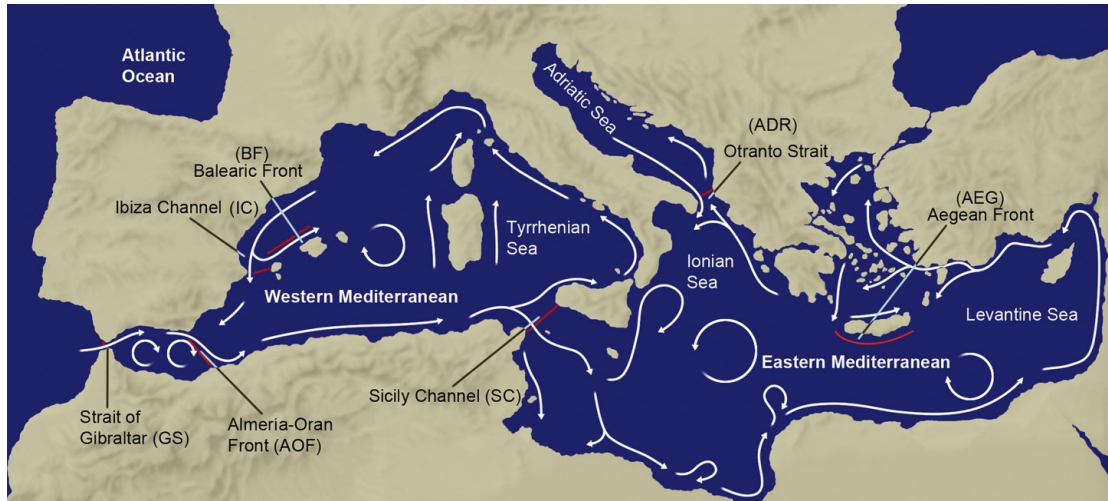


Figure 2.3.1 Simplified map of the Mediterranean Current (Pascual M, 2017)

The Mediterranean Sea is a semi-enclosed basin with a vigorous thermohaline circulation. It changes the sea water through the Strait of Gibraltar and the Turkish Strait and the Atlantic and Black Seas, respectively, the basin spans a maximum about 3860 km, and zonally it spans a maximum about 1600 km; its surface area is about 2,500,000 km<sup>2</sup>. It is an evaporative basin where its evaporation is greater than the freshwater input (Romanou et al., 2010), thus causing it to be anti- estuarine. Because of this particular environment, the sedimentation rate of the Mediterranean is relatively high, so sediments in the Mediterranean record higher resolution information, which is important for reconstructing paleoclimates.

The Mediterranean Sea is in the transition between the Subtropical High-Pressure Belt and the Temperate Westerlies. During the summer, the transition moves northward, resulting in dryness in the southeastern Mediterranean (Rohiling and Hilgen, 1991; Reghellin, 2015). During the winter, Most Genoan depressions move eastward along the southern Italian coast, across the Aegean Sea or northern Levantine Sea, and the low pressure formed in the process leads to the warmth and wetness of the Mediterranean winter.

The study area is located on the coast of the Northern Mediterranean, Ionian Sea, it is influenced by transit t water masses, the main water masses are: modified Atlantic Water (MAW, which crosses the Strait of Gibraltar from the Atlantic Ocean into the Mediterranean Sea, is in the upper layer of the ocean, contains lower temperature and

salinity. It is divided into two main streams as it passes through Sicily, one flowing northwest along the west coast of Italy, then southwest through the north coast of France and Spain and finally back to the Strait of Gibraltar; The other branch flows eastward through the long central axis of the Mediterranean, constantly evaporating water, thus increasing in density and sinking into LIW at the easternmost part of the Mediterranean. ); Levantine Intermediate water, LIW (Intermediate water, flowing counterclockwise from the easternmost edge of the Mediterranean Sea along the northern shore of the Mediterranean Sea and eventually returning to the Strait of Gibraltar. ).

In addition to this, until the Aswan High Dam was built in 1964, the Nile sent a large amount of fresh water to the Mediterranean Sea every year due to the influence of the African monsoon(Nof, 1979, Said, 1981, Wahby and Bishara, 1981, Béthoux, 1984, Rohling and Bryden, 1992). This had an important impact on the formation of Mediterranean deep-water (Rohling and Bryden, 1992, Boscolo and Bryden, 2001, Skliris and Lascaratos. , 2004, Skliris et al., 2007). Rossignol-Strick first described the time rework between the time of insolation-driven monsoon maxima and sapropel formation (Rossignol-Strick et al.,1982) and evaluated the formation time of sapropel from Miocene to the present. This is further evidence that sapropel in the central and eastern Mediterranean were commonly formed at times when perihelion falls in northern hemisphere summer. A precession minimum refers to an increase in summer insolation and a decrease in winter insolation, which increases the seasonal contrast and enhances summer monsoon intensity. Not every precession minimum form sapropel, but coincides with high-amplitude precession minima(insolation maxima) (Hilgen, 1991a, Hilgen, 1991b, Hilgen et al., 1993, Hilgen et al., 1995, Lourens et al., 1996, Lourens et al., 2001).

### 3. Stable isotope

As we all know, matter is composed of atoms, atoms are composed of nucleus and electrons. Nucleus are composed of protons and neutrons. The nucleus is positively charged due to the presence of protons, attracting negatively charged electrons outside the nucleus by binding force. We will place atoms with the same number of nuclear charges as a class of elements. We call different nuclides of the same element with the same number of protons and different numbers of neutrons as isotopes. Isotopes occupy the same place in the periodic table, their chemical properties are almost identical, but their physical properties (e.g., atomic mass, ability to diffuse in a gaseous state) is not the same as radiological transition. There are many ways to produce isotopes, which can be simply divided into naturally generation and artificially generated (bombardment with nuclear particles or neutrons). Isotopes are divided into two categories: stable and unstable. Some isotope atomic nuclear energy spontaneously emits particles or rays, releasing a certain amount of energy, while the number of protons or neutrons changes, thus transforming into the nucleus of another element. This property of the elements is called radioactivity, such a process is called radioactive decay, and these elements are called radioactive elements. Elements with an atomic number above 84 are radioactive isotopes, and there are 34 commonly used. Radioisotopes play a key role in experiments on absolute age determination of paleoclimatic archives.

A stable isotope is defined as an isotope of an element with a half-life greater than 10<sup>15</sup> years. These elements are not prone or extremely vulnerable to radioactive decay. There are currently 81 known stable isotopes for occurrence, and the total number of stable isotope species is now more than 300. Stable isotopes are often used to reconstruct paleoclimates and environments, such as carbon and oxygen isotopes to reconstruct paleoceanic temperatures. The isotopic composition of an element is often expressed as isotopic abundance, which is the ratio of the number of atoms of a particular isotope to the total number of atoms of an element in a mixture of isotopes. In general, although an element will have multiple isotopes, only one isotope occupies the main prevailing. For example, oxygen has three isotopes, and their relative abundances are: <sup>16</sup>O = 99.762%;

$^{17}\text{O} = 0.038\%$ ;  $^{18}\text{O} = 0.200\%$ 。

The isotope effect refers to the difference in the physical and chemical properties of isotopes with different masses and their compounds. In general, the greater the relative mass difference of the isotope of the element, the more significant the isotope effect. The partitioning of isotopes between different substances or phases in different proportions due to the isotope effect is called isotope fractionation (Hoefs, 1997; Criss, 1999).

Isotope fractionation is generally divided into two categories: equilibrium isotope fractionation and kinetic isotope fractionation. The former determined on differences of thermodynamics properties in molecules established by different isotopes (Urey, 1947). Because different isotopes have different chemical bonds, light chemical bonds are more likely to break than heavy chemical bonds during chemical and physical reactions. In kinetic isotope fractionation, react is unidirectional, which usually occurs during respiration and photosynthesis. Because light isotopes have higher mobility, they have a higher probability of collisions, so light isotopes react faster than heavy isotopes.

In geoscience experiments, we need to obtain information by comparing the concentrations of different isotopes, so we usually measure the relative abundance of samples through mass spectrometers, which are based on mass spectrometry - that is, the method of separating moving ions according to their mass-to-charge ratio with electric and magnetic fields. However, due to the limited sample mass and extremely small content, we often cannot accurately indicate the exact mass of the isotope, so in 1997 Hoefs introduced the concept of relative concentration: comparing the isotope concentration of the sample with the standard reference sample concentration. The isotope ratio  $R$  of the sample to be measured is compared with the isotope ratio  $R_{st}$  of the standard material, and the experimental results are expressed by delta ( $\delta$ ), which indicates the thousandth deviation of the isotope ratio of the sample relative to the isotope ratio of the standard sample. When the  $\delta$  is positive, it indicates that the sample is enriched with this isotope relative to the standard, and the opposite is true when the  $\delta$  is negative. When the  $\delta$  is 0, it indicates that the sample has the same ratio to the standard isotope.

$$\Delta (\text{‰}) = (R/R_{st} - 1) \times 1000$$

For different elements, there are many different standards for the standard samples

mentioned in the formula, each suitable for different analytical environments. When different criteria are selected, the  $\delta$  values are also different. For oxygen isotopes and hydrogen isotopes, there are two commonly used standards: SMOW (Standard Mean Ocean Water) and NBS-1 (National Standard Bureau). There is only one standard we commonly use for carbon isotopes, namely: PDB (Pee Dee Belemnite). For the S isotope standard: CDT (Canyon Diablo Troilite).

Among them, the general oxygen isotope analysis results are based on SMOW as the standard, but in the oxygen isotope analysis of carbonate samples related to paleotemperature, it is customary to use PDB standards. PDB is an American archery rock in the Cretaceous Pidi Formation of South Carolina, United States, originally prepared by the University of Chicago and now depleted, but it is still used in the literature as a standard for carbon isotopes.

### 3.1 Carbon isotope

Carbon is in the second period IVA group of the periodic table. The chemical symbol is C. The atomic weight of carbon is taken as the average value weighted by the abundance of two isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$ , and 12.01 is generally used in calculation.  $^{12}\text{C}$  is the scale defined by moles in the International System of Units, with 12 grams of  $^{12}\text{C}$  containing 1 mol of atoms. It is solid at room temperature and chemically stable. It is not easily reactive and exists in nature both in elemental form (EG. diamond, charcoal, graphite) and in the form of compounds (EG. carbon dioxide, calcium carbonate). It is widely distributed on Earth and is an important part of the composition of organic and inorganic matter. A series of carbon compounds are the foundation of organic matter, such as five-carbon sugars and proteins, and it also participates in important biochemical reactions such as respiration and photosynthesis like oxygen. Regarding inorganic substances, carbon also has a variety of allotropes, such as diamond, graphite, graphene, etc. In addition, carbon is one of the components of pig iron, wrought iron and steel, these allotropes are widely used in aviation, medical, petrochemical, defense, and other fields. Carbon can chemically self-combine to form many compounds, which are biologically and commercially important

molecules.

There are 15 isotopes of carbon, from  $^8\text{C}$  to  $^{22}\text{C}$ . Except for  $^{12}\text{C}$  and  $^{13}\text{C}$ , which are stable isotopes, the remaining 13 species are radioactive.  $^{12}\text{C}$  dominates among the isotopes of carbon, with a content of about 98.93%, followed by  $^{13}\text{C}$ , which has a content of about 1.07%.  $^{14}\text{C}$  has a half-life of about 5760 years and decays in  $\beta$  decay. C is one of the constituent elements of organic matter, when the organism is alive, the  $^{14}\text{C}$  content in the body is roughly unchanged. When the organism stops breathing after death, and the  $^{14}\text{C}$  in the body begins to decay and decrease. Therefore, one can estimate the absolute age of an antiquity by measuring its  $^{14}\text{C}$ , which is called carbon dating.

The amount of carbon on Earth is a valid constant, labeled Total carbon ( $C_{\text{tot}}$ ), which contains organic carbon ( $C_{\text{org}}$ ) and inorganic carbon ( $C_{\text{ing}}$ ). Most of this carbon is stored in the lithosphere, containing organic or inorganic carbon, mainly calcium carbonate. This part of the carbon is about 66 million Gt. The second largest carbon reservoir is the deep sea, which is much larger than the atmosphere and shallow sea, and is also closely connected to the atmosphere. The solubility of carbon dioxide depends on pressure, salinity and temperature, the higher the temperature, the lower the solubility, so it is released by seawater in the tropics and absorbed at the poles. The flow of carbon through the five global spheres constitutes the carbon cycle, and at the same time it also transitions between inorganic and organic matter many times, but most of the time it remains in the form of carbon dioxide. In shallow seas and on land, the exchange of carbon between the ocean and the atmosphere is very fast, and these processes react mainly through carbon dioxide (Vogel et al., 1970). The exchange of carbon between shallow and deep oceans is slow, measured in millennia, and relies mainly on thermocline and ocean current cycles. The longest carbon cycle involves the lithosphere, where animals and plants are buried after death, and organic carbon forms rocks such as black shale after geological processes measured in millions of years. There is also an erratic flux, which is a volcanic eruption produced by deep Earth. It rapidly releases large amounts of carbon dioxide from the lithosphere into the air, thus compensating for the slow rate of carbon exchange in the lithosphere and replenishing the amount of carbon dioxide in the atmosphere.

In the ocean, carbon comes in three main forms: Particulate Organic Carbon (POC), Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC). Their levels are, from highest to lowest: 37,000 Gt are DIC, 700 Gt are DOC, and 20 Gt are POC.

In the above, we mentioned that the carbon exchange between shallow waters and the atmosphere is mainly mediated by carbon dioxide, and in the photic zone, carbon dioxide dissolved in seawater is consumed by photosynthesis. And in this process, the priority is  $^{12}\text{C}$ , which is used to build the organism, and the shell is built with the precipitated  $^{13}\text{C}$ . Thus,  $^{12}\text{C}$  is enriched in photic zone microorganisms and  $^{13}\text{C}$  in photic zone seawater. Most of the organic matter is decomposed and consumed in the photic zone, and the remaining small amount of carbonaceous organic matter sinks into the deep sea with the "pelagic rain" and is oxidized. Therefore, there will be a gradient difference between the  $^{13}\text{C}$  concentration in shallow water and deep sea, and the larger the gap, the stronger the productivity of the photic zone (Shackleton et al., 1983). Also because of the existence of poor gradients, shallow planktonic foraminifera shells were enriched at  $^{13}\text{C}$ , and benthic foraminifera shells were enriched at  $^{12}\text{C}$  (Woodruff et al., 1980; Faul et al., 2000).

When the carbon on the seafloor is oxidized and respired, it is released again into the seawater and is carried back to the surface with rising currents and released into the atmosphere. This process is called the "ocean carbon pump" by Volk and Hoffer. It follows that the circulation of  $\delta^{13}\text{C}$  in the ocean depends on ocean circulation, which is a slow and complex process (Kroopnick et al., 1972; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz and Fairbanks, 1994).

In summary, the  $^{13}\text{C}$  content in the foraminifera shell is always in balance with the  $^{13}\text{C}$  content in the surrounding seawater, so when we measure the  $^{13}\text{C}$  information, we can understand its variations in primary productivity, oceanic circulation, and rotation of glacial and interglacial periods (Shackleton, 1977).

But in fact, when  $^{13}\text{C}$  is used as a climate proxy, it cannot clearly indicate a change in certain conditions, because it is affected by many factors, such as surface runoff, ocean circulation, etc. So, my interpretation of it is inferential. When the gap between  $\delta^{13}\text{C}$  in planktonic foraminifera and benthic foraminifera increases, or when benthic foraminifera  $\delta^{13}\text{C}$  becomes "light", it represents an increase in primary productivity, which may correspond



to possible factors such as melting glaciers, increased monsoon intensity, or weakened ventilation on the seabed. It is easy to understand that when glaciers melt or monsoon intensities increase, they cause increased river runoff, which allows rivers to carry more nutrients into the ocean, thus promoting the rapid reproduction of photic zone foraminifera. Especially when glaciers melt, forests and vegetation cover are small, which allows rivers to deliver nutrients directly to the ocean. When photic zone foraminifera multiplies rapidly, primary productivity increases, and the  $^{13}\text{C}$  content of the surface water increases, and correspondingly, the  $^{13}\text{C}$  content of the seafloor decreases.

Another possibility, when the thermohaline circulation strength decreases, the oxygen in the bottom water cannot be replenished in time, resulting in a poorly ventilated and oxygen-deprived environment. In this environment, the  $^{12}\text{C}$  produced by biological respiration is used to construct calcium carbonate, the shell of the foraminifera, thus forming a case of light  $\delta^{13}\text{C}$ .

### 3.2 Oxygen isotope

Oxygen, the element symbol O, is in group VIA of the second period of the periodic table. Oxygen is the most abundant element in the earth's crust, its content is about 48.6%, and it is also an important part of organisms and plants, participating in important biochemical reactions such as photosynthesis and respiration.

There are three isotopes of oxygen,  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ . Among them, the most abundant is  $^{16}\text{O}$ , which occupies an absolute dominant position, its content is 99.762%, it has 8 protons and 8 neutrons, called light oxygen. This is followed by  $^{18}\text{O}$ , which is called heavy oxygen, which has 2 more neutrons than  $^{16}\text{O}$ , and its content is about 0.200%. The rarest is  $^{17}\text{O}$ , which has a content of 0.038%.

The amount of oxygen isotopes varies greatly in different regions and in different processes, and it varies from -2‰ to -22‰, which is called "Rayleigh distillation" (Gat, 1966). For example, water molecules composed of  $^{16}\text{O}$  are more volatile due to different chemical bonds, because "light water" has a higher vapor pressure than "heavy water". Therefore, when seawater is heated and evaporated, the  $\delta^{16}\text{O}$  value in the water vapor is

greater than the  $\delta^{18}\text{O}$  value, and  $\delta^{16}\text{O}$  is enriched. In contrast, in the process of precipitation, "heavy water" is more likely to be released, so the  $\delta^{16}\text{O}$  value in rainfall is less than the  $\delta^{18}\text{O}$  value. This property binds to dimensions to produce a "Latitudinal Effect", meaning that isotopes are depleted as the dimension increases. This is a concept that Dansgaard proposed in 1964. Due to the hydrological cycle and atmospheric circulation, the  $^{16}\text{O}$ -enriched water will continue to evaporate from the seawater, continuously releasing "heavy water" during the journey to high latitudes, and finally releasing  $^{16}\text{O}$ -enriched light water at high latitudes as  $^{18}\text{O}$  is depleted. When it is called polar snowfall, a very low  $\delta^{18}\text{O}$  value is recorded in the ice core. This difference in isotopic content is closely related to other factors such as dimension, salinity and so on. Therefore, when the climate changes, the ice cores of the polar regions and the oxygen isotopes in the foraminifera that live in seawater are recorded as good carriers.

As early as the 40s of the last centuries, Urey pioneered the work of restoring paleotemperature using foraminifera oxygen isotopes. Urey noticed that certain effects in nature lead to isotope enrichment, and foraminifera that secrete calcium carbonate in water use oxygen during metabolism and tend to enrich  $^{18}\text{O}$ . For example, the  $^{18}\text{O}/^{16}\text{O}$  ratio of water is 1/500, and at 0 °C, when the equilibrium of water and calcium carbonate exchange oxygen isotopes, the  $^{18}\text{O}/^{16}\text{O}$  ratio of calcium carbonate is 1.026/500, and at 25 °C, the  $^{18}\text{O}/^{16}\text{O}$  ratio of calcium carbonate is 1.022/500. This indicates that the isotopic composition of calcium carbonate is related to the temperature and composition of its precipitated aqueous solution. He made a hypothesis that when we know the ratio of oxygen isotopes, we can infer the ambient temperature of the period in which the foraminifera lived. Thus, they published the Epstein formula a few years later:

$$T=16.5-4.3(\delta_{\text{carbonate}}-\delta_{\text{seawater}})+0.14(\delta_{\text{carbonate}}-\delta_{\text{seawater}})^2$$

But it still has some problems, such as the isotopic values of seawater in the past. As people's understanding deepened, the formula was continuously improved in the following years.

In the 50s, Emiliani for the first time identified the cold and warm cycles recorded by oxygen isotope information based on foraminifera species changes. This also confirms that oxygen isotopes are one of the potentially effective proxies for studying paleoclimate.

But until the 70s, most Quaternary workers did not accept the gyration information recorded by deep-sea drills, and still relied on the four ice ages identified by continental glaciers. It was not until Hay first completely extracted eccentricity, slope, and precession cycles from foraminifera oxygen isotopes in 1976 that the cold and warm cycles corresponding to foraminifera oxygen isotopes were gradually accepted, and Milankovic's theory gradually became the mainstream theory of Quaternary climate from this point on. After that, a lot of high-resolution oxygen isotope records were published, such as the work of Lisiecki and Raymo in 2005, after compiling various drilling data of the past 5300ka, the climate change revealed by the oxygen isotope of benthic foraminifera was summarized: the overall manifestation of the past 5.3 Ma climate showed a cooling trend, and the amplitude of oxygen isotopes continued to increase; the main control period of the rotation changed from 1.2 Ma to 100ka; the climate rotation change was "canine-like". Rapid end of ice ages; Since the late Pleistocene, glacial change in the Northern Hemisphere precedes climate change. In studies of the Pleistocene, isotopes were used to reconstruct paleotemperature versus the extent of the Northern Hemisphere ice sheet (Shackleton Nj. 1967)

In the study of paleotemperature, we must first select the appropriate isotope standard, and then convert the oxygen isotope into relative concentration according to the formula mentioned in the previous chapter and divide it into "light" and "heavy" according to its value. According to the oxygen isotope properties mentioned above, during the ice age, due to the increase in snowfall and the growth of glaciers, more and more water molecules composed of  $^{16}\text{O}$  are carried into the ice cores at the poles with precipitation, leaving a "light" oxygen isotope record. In contrast, due to the loss of  $^{16}\text{O}$ , the content of  $^{18}\text{O}$  in seawater gradually increases, thus leaving a "heavy" record in the record of foraminifera. In interglacial periods, the opposite is true. As temperatures rise, glaciers at the poles and continents melt one after another, and sea levels rise bring with it a large amount of fresh water composed of  $^{16}\text{O}$ , so the "heavy" record in seawater falls back and slides to the more "light" side.

At the same time, it is also a good indicator of freshwater influx. The delta  $^{18}\text{O}$  value in freshwater, especially heavy precipitation caused by monsoons, is much smaller than in

seawater (Abell and Hoelzmann, 2000, Gasse, 2000, Hoelzmann et al., 2000, Rodrigues et al., 2000, Beuning et al., 2002). Therefore, the  $\delta^{18}\text{O}$  data of the planktonic foraminifera shell at this time will show a lower value.

Due to the close response of deep-sea oxygen isotopes to orbital parameters, oxygen isotope cyclostratigraphy has also gradually developed, and by comparing the results of magnetic stratigraphy and biostratigraphy, a precise chronological sequence of deep-sea sedimentation can be established. Oxygen isotope stratigraphy is extrapolated to other indicators, such as ice cores and stalagmites, which not only provides a high-resolution time scale for these excellent paleoclimatic records, but also provides a basis for comparing climate change of different indicators.

## 4. Astrochronology

Astrochronology consists in dating sedimentary units by means of their calibration with the time series deriving from orbital parameters. This theory is based on the assumption that the gravitational force between the Sun-Earth-Moon system and the Earth and other planets in the Solar System can generate periodic changes in the parameters of the Earth's orbit and rotation parameters.

The orbital structure and main astronomical parameters of the Earth-Sun system basically depend on three parameters: eccentricity, obliquity, and precession.

-Eccentricity:

The Earth orbits the Sun in an elliptical orbit, the shape of which is not fixed, and the degree of its "circle" or "flat" is expressed by eccentricity ( $e$ ), with  $E$  varying from 0- to 0.07. Smaller  $e$  indicates closer to the circle orbit and larger  $e$  indicates flat orbit. The current eccentricity of the Earth's orbit  $e = 0.0167$ . Its periods of change are 100,000 years and 400,000 years.

-Obliquity:

The angle between the Earth's axis of rotation and the axis of rotation, also known as the tilt of the Earth's axis, slowly changes between  $21.5^{\circ}$ - $24.5^{\circ}$ , with a period of about 41,000 years; the change of inclination affects the difference in incidence of solar radiation between the latitudes of the earth, and the smaller inclination of the Earth's axis means that the high latitude region receives more solar radiation, such as increased insolation in the polar regions and decreased insolation in low latitudes.

- Precession:

Due to the gravitational pull of the Sun, Moon and other celestial bodies, the position of the Earth's axis is constantly moving, and this movement is not parallel, but a "shaking head motion" around a certain axis (yellow pole). "Precession is used to describe how much the Earth's axis changes in motion. When the geo-axis sways, the corresponding equatorial plane and ecliptic plane also move slowly, resulting in the position of the spring and autumn equinox on the ecliptic plane. Its precession period is about 2.6 and 19,000 years; Precession is the main cause of seasonal climate variation, causing the four seasons

to be opposite in the northern and southern hemispheres.

At the beginning of the 20th century, the astronomical community grasped the law of the three elements of the Earth's orbit over the past 600,000 years. Milankovic believed that changes in the orbit of the three elements would lead to changes in the amount of solar insolation received by the Earth, and thus changes in climate. In order to test this conjecture, he calculated the change curve of the total amount of astronomical radiation in the summer and winter half of the year caused by the changes in the three elements of the Earth's orbit at different latitudes in the past 600,000 years. Milankovic compared the solar radiation change curve with the model of Quaternary climate change provided by geologists and found similarities between the two, so he proposed Milankovic's theory to prove that the growth and decline of ice sheets are related to sunlight.

In the 1970s, scientists obtained an oxygen isotope record of foraminifera in deep-sea sediments, revealing that Pleistocene climate change has 100,000, 40,000, and 20,000-year cycles, confirming that changes in Earth's orbital parameters are pacemakers for glacial cycles (Hays et al., 1976). At the same time, astrochronology is very effective and accurate as a method for dating sedimentary sequences, and most of the isotopes and sedimentary sequences of nearly 60 Ma can be calibrated with the representative time series The climatic oscillations caused by theorbital parameters. (Hays et al., 1976).

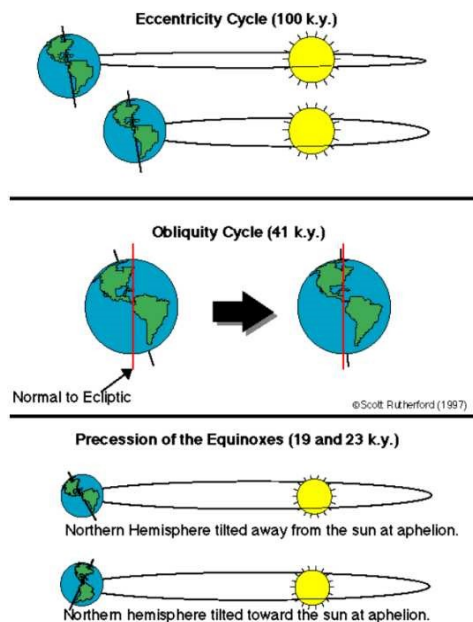


Figure 4.1 Main orbital parameters, (S. Rutherford, 1997).

## 5. The foraminifera

### 5. 1 The foraminifera

To date, there are about 6,000 officially described living foraminifera, and the known fossil species greatly exceed this number.

Foraminifera are eukaryotic protists found in both fresh and salt water, but most foraminifera live in salt water. Most of them are about a millimeter in diameter. They consist of multiple chambers, connected by "foramen" on the septa between each chamber, hence the name foraminifera. The organism of the foraminifera is a single cell formed by protoplasm, divided into two parts: the peripheral ectoplasm and the middle endoplasm, which extends out of the filamentous or branched pseudopodia, has the function of preying (e.g., organic matter, bacteria, diatoms), and can promote the movement of foraminifera; endoplasm contains nuclei and food bubbles.

According to the composition of the shell, foraminifera can be roughly divided into three categories: organic test, Agglutinated or Arenaceous test and Calcitic test.

Organic test is composed by a proteinaceous mucopolysaccharide, the test is thin and flexible, it can change its shape. Agglutinated or Arenaceous test is the application of foreign particles (e.g., Sand, diatoms, calcareous nannofossils, etc.) are made with organic, siliceous or calcite glued together. Calcific tests are composed of tiny, closely packed grains of calcium carbonate, but with no obvious cement. In general, the concentration of carbon-oxygen isotopes in the shell is in balance with the carbon-oxygen isotopes in their living environment.

According to the ecological taxa, foraminifera can be divided into two categories: planktonic foraminifera and benthic foraminifera.

Modern planktonic live in water bodies from the surface layer to depths of more than 1000 meters, they are very sensitive to the surface temperature of seawater, and their populations have obvious characteristic changes with dimensional changes and can reconstruct the paleoprimary productivity change curve according to their  $\delta^{13}\text{C}$  changes or use their  $\delta^{18}\text{O}$  to reduce sea surface temperature.

Benthic foraminifera live at the junction of seafloor sediment and water, the temperature of the seabed water mass is low, the physical and chemical properties are relatively stable,

and it is easy to evolve a highly specialized benthic foraminifera population, so it can restore the physicochemical interest of the paleo water mass according to its population characteristics. Dissolved oxygen content and organic matter flux in seawater are two important parameters to control the community composition of benthic foraminifera and the distribution of benthic foraminifera in sediments. (Jorissen et al., 1995) Subdivide benthic foraminifera into three types according to their depth of life in sediments: epifauna, shallow infauna, and deep infauna. Jorissen et al. (1995) summarized the relationship between dissolved oxygen content, nutrient capacity, sedimentation, and distribution of benthic foraminifera in seawater, and established the TROX model (Figure 5.1)

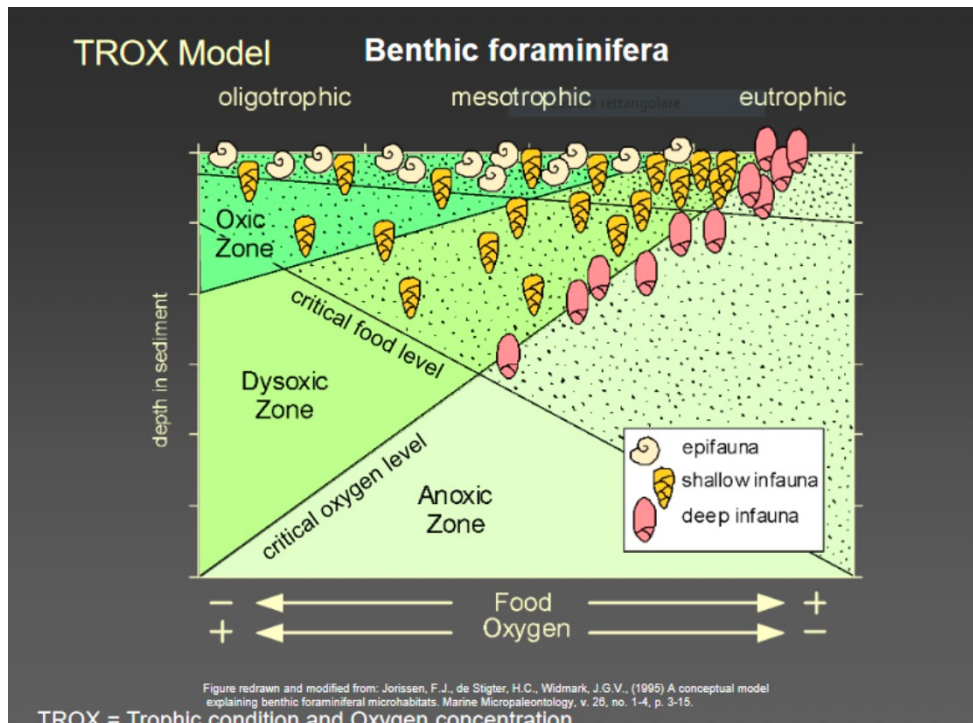


Figure 5.1 Diagram of the vertical variability of distribution of infaunal benthic foraminifera, based on the amount of oxygen present within the sediment (Van derZwaan et al., 1990)

The model reflects the relationship between high dissolved oxygen content in seawater, organic matter flux, and distribution of benthic foraminifera.

Through the analysis of benthic foraminifera isotopes, relative abundance, foraminiferal assemblages, we can learn the physicochemical information of paleo seawater. Such as: changes in organic matter flux in seawater. Its indicators mainly include benthic



foraminifera accumulation rate (BFAR) and "U+B" content. Herguera and Berger proposed this concept in 1991, for every 1 mg of organic carbon entered the seafloor, a benthic foraminifera > 150 µm in size is generated. The "U+B" content refers to the proportion of *Uvigerina peregrina* and *Bulimina aculeata* to the entire benthic foraminifera community. In addition, the most important thing is the establishment of an oxygen isotope underlying framework by benthic foraminifera shell  $\delta^{18}O$  and the reconstruction of global climate change trends over geological time.

However, foraminifera are greatly affected by water masses, and local changes in water temperature or physicochemistry can also have significant effects, sometimes these changes are not related to climate change. And the indicator of foraminifera has limitations, such as BFAR is available in the South Sea of China, but not necessarily effective in the Mediterranean. It is difficult for a single indicator to cover all the influencing factors and cannot comprehensively reconstruct the paleoenvironmental information, so the paleoenvironment and paleoclimate change can be accurately constrained by establishing a comparison of multiple climate record indicators. At present, the most ideal research methods should be: organic indicators, inorganic indicators and simulated climate models. Integrate all indicators and exclude inaccurate information on a single indicator.

#### *Uvigerina peregrina*

The carbon-oxygen isotopes analyzed in this paper are from *Uvigerina peregrina*. It is an infaunal and therefore can provide information on seafloor water masses. It often lives in high organic fluxes and high concentrations of bacteria (Mackensen et al., 1995) and low temperatures (Altenbach and Sarnthein, 1989). The foraminifera of this family all have similar characteristics. It has a transparent shell characterized by a triserial test, a terminal aperture with a neck, and a phyaline lip (Loeblich and Tappan, 1988).

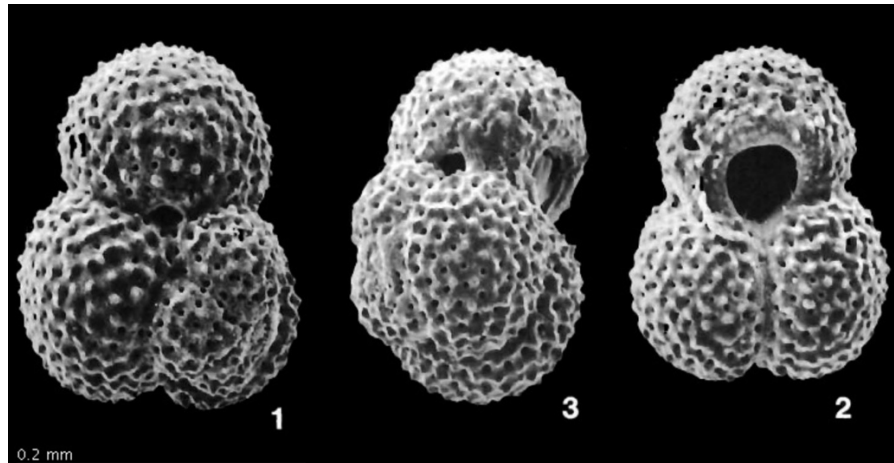


Figure 5.1.1 different views of the “normal” morphotype *Globigerinoides ruber* . Test size is ca. 200  $\mu$ m  
(Modified from Kennett & Srinivasan, 1983).

### *Globigerinoides ruber*

It is a kind of planktonic foraminifer. Reghellin used it in 2010 to obtain the carbon-oxygen isotope curves of PCS cores with *Uvigerina peregrina*. (Reghellin, 2010) Similar to *Uvigerina peregrina*, it also lives in high organic matter fluxes. But unlike *Uvigerina peregrina*, *Globigerinoides ruber* usually lives in warm waters, such as tropical and subtropical waters. It is usually white, but sometimes pink and varies greatly in morphology. Therefore, its specific classification has been controversial (Aurahs et al., 2011). It is extensively used to reconstruct past sea-surface temperature (SST) and paleoproductivity.

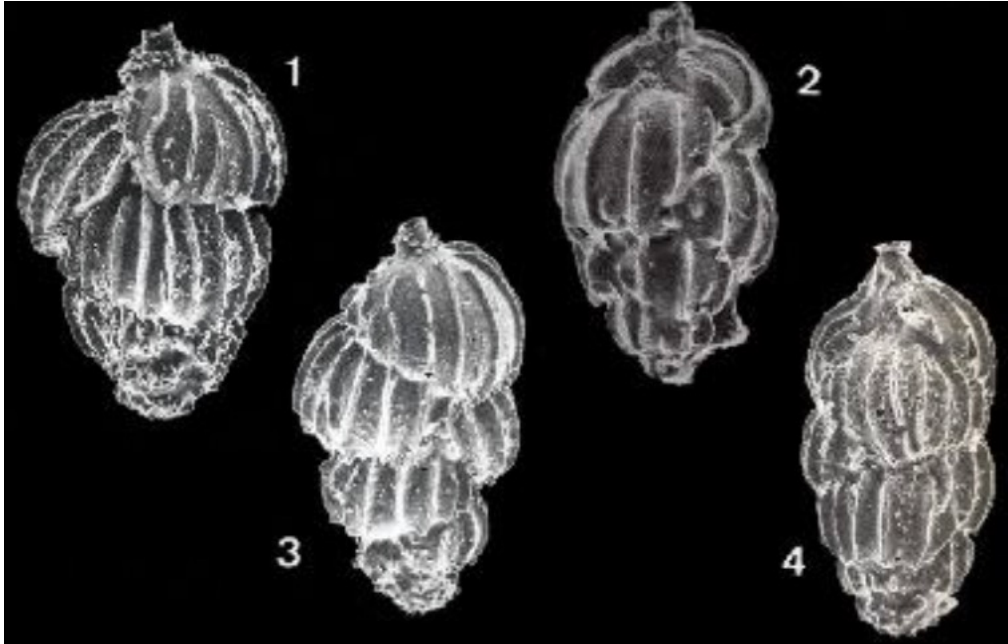


Figure 5.1.2 Different views of *Uvigerina peregrina*. Test sizes are ca. 250  $\mu$ m (Modified from Boersma, 1984)

## 5.2 Productivity

Biological productivity refers to the ability of organisms to produce (or accumulate) organic matter through assimilation. It includes: primary productivity, the rate at which autotrophic organisms produce organic matter through photosynthesis or chemical synthesis; secondary productivity, the rate at which consumers at all levels, other than producers, directly or indirectly use the organic matter already produced through assimilation and absorption and conversion into their own substances; Net community productivity, storage rate of organic matter that has not been heterotrophic during the production season or during the study period of one year.

There are three main factors that affect the primary productivity of the ocean: light, nutrients and temperature.

The impact of light on primary productivity is mainly divided into two parts: irradiation intensity and compensation depth. Under low irradiation conditions, the light is limited, the speed of photosynthesis is limited by the photochemical reaction, and the photosynthetic production is proportional to the light intensity; under slightly stronger irradiance, the photosynthesis curve bends and gradually becomes parallel to the

horizontal illumination intensity axis, which is that photosynthesis is limited by the speed of enzymatic reaction, and photosynthesis reaches saturation; the irradiance continues to increase, and the overall rate of photosynthesis decreases. Compensation depth refers to the depth at which solar radiation enters seawater and weakens with increasing depth, when the amount of oxygen produced by photosynthesis is exactly equal to the amount consumed during its respiration.

The main types of nutrients are nitrate, phosphate, and some trace elements such as Fe, Mn, Cu, etc. In the ocean, additional sources of this class of nutrients are usually surface runoff (river input) and rising currents.

In tropical seas, the stratification of water bodies caused by temperature will affect the rise of nutrients, etc., so that the primary productivity of the upper water is maintained at a low and stable level. In temperate regions, there is usually only temporary stratification.

In this thesis, I am discussion about bottom water biological productivity, the limiting factors of which I simplify to carbon flux and oxygen, and in the study of Reghellin (2011), he found that in the clays immediately underlying the laminated intervals, dramatic turnovers in the benthic microfauna document a transition of the sedimentation area to anoxic conditions. This also proves that oxygen is a stronger restriction in the bottom water in the study area than overall carbon fluxes. Therefore, in this discussion, bottom water ventilation is used as a limiting condition for seabed biological productivity. When  $^{13}\text{C}$  is raised, it represents increased ventilation and increased biological productivity of bottom water; When  $^{13}\text{C}$  decreases, it represents a decrease in the biological productivity of the bottom water.

## 6. Mediterranean Sapropel

The word SAPROPELS was first coined in 1904 by Potonié, which is derived from the Greek word meaning decomposed and mud. His interpretation of the term is an organic-rich dark sediment deposited under stagnant water. Initially, sapropel was thought to be a black shale. But alternating black layers rich in organic matter were found in cores obtained by a Swedish deep-sea drilling team in 1947, which were not black shale after lithological chemical composition. Eventually, in the Deep-Sea Drilling Program (DSDP), researchers discovered more layers of dark organic matter, and by studying their composition, they came up with the official definition of sapropel. Its official definition is "a discrete layer, greater than 1 cm in thickness, set in open marine pelagic conditions, and containing greater than 2.0% organic carbon by weight" (Kidd et al., 1978).

It is widely found in the Eastern Mediterranean and is a sign of hypoxia and poor ventilation on the seabed. At the end of the last century, many scientists studied Sapropel in the Eastern Mediterranean. They are often thought to have been caused by the strengthening African summer monsoon during the time of Precession Minima. When the monsoon strengthens, precipitation increases and runoff from the Nile increases, resulting in large amounts of fresh water flowing into the Eastern Mediterranean. Low-density fresh water will stratify with resident high-density seawater, weakening the exchange of substances between surface water and deep water, preventing oxygen supplementation, thus forming anoxia environment, preserved, and deposited organic matter. At the same time, nutrition brought by the Nile also increases primary production and increases oxygen consumption on the seafloor (Calvert et al., 1992). In addition to the strengthening of the monsoon, Rohling also believes that rising planes are also responsible for the formation of sapropel (Rohling et al., 2015, for sapropel S1).

As for the causes of sapropels, although many experiments and modeling have been conducted, the exact answer remains unknown. But based on these experiments, there is some speculation that its formation is related to the Haitian ventilation environment and biological productivity. In 2006, Bianchi proposed two models, the stagnation model and the increased biological productivity model.

In the Stagnation model, the sharp increase in freshwater, because the salinity of

freshwater is less than that of Mediterranean native seawater, resulting in stratification between water masses, weakening the oxygen exchange between the upper and lower water layers, and the oxygen consumed by the lower water cannot be replenished, so it stagnates and becomes an oxygen-deficient environment, and the remaining organic matter cannot be decomposed and preserved. The increase in freshwater may be due to increased precipitation due to enhanced monsoons, increased river runoffs, or melting glaciers. An increase in the elemental content of Be and the  $\delta^{18}\text{O}$  value of planktonic foraminifera can attest to the occurrence of this process.

In the increased biological, the increase in nutrients in the surface water causes the microbes in the photic zone to multiply, increasing primary production, and then more organic matter flowing to the ocean floor through "pelagic rain." Because there is too much organic matter flowing to the seafloor to be completely decomposed, there is a chance that it can be buried quickly. The increase in nutrients may be due to an increase in river runoffs.

The low nutrient content of the surface water in the Mediterranean and the good ventilation of the bottom layer make it difficult for organic matter to be preserved on the seabed, so the original hydrological balance needs to be upset to form sapropel. Changes in ocean currents are a response to changes in the climate system. At the same time, because of its semi-enclosed nature, the Mediterranean Sea is particularly sensitive to climate response, so good climate data and regularities on thermohaline circulation and gateway control have been recorded organic-rich sapropels (Dirksen, J.P., 2020; Rossignol-Strick, 1985; Rohling et al., 2015; Hilgen, 1991; Lourens et al., 1996; Cramp and O'Sullivan, 1999). In the current study, people are more inclined to think that the formation of sapropels is related to max. eccentricity, min. Precession related. This is easy to understand, and in the two models mentioned above, drastic changes in hydrological balance are key to causing sapropels to form. When the intensity of sunlight increases, it causes an increase in the thermal difference between sea and land (Rohling et al., 1991), so the monsoon in the southern Mediterranean intensifies, thereby increasing precipitation and river runoff. The intensity of sunlight is closely related to orbital parameters, and it has a precessional frequency with a lag of thousand years. So sapropels

may also be a potential new chronological tool.

## 7. Material and method

### 7.1 Material

Core PCS was collected by Luca Capraro et al., which is a ca. 90 m-long sediment core drilled immediately north of the village of Crosia, Cosenza province, Calabria, Southern Italy. Our sample starts from the lower 50m of the Core PCS and is called Lower Core PCS. The sampling interval is 10 cm, so the experiment has high resolution.



Figure 7.1 PCS core samples stored separately in plastic bags.

### 7.2 Preparation for sampling

The samples we used which are light brown, were individually packed in plastic bags, numbered from CCR700 to CCR964, CCR is abbreviation for “Carota Crosia”. The preprocessing work was carried out in the Micropaleontology lab of the University of Padua. We took a portion of each of the above samples as future samples for preprocessing, a total of 260, and weighed them to get total weight, initial weight. After weighing, the samples were individually placed in beakers and soaked for approximately 16 hours.

We wash the samples with water and filter them with sieves, The sieves are in two sizes, 2mm and 63 $\mu$ m. Ensure that leaving samples larger than 63  $\mu$ m in size, removing muddy and sandy deposits. The standard of cleaning is that the water flowing from the sieve becomes clean and free of suspended solids. After each cleaning of the sieve, soak the



sieves in copper sulfate solution for twenty seconds to dye the possible residual foraminifera blue. We dry these samples by drying oven at 50°C for 24h and weigh them to get a dry weight. Finally, we put the samples individually into antistatic plastic bags and mark them with numbers from CCR700 to CCR964.



Figure 7.2 Sample in evaporation dish and antistatic plastic

### 7.3 Picking

We transferred samples to an Earth science laboratory for picking by using an optical microscope. Firstly, we cleaned the sieve with a 150  $\mu\text{m}$  pore size by a dry brush to ensure that there is no residue. Then we used it to screen the samples, leaving particles between 150  $\mu\text{m}$  and 250  $\mu\text{m}$  in size. The samples were then evenly sprinkled on a tray, we picked *Uvigerina peregrina* with a brush dipped in deionized water under a light microscope. We select clean, complete, and large foraminifera, the standard is 10-15. Try to select foraminifera with no black deposits in the shell and no calcium carbonate coating outside the shell. We placed the selected foraminifera on glass slides and mark the corresponding number and recorded the characteristics of the sample and the number of foraminifera selected. When the amount of *Uvigerina peregrina* in the sample is very small, the smaller or broken ones can be selected as appropriate. But we tried not to pick black and blue foraminifera. Black means that it contains organic matter, which may interfere the isotope signal. Blue means that it is the foraminifera that remains on the sieve during the

preprocessing step and is not part of these samples. But in our experiments, CCR827-CCR844 did not have any *Uvigerina peregrina*. We put these samples into an ultrasound instrument in the Palynology lab to remove the encrustation and looked at them again under an optical microscope, but still did not find *Uvigerina peregrina*.

#### 7.4 Preparation for isotope analysis

After picking, we transferred the foraminifera to clean tubes with a brush dipped in deionized water, marked the corresponding label and the foraminifera number. Then we carry out the filling of MAQ1 for standard samples. MAQ1 is Carrara marble derived from the so-called "cava di Altissimo", a quarry that was owned by Michelangelo in person. Among the different available samples, the very first one provided the best and the cleanest chemical analyses. They are often used for the analysis control. Another standard sample is GR1, it is usually used for the calibration. This step is performed in the Spectroscopic Analysis Laboratory of the Department of Earth Sciences, where we load a standard sample measuring about 0.250 mg with a balance into test tubes and record the number of grams. When all samples and standard sets were filled, arranged the tubes in the order shown in the Figure 7.5. Placed the tube racks into the mass spectrometer rack for isotope analysis.

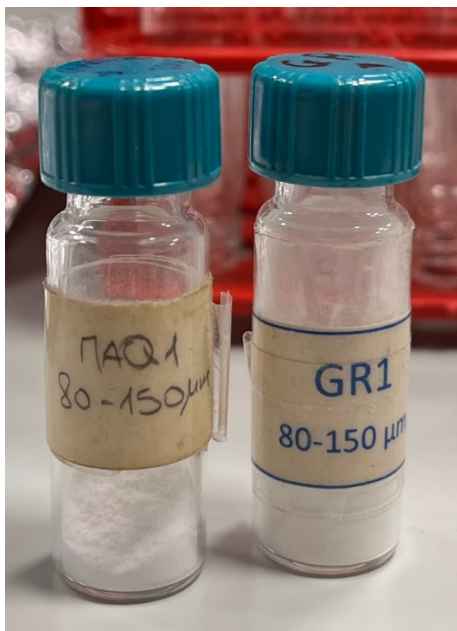


Figure 7.4 Standard samples GR1 and MAQ1

## 7.5 Analysis by mass spectrometer

The instrument used for this isotope analysis is the Thermo Scientific Delta V Advantage IRMS (Isotope Ratio Mass Spectrometer), which is connected to the GasBench II. The first step is to penetrate the rubber septum of the test tube through the thin needle, and helium flows into the test tube through the thin needle to isolate the air and drive away the existing carbon dioxide in the test tube. The second step is to inject phosphoric acid, which reacts with calcite in the foraminifera shell to release water and carbon dioxide. This step of the reaction needs to be carried out at 70°C and lasts about three hours. In the end, only Helium and Anhydride remain in the tube, which Products analyzes with a mass spectrometer.

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USER \_\_\_\_\_ DATE OF FLUSH \_\_\_\_\_  
 DATE OF SAMPLING \_\_\_\_\_ DATE OF ANALYSIS \_\_\_\_\_

1	VOID	17	25	33	41	49	57	65	73	81	89	
2	MAQ1 10	MAQ1 18	MAQ1 26	MAQ1 34	MAQ1 42	MAQ1 50	MAQ1 58	MAQ1 66	MAQ1 74		90	
3	MAQ1 11	19	27	35	43	51	59	67	75	83	91	
4	12	20	CR-1 28	36	44	52	60	68	76	84	92	
5	13	21	29	37	45	53	CR-1 61	69	77	85	93	
6	14	22	30	38	46	54	62	70	MAQ1 78	86	94	
7	15	23	31	39	47	55	63	71	MAQ1 79	87	95	
8	16	24	32	40	48	56	64	72	VOID 80	88	96	

Figure 7.5 The standard sample MAQ1 is placed in the marked position. Blank positions place experimental samples sequentially.

## 8.Result

In this experiment, we analyzed oxygen isotope and carbon isotope. The oxygen isotope curve of *Uvigerina peregrina* reflects the bottom water temperature on the continental shelf. Variation in oxygen isotope curve show significant fluctuations, such as the gyration between glacial and interglacial periods. During glacial periods, the lighter  $^{16}\text{O}$  first moves from the ocean to the land through precipitation, forming the ice sheet, so that  $\delta^{16}\text{O}$  in seawater decreases and  $\delta^{18}\text{O}$  increases. In general, heavier  $\delta^{18}\text{O}$  values represent glacial periods and lighter values represent interglacial periods.

In this study, I used the carbon isotope curve of *Uvigerina peregrina* as an indicator of the conditions of bottom water ventilation, and the lighter  $\delta^{13}\text{C}$  value represents a hypoxic environment with weak thermohaline circulation; A heavier  $\delta^{13}\text{C}$  value indicates a well-ventilated seabed.

Although the Mediterranean is a unique and special basin whose isotopic signal is strongly influenced by local evaporation and precipitation, glacioeustatic fluctuations still dominate among these factors. There was a good correlation between open ocean and Mediterranean reconstructed foraminifera signaling (e.g., Lisiecki and Raymo, 2005)。

We obtained the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  curves as shown by isotopic analysis of *Uvigerina peregrina*, as Figure 8.1 and Figure 8.2.

### 8.1 Oxygen isotope

In the figure, we can see that the  $\delta^{18}\text{O}$  values drift between 1.6‰ and 3.8‰, and the average of this set of data is 2.6‰. In this set of data, I define parts close to 4‰ as glacial periods and continuous portions less than 2‰ or less as complete interglacial periods. I can observe three glacial periods in GP1, GP2 and GP3, a complete interglacial period IP2, and three brief warm events IPA, IPB, IPC.

At -50m, the  $\delta^{18}\text{O}$  value is close to -3.5‰ at a high level, so it is called glacial GP1.  $\delta^{18}\text{O}$  then drops rapidly to about 1.8‰, but because it only drops briefly and then returns quickly, it is called a brief warm event IPA. Then  $\delta^{18}\text{O}$  returned to high values and entered the glacial GP2. But there were two warm events during the glacial period, and the  $\delta^{18}\text{O}$

value fell to about 2.3‰, which I call warm event ipc together. It is worth noting that sapropel also occurred during this interglacial period. At the bottom of the sample, the  $\delta^{18}\text{O}$  value rises to about 3.8‰ and enters the glacial GP3, but there is a brief warm event ipb during this period.

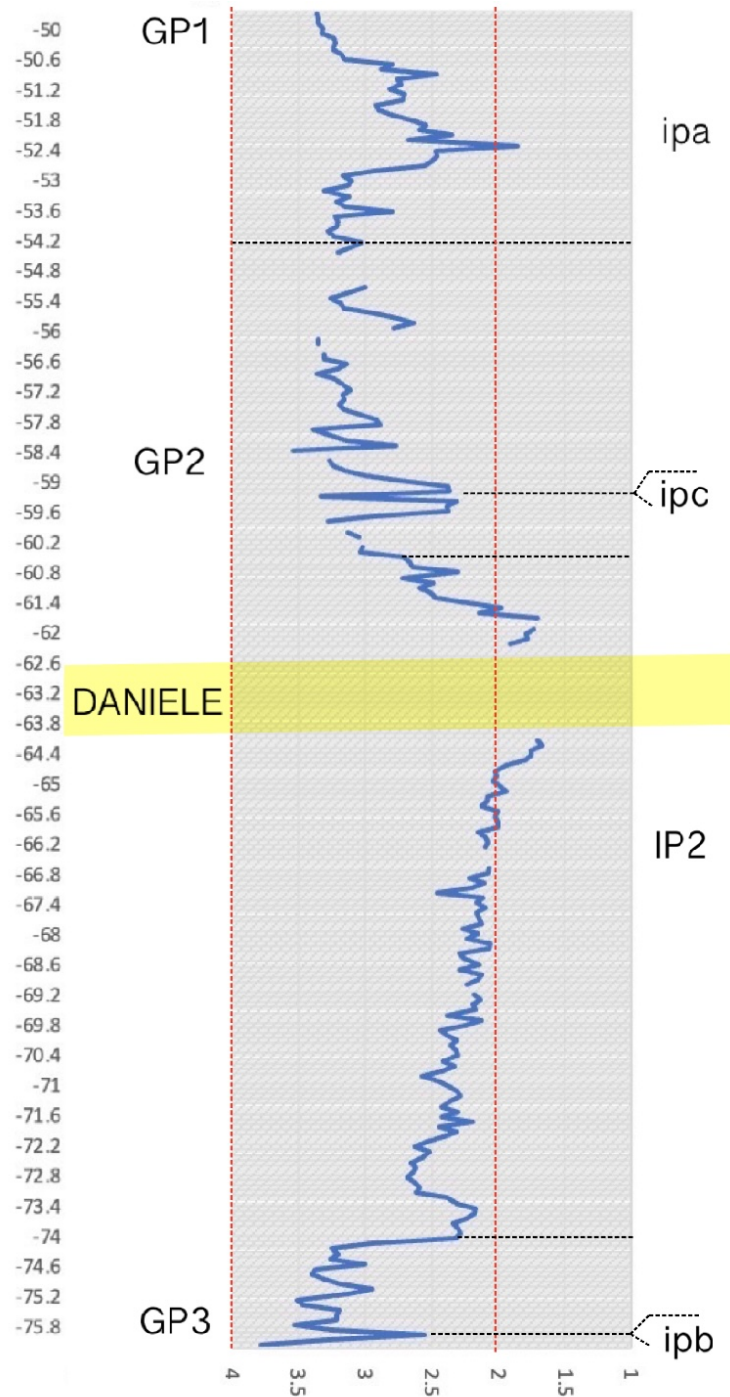


Figure 8.1 Benthic foraminifera *Uvigerina peregrina*  $\delta^{18}\text{O}$  record of the lower ca. 27 m of the PCS core.

## 8.2 Carbon isotope

In the study of Reghellin (2011), it was found that in the cays immediately underlying the laminated intervals, dramatic turnovers in the benthic microfauna document a transition of the sedimentation area to anoxic conditions. This also proves that oxygen is a stronger restriction in the bottom water in the study area than overall carbon fluxes. Therefore, in this discussion, bottom water ventilation is used as a limiting condition for bottom water biological productivity. When  $^{13}\text{C}$  is raised, it represents increased ventilation and increased biological productivity of bottom water; When  $^{13}\text{C}$  decreases, it represents a decrease in the biological productivity of the bottom water.

In the  $\delta^{13}\text{C}$  curve of this study (Figure 8.2), the maximum value is about 0.16‰, the minimum is about -1.5‰, and the maximum amplitude is about 1‰, but most of the data oscillates within -0.2‰ to -0.9‰. There are two peaks in the figure, one is the maximum at -58m, which is about 0.1‰, and the other is the lowest value at -73.4m, which is about -1.5‰.

Overall, PCS core's  $^{13}\text{C}$  record does not fluctuate much. From the top of the sample to the top of the sand layer, the bottom water  $\delta^{13}\text{C}$  value rises slightly. There are two large undulations between the bottom of the sand layer and the top of the sapropel, and the  $\delta^{13}\text{C}$  value increases from about -0.8‰ to about 0.1‰, and rapidly decreases to about -0.5‰, and then rapidly rises again to the highest value, about 0.16‰. The  $\delta^{13}\text{C}$  value begins to decline at -71.6 m, reaches a minimum at -74.4 m, about -1.5‰, and then gradually returns to the general level. In this period, the overall fluctuation of biological productivity is not large, but it increases and decreases significantly at -58m and -73.4m, respectively.



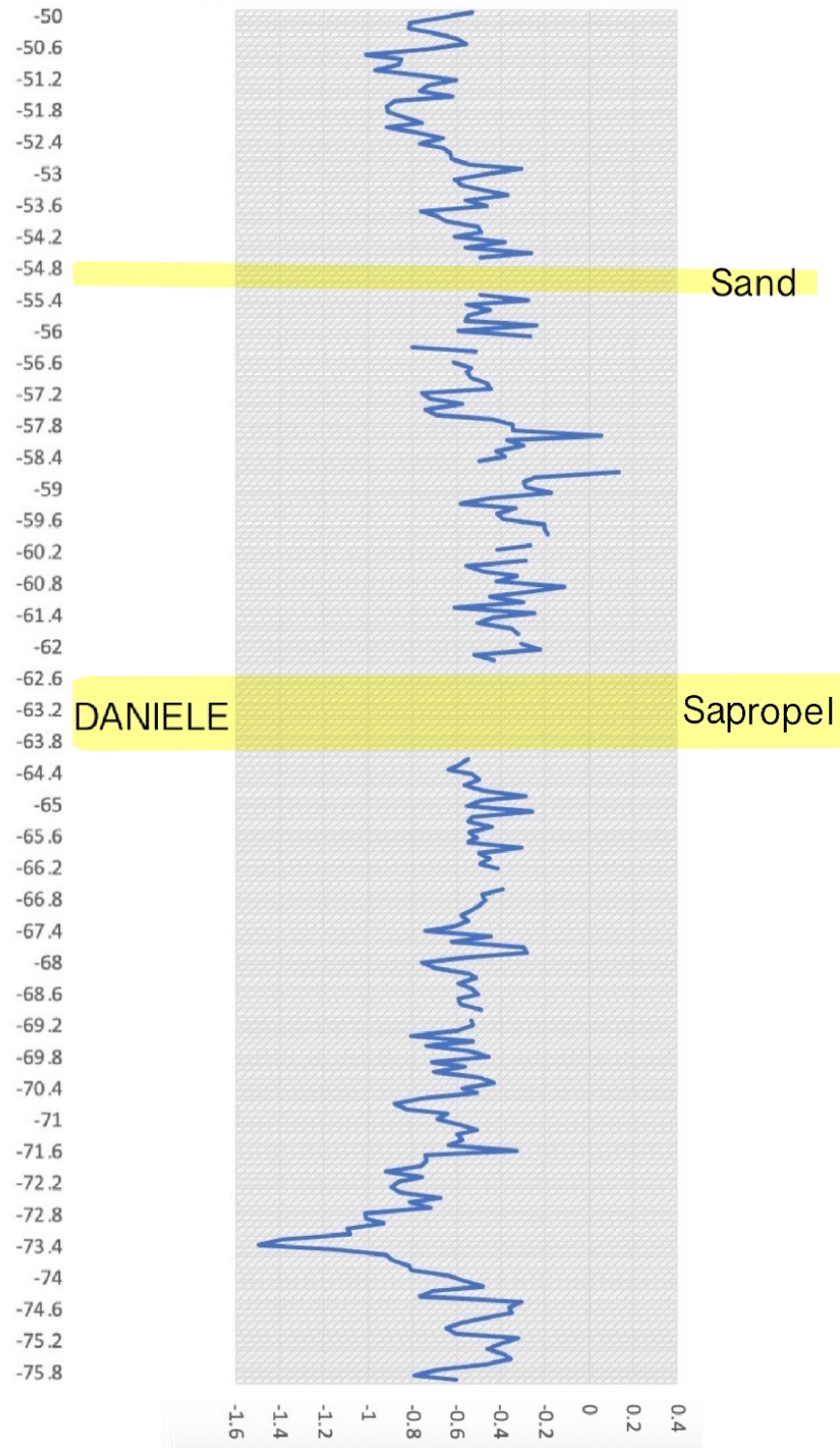


Figure 8.2 Benthic foraminifera *Uvigerina peregrina*  $\delta^{13}\text{C}$  record of the lower ca. 27 m of the PCS core.

There are two notable layers in this section of the sample, the sand layer and the sapropel layer.

The Sand layer is located at -55m. At this layer, the  $\delta^{13}\text{C}$  value shows a downward trend. In Figure 8.1, it corresponds to an ice age, which can be interpreted as an event during an ice age in which a great amount of basin sediments is imported into the ocean. This is also the reason for the occurrence of the "light"  $\delta^{13}\text{C}$  value, basin sediments are usually composed of sand and organic matter fragments (e.g., wood, leaves, animal bones), when this sediment is transported into the ocean, bringing with it a large amount of terrestrial organic matter with a lower  $\delta^{13}\text{C}$  value, which is usually characterized by a decrease in the  $\delta^{13}\text{C}$  value of benthic foraminifera.

The sapropel formation phase corresponds to a warm interglacial period in Figure 8.1, which coincides with the expected warm Mediterranean climate of the sapropel formation stage. Similarly, the  $\delta^{13}\text{C}$  value during the formation of sapropel in this figure also shows a trend of lightening, due to the reduced bottom water ventilation during its formation period. At this stage, biological productivity decreases due to reduced ventilation on the bottom water.



## 9.conclusion

In benthic foraminifera recordings from -50 m to -76.2 m in the lower part of the PCS, bottom water biological productivity slowly rises from -50 m to -53 m, then remains stable until it rises again at -59 m, falls back to the general level at -59.6 m and holds. Until the formation of Sapropel, the biological productivity decreased due to decreased bottom water ventilation. After that, the biological productivity continued to level off until it began to decrease at -72m, reaching a minimum at -73.4m and gradually returning to normal levels.

Two of these layers are noteworthy. At the sand layer, the decrease in  $\delta^{13}\text{C}$  is since sediments imported into the ocean from the basin are mixed with many organic debris (e.g., wood, leaves, animal remains, etc.), while land-based organic matter tends to have a lighter  $\delta^{13}\text{C}$  value. During sapropel formation, the decrease in  $\delta^{13}\text{C}$  is due to a decrease in bottom water ventilation, which coincides with expectations. At the same time, the formation period of sapropel also corresponds to the warm period of the Mediterranean, which is also consistent with the predictions of predecessors.

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## Bibliography

Bottrell, S.H. (2003). CRISS, R. E. 1999. Principles of Stable Isotope Distribution. x + 254 pp.

New York, Oxford: Oxford University Press. Price £47.50 (hard covers). ISBN 0 19 511775

1. *Geological Magazine*, 140, 233 - 233.

Broecker, W.S., & Maier-Reimer, E. (1992). The influence of air and sea exchange on the carbon isotope distribution in the sea. *Global Biogeochemical Cycles*, 6, 315-320.

Calvert, S.E., Nielsen, B., & Fontugne, M. (1992). Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels. *Nature*, 359, 223-225.

Cramp, A., & O'Sullivan, G. (1999). Neogene sapropels in the Mediterranean: a review. *Marine Geology*, 153, 11-28.

Dijk, J.V., Bello, M.I., Brancaleoni, G., Cantarella, G., Costa, V.S., Frixia, A., Golfetto, F., Merlini, S., Riva, M., Torricelli, S., Toscano, C., & Zerilli, A. (2000). A regional structural model for the northern sector of the Calabrian Arc (southern Italy). *Tectonophysics*, 324, 267-320.

Dirksen, J.P., & Meijer, P.T. (2019). The mechanism of sapropel formation in the Mediterranean Sea: insight from long-duration box model experiments. *Climate of the Past*.

Dirksen, J.P., Hennekam, R., Geerken, E., & Reichert, G. (2019). A Novel Approach Using Time-Depth Distortions to Assess Multicentennial Variability in Deep-Sea Oxygen Deficiency in the Eastern Mediterranean Sea During Sapropel S5. *Paleoceanography and Paleoclimatology*, 34, 774 - 786.

Faul, K., Ravelo, A.C., & Delaney, M.L. (2000). RECONSTRUCTIONS OF UPWELLING, PRODUCTIVITY, AND PHOTIC ZONE DEPTH IN THE EASTERN EQUATORIAL PACIFIC OCEAN USING PLANKTONIC FORAMINIFERAL STABLE ISOTOPES AND ABUNDANCES. *Journal of Foraminiferal Research*, 30, 110-125.

Hilgen, F.J. (1991). Extension of the astronomically calibrated (polarity) time scale to the Miocene/Pliocene boundary. *Earth and Planetary Science Letters*, 107, 349-368.

Hoefs, J. (2021). Stable Isotope Geochemistry. *Stable Isotope Geochemistry*.

Kappelman, J. (1986). Plio-Pleistocene Marine-Continental Correlation using Habitat

Indicators from Olduvai Gorge, Tanzania. *Quaternary Research*, 25(2), 141-149.  
doi:10.1016/0033-5894(86)90052-9

KIDD, R.B., CITA, M.B. & RYAN, W.B.F.(1978). Stratigraphy of eastern Mediterranean sapropel sequences recovered during DSDP Leg 42A and their paleoenvironmental significance. *Initial Reports DSDP*, 42, 412-443.

Loeblich, A.R., & Tappan, H.N. (1988). *Foraminiferal Genera and Their Classification*.

Lynch-Stieglitz, J., & Fairbanks, R.G. (1994). A conservative tracer for glacial ocean circulation from carbon isotope and palaeo-nutrient measurements in benthic foraminifera. *Nature*, 369, 308-310.

Pascual, M., Rives, B., Schunter, C., & Macpherson, E. (2017). Impact of life history traits on gene flow: A multispecies systematic review across oceanographic barriers in the Mediterranean Sea. *PLoS ONE*, 12.

Rohling, E.J., & Gieskes, W.W. (1989). Late Quaternary changes in Mediterranean intermediate water density and formation rate. *Paleoceanography*, 4, 531-545.

Rohling, E.J., & Hilgen, F.J. (2007). The eastern Mediterranean climate at times of sapropel formation: a review. *Geologie En Mijnbouw*.

Rohling, E.J., Cane, T., Cooke, S., Sprovieri, M., Bouloubassi, I., Emeis, K.C., Schiebel, R., Kroon, D., Jorissen, F.J., Lorre, A., & Kemp, A.E. (2002). African monsoon variability during the previous interglacial maximum. *Earth and Planetary Science Letters*, 202, 61-75.

Romanou, A., Tselioudis, G., Zerefos, C.S., Clayson, C.A., Curry, J.A., & Andersson, A. (2010). Evaporation–Precipitation Variability over the Mediterranean and the Black Seas from Satellite and Reanalysis Estimates. *Journal of Climate*, 23, 5268-5287.

Shackleton, N.J. (1967). Oxygen Isotope Analyses and Pleistocene Temperatures Re-assessed. *Nature*, 215, 15-17.

Urey, H.C. (1947). The thermodynamic properties of isotopic substances. *Journal of the Chemical Society*, 562-81 .

Vogel, J.C., Grootes, P.M., & Mook, W.G. (1970). Isotopic fractionation between gaseous and dissolved carbon dioxide. *Zeitschrift für Physik A Hadrons and nuclei*, 230, 225-238.

Woodruff, F., Savin, S.M., & Douglas, R.G. (1980). Biological fractionation of oxygen and carbon isotopes by recent benthic foraminifera. *Marine Micropaleontology*, 5, 3-11.

Nof, D. (1979). On man-induced variations in the circulation of the Mediterranean Sea. *Tellus A*, 31, 558-564.

Said, R. (1981). The geological evolution of the river Nile. *GeoJournal*, 8, 184.

Wahby, S.D., & Fisheries, A.E. (1981). The effect of the River Nile on Mediterranean water, before and after the construction of the High Dam at Aswan [Egypt].

Rohling, E.J., & Bryden, H.L. (1992). Man-induced salinity and temperature increases in western Mediterranean deep water. (Reannouncement with new availability information).

Bethoux, J.P. (1984). Paléo-hydrologie de la Méditerranée au cours des derniers 20 000 ans. *Oceanologica Acta*, 7, 43-48.

Rohling, E.J., & Bryden, H.L. (1994). Estimating past changes in the Eastern Mediterranean freshwater budget, using reconstructions of sea level and hydrography.

Boscolo, R., & Bryden, H.L. (2001). Causes of long-term changes in Aegean sea deep water. *Oceanologica Acta*, 24, 519-527.

Skliris, N., Sofianos, S.S., & Lascaratos, A. (2007). Hydrological changes in the Mediterranean Sea in relation to changes in the freshwater budget: A numerical modelling study. *Journal of Marine Systems*, 65, 400-416.

Shackleton, N.J., Hall, M.A., Line, J.M., & Shuxi, C. (1983). Carbon isotope data in core V19-30 confirm reduced carbon dioxide concentration in the ice age atmosphere. *Nature*, 306, 319-322.

Rosignol-Strick, M. (1985). Mediterranean Quaternary sapropels, an immediate response of the african monsoon to variation of insolation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 49, 237-263.

Mackensen, A., Schumacher, S., Radke, J., & Schmidt, D.N. (2000). Microhabitat preferences and stable carbon isotopes of endobenthic Foraminifera: clue to quantitative reconstruction of oceanic new production? *Marine Micropaleontology*, 40, 233-258.

SEGALLA, M.(2007). Stratigraphic, chronological and palaeoenvironmental characterization of the Pleistocene succession of Crosia - Calopezzati (Ionian Calabria). Master Degree Thesis in Natural Sciences, University of Padua.

Aurahs, R., Treis, Y., Darling, K., & Kučera, M. (2011). A revised taxonomic and phylogenetic concept for the planktonic foraminifer species Globigerinoides. *Fuel and Energy Abstracts*.

Rohling, E.J., Rohling, E.J., Marino, G., & Grant, K.M. (2015). Mediterranean climate and oceanography, and the periodic development of anoxic events (sapropels). *Earth-Science Reviews*, 143, 62-97.

Kroopnick, P.M., Weiss, R.F., & Craig, H. (1972). Total CO<sub>2</sub>, <sup>13</sup>C, and dissolved oxygen -18O at Geosecs II in the North Atlantic. *Earth and Planetary*