Specifications for carbonate content quantification in recent marine sediments using Rock-Eval pyrolysis.

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Abstract

The amount of $CaCO_3$ in sediments and/or sedimentary rocks is usually measured by calcimetry while the nature of the carbonates is determined by X-ray diffraction. Recently, a carbonate recognition method based on the results of Rock-Eval pyrolysis was proposed in 2014 by Pillot *et al.* [1]. Rock-Eval pyrolysis is also widely used for the characterization of recent sediments. However, later in 2015 Baudin *et al.* [2] noticed that some of the characteristics of recent sediments tended to produce different results from those of more classical Rock-Eval analyses, causing bias in interpretations.
In this study, the thermal stability of fossil and recent marine carbonated sediments was analyzed to identify differences in carbonate decomposition and to underline the importance of accounting for them in Rock-Eval analyses. The state of calcite preservation in recent marine sediments and sedimentary rocks at temperatures between 400 °C and 600 °C was characterized using different techniques (calcimetry, XRD, SEM imaging, etc.) for better interpretation of data obtained with Rock-Eval.
Our results highlight a clear difference in the range of calcite decomposition temperatures during Rock-Eval analysis: between 550 °C and 775 °C for bulk clayey hemipelagic sediments versus 650 °C to 840 °C after the same sediments were rinsed to get rid of the salt. During heating, water and hydroxide anions are released from clay minerals and react with salt crystals to form acid vapor. This acid vapor reacts with carbonates to produce CO_2. The chemical decomposition of carbonate starts at temperatures that are lower than the typical range of decomposition temperatures, leading to overestimation of mineral carbon content (overestimation of the S5 peak) and to underestimation of organic carbon content (underestimation of the $S4CO_2$ peak) with the Rock-Eval method. In the absence of clay minerals, such as in recent marine pure carbonate oozes, there is no evidence for this effect. It is therefore essential to prepare and rinse recent clay-rich carbonated sediment samples before Rock-Eval analysis to avoid misinterpretation.

Keywords

Rock-Eval - Pyrolysis - Recent sediments - Carbonates decomposition - Acid attack

Introduction

The abundance of carbonates in rocks, sediments and soils is an important parameter for many geological, pedological and environmental studies. Several approaches enable the evaluation of the carbonate content in selected samples, including wet chemical dissolution, spectral techniques, and analysis of gas that evolves during thermal decomposition. For wet-chemistry, total carbonate content is determined via acid digestion of the various carbonate minerals (calcite, dolomite, siderite, ankerite, rhodochrosite, etc.) present in the sample. Hydrochloric acid is usually used at room temperature or under moderate heating, to digest the carbonate minerals. Total carbonate contents are determined by measuring either (1) the weight loss of the sample after decarbonatation, (2) the acid consumption needed for the complete destabilization of carbonates, or (3) CO_2 pressure during decarbonatation using a Bernard calcimeter or a Mélières manocalcimeter.

Rock-Eval analyses are also widely used in the petroleum industry because they make it possible to obtain the percentage of organic matter in a rock and many other parameters that are useful for the characterization of oil potential. The Rock-Eval method was primarily developed by the *Institut Français du Pétrole* for compacted (fossil) sediments [3,4] but is now being increasingly used for the characterization of recent lacustrine and marine sediments [5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20 and others] as well as soils

[21,22,23,24,25,26,27 and others]. In 2014, a qualitative and quantitative carbonate recognition method based on the results of Rock-Eval pyrolysis was proposed [1]. According to this method the morphology of the CO_2 production curve obtained during thermal destabilization of carbonated minerals also allows the identification of the type of carbonates present in the rock.

However, in a previous study [2] we demonstrated that for Rock-Eval analyses of some recent marine sediments are biased, which can lead to misinterpretation of the results (organic matter and / or carbonate content). The aim of the present study was thus to identify the cause of the differences in recent marine sediments. The stability of recent carbonate natural samples subjected to heat treatment (such as those used in Rock-Eval pyrolysis) was compared to the same sample set but previously desalted.
In parallel, different sample characterization techniques (calcimetry, XRD, scanning electron microscope imaging, etc.) were carried out to insure a better interpretation of the data obtained by the Rock-Eval and to propose specific conditions for analysis and/or the preparation of recent sediments.

1. Materials and methods

1.1 Material

As the purpose of this study was to understand the thermal behavior of carbonates in recent sediments, we chose samples of different sedimentary rocks with similar carbonate composition (content, mineralogy) to better identify the origin of the phenomenon. We chose consolidated sedimentary rock samples, recent clay-rich sediment samples and pure carbonate ooze samples. The following samples were analyzed:

Douvrend
Douvrend corresponds to the last fifteen centimeters of the upper Cenomanian "Craie de Rouen" Formation (Marnière de Douvrend section, Renouval Quarry, Dieppe region, France). It is a white to light beige marly chalk mainly made of coccoliths and foraminifera. It contains very little organic matter (TOC<0.3%) and is characterized by approximately 90.42±2% $CaCO_3$ (calcite) content [28]. The sample is in the form of a homogeneous powder and used as ISTeP laboratory internal standard for stable carbon and oxygen isotope measurements and trace element analyses.

MD01-2376 core
The MD01-2376 core was taken in the Timor Sea (12.314°S, 121.192°E) at a depth of 2906 m below the surface during the IMAGES VII MD122 (WEPAMA) cruise in May 2001 and penetrated the sediment to a depth of 27.90 m. Based on visual examination and smear slide observations the sediment is composed of a siliceous (10-30% diatomaceous) and carbonated (20-45% coccoliths and foraminifera) biogenic phases, clay minerals (25-45%) and organic matter (~ 1%). The color of the sediment (sometimes bioturbed) varies from light to olive gray [29].
Since its recovery and opening, the MD01-2376 core has been stored in the cold and humid core repository of the French National Museum of Natural History in Paris. Around 5 cc of wet sediment were collected at approximately 10 cm intervals along the MD01-2376 core from its top down to 27.90 m (260 samples). Three larger samples (15 cc corresponding to a 2 cm thick interval) were collected at different depths of the core: 464-466 cm, 1914-1916 cm and 2345-2347 cm, in order to dispose of a sufficient quantity of material for additional analyses (see below). In the present paper, samples from this core are hereafter referred to as “bulk clayey hemipelagic ooze” and “rinsed clayey hemipelagic ooze”, respectively.

SU90-08 core
These samples were collected from the top of the core (0.2 first meters) extracted with the Suroît (Ifremer) research vessel in 1990 during the PALEOCINAT drilling campaign at a depth of 3080 m below the surface north of the Azores (43.353N, -30.408W), in the Atlantic Ocean [30,31]. The pelagic sediment in this zone is characterized by approximately 90% calcite content, low TOC (<0.2%) and a very small proportion of clay minerals. Samples from this core are hereafter referred to as “nannofossil pelagic ooze”.

1.2 Methods

The first batch of sediment was dried at 50 °C in a stove and then crushed with an agate mortar. The second batch was rinsed twice in deionized water to remove residual salt from marine pore water. Conductivity was measured to insure the rinses were effective. The samples were then centrifuged and finally dried in a stove at 50 °C for 10 hours. We believe that this rinsing has no influence on the carbonate content because the procedure is fast (2 minutes maximum before centrifugation) and made with a neutral pH water.

Off-line thermal decomposition

Both bulk and rinsed samples were subjected to the following thermal protocol:

- 11 mid-ramp isothermal sections in increments of 20 °C (from 400 °C to 600 °C) at 30 min intervals;
- Each powdered sample was divided into 11 aliquots each weighing 0.6 g;
- The aliquots were placed together in a muffle furnace at ambient temperature and ambient air atmosphere;
- The furnace was then heated to 400 °C;
- Then, for each isothermal section, the temperature was stabilized for 30 minutes;
- At the end of each isothermal section, an aliquot was removed from the oven, cooled and weighed.

This protocol was repeated for each sample, and a total of 60 aliquots (including raw samples) were prepared and analyzed.

Calcimetry

The measuring instrument used in this study was a Mélières manocalcimeter. The calcium carbonate dosage is based on acid attack (here with 30% volume HCl) of 100 mg of sample at ambient temperature. The calcimeter was previously calibrated with pure calcite. The volume of CO_2 released during the following reaction was measured with a manometer:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2$$

XRF Ca counts

High-resolution geochemical elemental composition records were measured on the archive slab core MD01-2376 surface with an Avaatech XRF Core Scanner at the EPOC Laboratory (University of Bordeaux). After cleaning and preparation of the surface, three separate runs (10, 30 and 50 kV, with currents of 0.6, 1.5 and 2.0 mA, respectively) were performed every cm down-core with a down-core slit size of 1cm. Sampling time was set to 10 s at 10 kV, 15 s at 30 kV and 20 s at 50 kV. The slab surface was covered with a 4mm thick SPEXCerti Prep Ultralene1 foil to avoid contamination of the XRF measurement unit and desiccation of the sediment. Raw data spectra were processed by analysis of the X-ray spectra using the iterative least squares software (WIN AXIL) package from Canberra Eurisys. The elements analyzed included a broad range, from aluminum through uranium [32, 33]. In this paper, we only focus on calcium (Ca) results as a marker for carbonates assuming the absence of other calcium rich detrital minerals.

X-ray diffraction

In this study, XRD was used to monitor the amount of calcite present in the samples at each temperature step. All the samples were analyzed after thermal treatment (except for raw samples). Diffractograms provided information on the mineral nature of each sample. Once calcite was identified, intensity, width at half height and (1, 0, 4) peak surface were measured with MacDiff software.

The diffractometer used in this study was a Bruker D2 Phaser equipped with a copper anticathode (CuKα radiation). Analyses were carried out according to the so-called "powders" method established by Moore & Reynolds [34].

Aliquots of the three samples selected from core MD01-2376 (for both bulk and rinsed clayey hemipelagic oozes) were crushed, and part of the powder (grain size less than 50 µm) was added to deionized water to form mineral suspensions, that were then dispersed ultrasonically for 2 minutes. The fraction of the sediments less than 2µm in size was collected by sedimentation, and clay minerals were characterized from the XRD patterns of the oriented preparations acquired in air-dried conditions, after ethylene glycol solvation and heating at 490 °C for 2 hours. XRD analyses were performed using a Bruker D4 Endeavor X-Ray diffractometer (CuKα radiation). The oriented preparation of the fraction less than 2 µm in size was analyzed from 2° to 30° 2θ for the detailed characterization of the d_{001} diffractions of phyllosilicates.

Rock-Eval

We used a Turbo Rock-Eval 6 [4]. Each individual sample was analyzed according to the Rock-Eval "Basic" cycle in which they are subjected to open pyrolysis at 300 °C to 650 °C with a 25 °C/min ramp and then to oxidation at 300 °C to 850 °C with a 20 °C/min ramp [3, 35]. Core samples were also analyzed with the method of Baudin *et al.* [2] using a pyrolysis that starts at 180 °C and a ramp of 30 °C/min.
Total organic carbon (TOC) was calculated from the hydrocarbons expelled from the sample during pyrolysis as well as from the amounts of CO and CO_2 emitted during the pyrolysis and oxidation phases. The amount of mineral carbon (MinC) was calculated with Rock-Eval 6 as the sum of CO_2 released during pyrolysis, at more than 400 °C, and the CO_2 released by carbonate decomposition during oxidation, between 650 °C and 850 °C (for further explanations, see [35]).

Scanning Electron Microscopy
In this study, we observed only core samples using a Zeiss Ultra 55 Field Emission Scanning Electron Microscope. Three samples corresponding to different isothermal sections for both bulk and rinsed clayey hemipelagic oozes were analyzed by SEM to characterize calcite preservation state during heating at 400 °C, 480 °C and 540 °C (isothermal sections were chosen after XRD analysis to insure we focused on the temperature range of interest).

2. Results and interpretations

2.1 Calcimetry

The results of calcimetry during heating showed a quasi-steady state of the $CaCO_3$ content of the Douvrend chalk sample in the temperature range studied (loss < 5% at the final temperature) whereas the bulk clayey hemipelagic ooze samples (3 samples taken at different depths of the core) showed a marked decrease in $\%CaCO_3$ starting at around 440 °C to reach almost 100% loss at around 600 °C (Fig. 1). However, the decrease in the rinsed clayey hemipelagic ooze samples was much less pronounced, started later (>520-540 °C) and reached a maximum of 30% loss at 600 °C. It is thus clear that rinsing the sediment influences the decomposition of $CaCO_3$ content with increasing temperature.

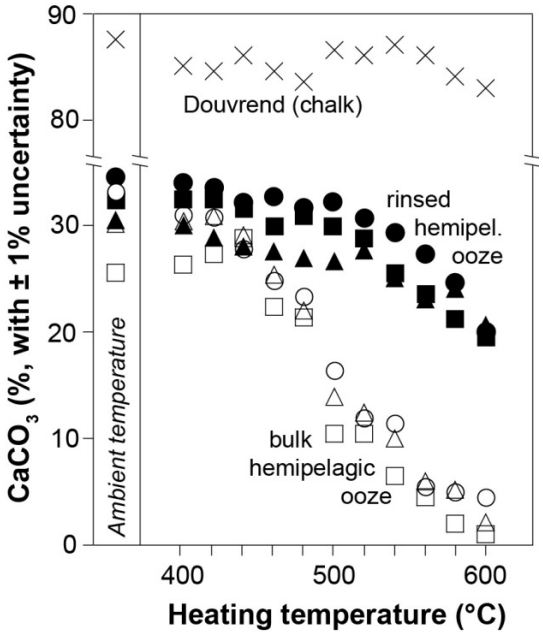

Fig. 1 – Variations in $CaCO_3$ content (determined using manocalcimetry) in a Cretaceous chalk indurated sample (Douvrend) and in bulk and rinsed recent clayey hemipelagic oozes from the Timor Sea, by increasing the temperature from 400 °C to 600 °C in 20 °C increments in a muffle furnace. Three samples corresponding to different core depths (triangles, squares and dots) were used for the recent clayey hemipelagic oozes from the Timor Sea.

2.2 X-ray diffraction

Considering the observations made with calcimetry, we thought it would be interesting to analyze the behavior of calcite and sodium chloride (NaCl), the only mineral present in the bulk hemipelagic ooze and absent in the rinsed hemipelagic ooze. The major peaks of calcite (104) and halite (200) of the bulk clayey hemipelagic ooze samples tumbled completely and synchronously between 400 °C and 600 °C (Fig. 2) whereas the intensity of the quartz peak (101) remained steady throughout the heating cycle. These diffractograms highlight the obvious relationship between the presence of salt in the samples and the early decomposition of calcite (at low temperatures) even if they do not make it possible to accurately measure the quantities.
The diffractograms of the rinsed clayey hemipelagic ooze showed a slight decrease in the intensity of the calcite peak between 400 °C and 500 °C and a more significant decrease between 500 °C and 600 °C but never above 30% loss at these temperatures. Thus, when salt was removed by successive rinses and the same temperature ranges were used, the intensity of the calcite peak only decreased by half when it tumbled down to zero in the presence of salt.

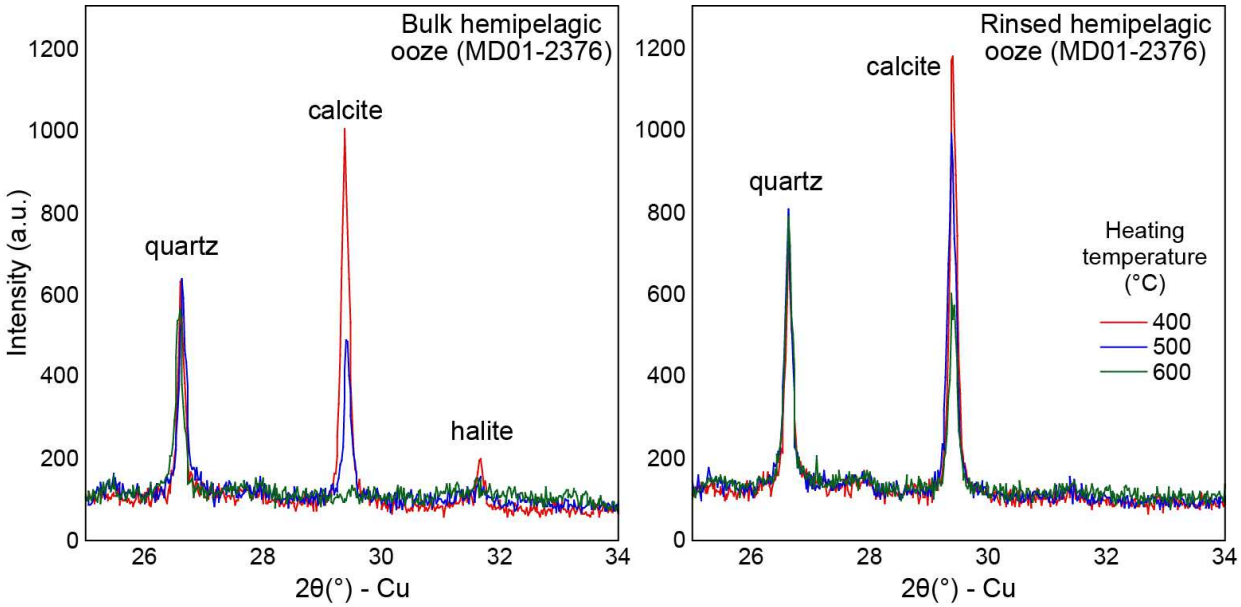

Fig. 2 – Comparison of X-ray diffractograms of a bulk and rinsed clayey hemipelagic ooze from the Timor Sea at three stages of a heating experiment. Note the sharp decrease in the calcite peak (104) and in the halite peak (200) between 400 °C and 500 °C and its disappearence at 600 °C in the bulk sample. COLOR FIGURE.

The main components of the clay fraction of the hemipelagic ooze were of R0 type illite/smectite mixed-layers hereafter referred to as smectite (about 70%), illite (15%), chlorite (5-10%) and kaolinite (10%) (Fig. 3). Traces of R1 type illite-smectite mixed layers and chlorite-smectite mixed-layer were probably also present. Quartz and traces of feldspars equally occur in the clay fraction.

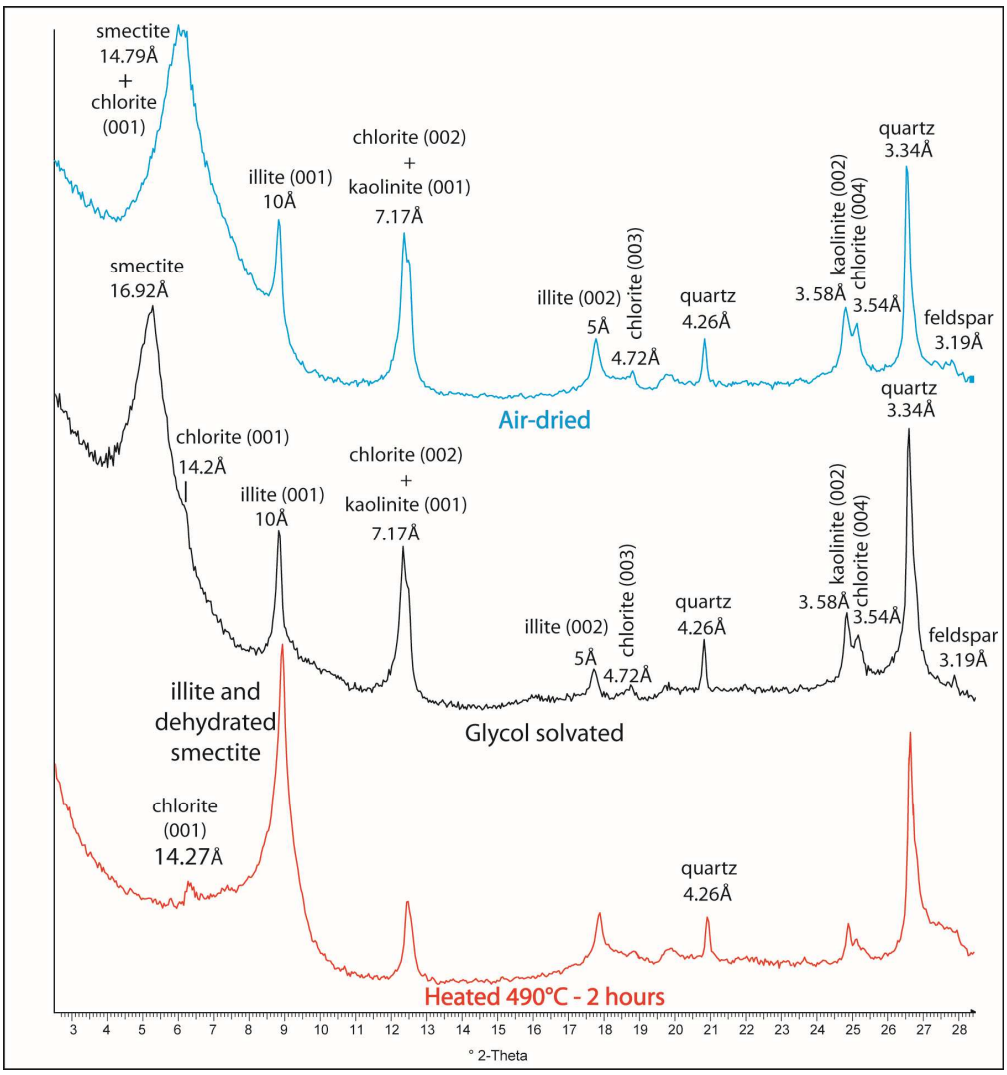

Fig. 3 X-ray diffractograms of the clay fraction of hemipelagic oozes samples in core MD01-2376.

2.3 Scanning Electron Microscopy

SEM observations confirmed that the carbonate fraction of clayey hemipelagic oozes was mainly composed of coccoliths and foraminifera, and subordinate micrometric calcite crystals of indeterminate origin.
The coccoliths observed belong to the species *Gephyrocapsa oceanica*, characterized by a crossbar in the center of the coccolith ring. When we examined the conservation status of the nannofossil at the three temperatures previously used for the XRD on the same bulk and rinsed sediment, the differences were drastic. The bulk clayey hemipelagic ooze was subjected to severe degradation of its coccolithic content between 400 °C and 480 °C and even more at 540 °C (temperature at which it becomes almost impossible to identify the organism). Moreover, the coccolith crossbar already decomposed 480 °C. Conversely, the coccoliths in the rinsed clayey hemipelagic ooze were much better conserved with increasing temperature, the structure of the coccolith and even the crossbars were still visible at 540 °C (Fig. 4). This microscopic observation points in the same direction as the XRD results: the presence of seawater and therefore of sodium chloride is correlated with the decomposition of carbonated elements.

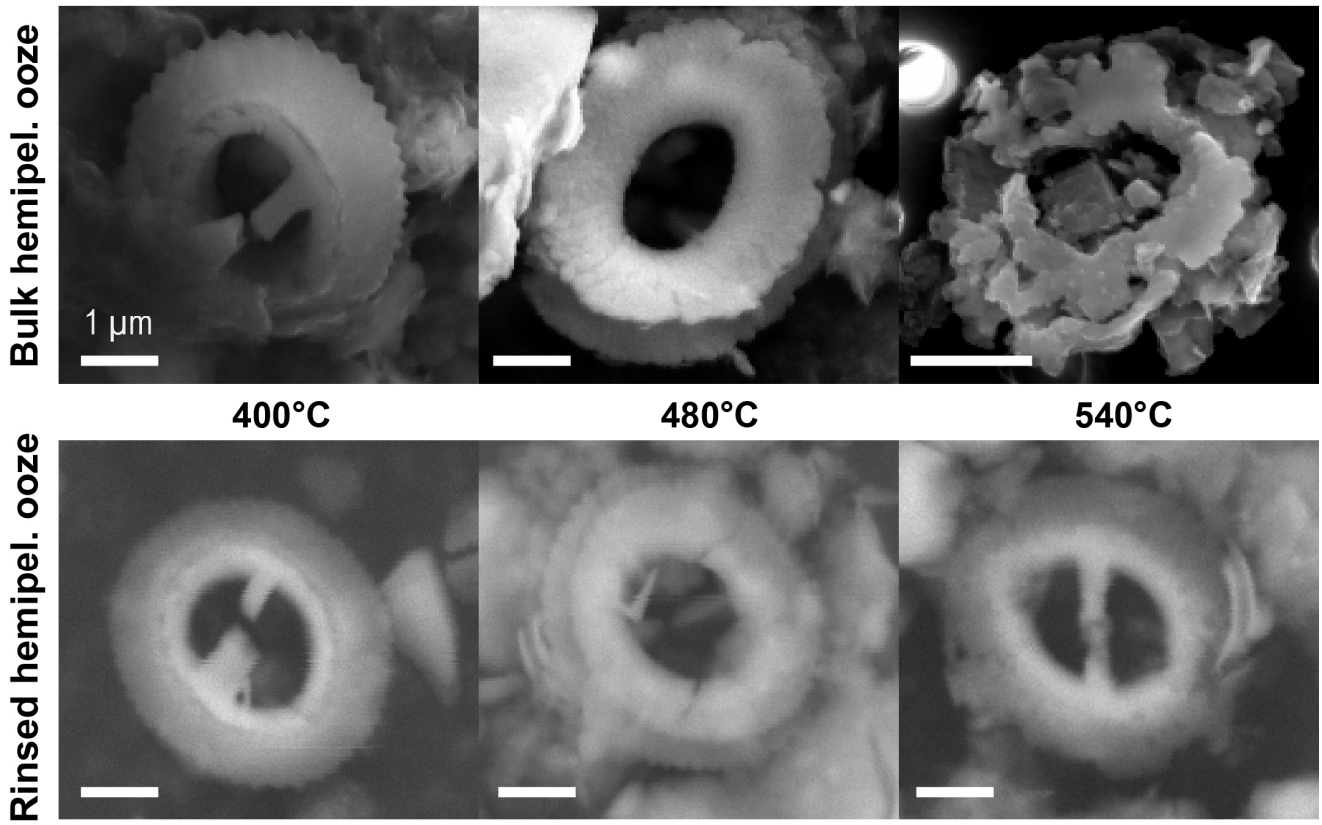

Fig. 4 – SEM images of a coccolith of the same species (*Gephyrocapsa oceanica*) at three stages (400 °C, 480 °C and 540 °C) of a heating experiment conducted with bulk and rinsed (desalted) powdered sediment from the Timor Sea.

2.4 Rock-Eval

The results of Rock-Eval in this study highlight the difference in the behavior of sediments components subjected to heating cycles. Looking at the CO_2 curves corresponding to decomposition of carbonates during the oxidation step (the so-called S5 peak) we observed two clearly different behaviors. Decomposition of the calcite in the fossil sediment samples Douvrend and IFP160000 (used as Rock-Eval standard) started at around 650 °C and reached zero around 830 °C, as also demonstrated by Pillot *et al.* [1]. The nannofossil pelagic ooze (SU90-08) had almost exactly the same CO_2 signature whether it was rinsed or not. The S5 peak of all the samples showed very similar shapes. On the other hand, our results revealed a disparity between the bulk and the rinsed clayey hemipelagic ooze. While the rinsed sample signal was almost identical to those discussed previously, the bulk signal shifted on the temperature scale. In the bulk clayey hemipelagic ooze, carbonate decomposition started early at around 400 °C increased at around 550 °C and peaked at 680 °C (Fig. 5).

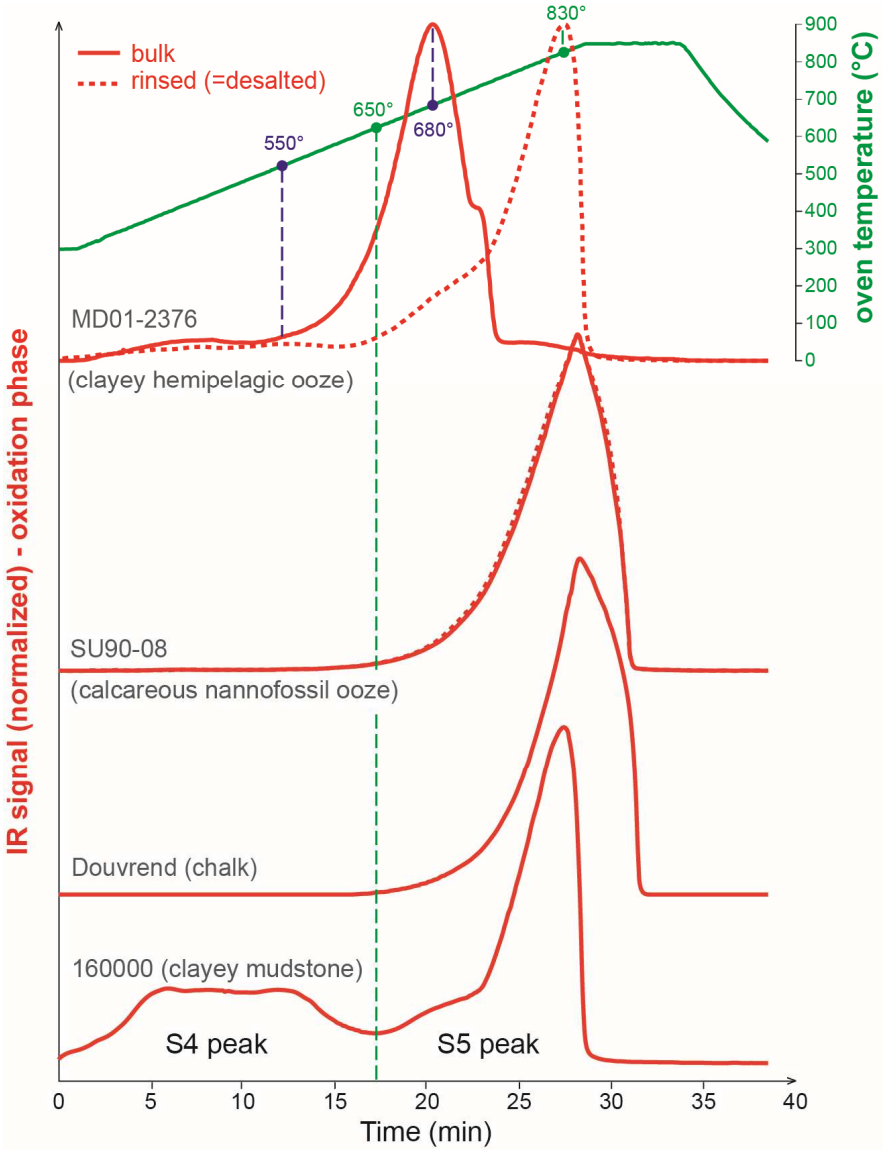

Fig. 5 – Infrared CO_2 cell-detector response (corresponding to the $S4CO_2$ and S5 peaks of Rock-Eval) for two recent sediment samples, one from the Timor Sea (clayey hemipelagic ooze/MD01-2376, ~30% $CaCO_3$) and the other from the central Atlantic Ocean (nannofossil pelagic ooze/SU90-08, ~90% $CaCO_3$). Each sample was analyzed before (as bulk sediment, solid line) and after rinsing (desalted sediment, dashed line). The $S4CO_2$ and S5 peaks for the chalk sample (Douvrend) and the IFP 160000 are shown for the sake of comparison. COLOR FIGURE.

3. Discussion

When a sediment or a sedimentary rock is heated, several modifications take place and are accompanied by mass loss. The loss of mass may be due to the moisture in the sample, the presence of structural water or hydroxide (OH^-) anions in minerals such as clays, destruction of both organic and mineral phases, etc.

The organic phase is often the first to be destroyed, followed by the decomposition and/or the neoformation of mineral phases. This study focused on identifying the factors responsible for the early thermal destruction of carbonates.

This study highlight the relationship between the presence of salt (NaCl) in the samples and the early decomposition of calcite. Therefore, the hypothesis we proposed in a previous study [2] according to which the thermally labile character of poorly crystallized minerals in recent sediments are responsible for the early decomposition of carbonates is not validated. This study revealed different calcite decomposition behaviors in

two different recent sediments: a nannofossil pelagic ooze and a clayey hemipelagic ooze (Fig. 5). Calcite decomposition in the nannofossil pelagic ooze occured in the same temperature ranges as fossil sediments such as Douvrend (chalk) and IFP16000, whether bulk or rinsed. On the other hand, the bulk clayey hemipelagic ooze calcite decomposed at lower temperatures although with a similar curve shape. This observation led us to the crucial identification of the cause of these different behaviors, i.e. the presence or absence of clays and hence of structural water and hydroxyl groups in the sediment.

The other methods of analysis used in this study confirmed the responsibility not only of the presence of salt in the sediments but particularly the water and/or hydroxide anions in the early stage of decomposition of the carbonates. XRD analysis (Fig. 2) showed that in the rinsed clayey hemipelagic ooze, the decomposition of calcite is not early even if a small amount of salt remains in the sample. However a small reduction in the calcite principal peak (104) intensity at 600 °C was observed corresponding the classical thermal decomposition ranges of this mineral [1]. On the other hand, the bulk clayey hemipelagic ooze calcite started decomposing between 400 °C and 500 °C and was already absent from the sample at 600 °C. These observations were visually confirmed by SEM and calcimetry analyses (respectively Fig. 4 and 1). According to the results of calcimetry based on the samples heated in the muffle furnace, the calcite content of the fossil sample (Douvrend) and rinsed clayey hemipelagic ooze started decreasing around 550 °C (in agreement with the onset reported by Pillot *et al.* [1]), whereas in the bulk clayey hemipelagic ooze, carbonate content reached almost zero at the same temperature. When the sample was rinsed and dried the water present in it evaporated. It is therefore the presence of water and/or hydroxide anions combined with chloride salt in our samples that triggered the early decomposition of carbonates.

It is also interesting to note the difference between the temperature of calcite decomposition in the bulk clayey hemipelagic ooze sample between calcimetry (around 450 °C) and the Rock-Eval oxidation cycle (starting around 450 °C but only becoming significant at around 550 °C). This shift in carbonate decomposition temperatures can be simply explained by the pyrolysis phase undergone before oxidation during the Rock-Eval analysis. Considering this cycle brings the sample up to a temperature of 650 °C (Fig. 6), unlike the calcimetry and SEM post thermal protocol analyses, some of the carbonates have already been attacked during pyrolysis. Rock-Eval analyses of rinsed clayey hemipelagic ooze confirmed this observation by showing lower mineral CO_2 values during pyrolysis and standard degradation of calcite in chalk-like temperature ranges. Moreover, the difference in pyroMINC values between rinsed and bulk samples decreased in accordance with the depth of the sample (factor of about 2.5 between pyroMINC values for a sample located at 120cm from the top of the core versus 2 for a deeper sample located at 2260cm from the top of the core), which is to be expected since the sediments contain progressively less water and salt with compaction due to the depth.

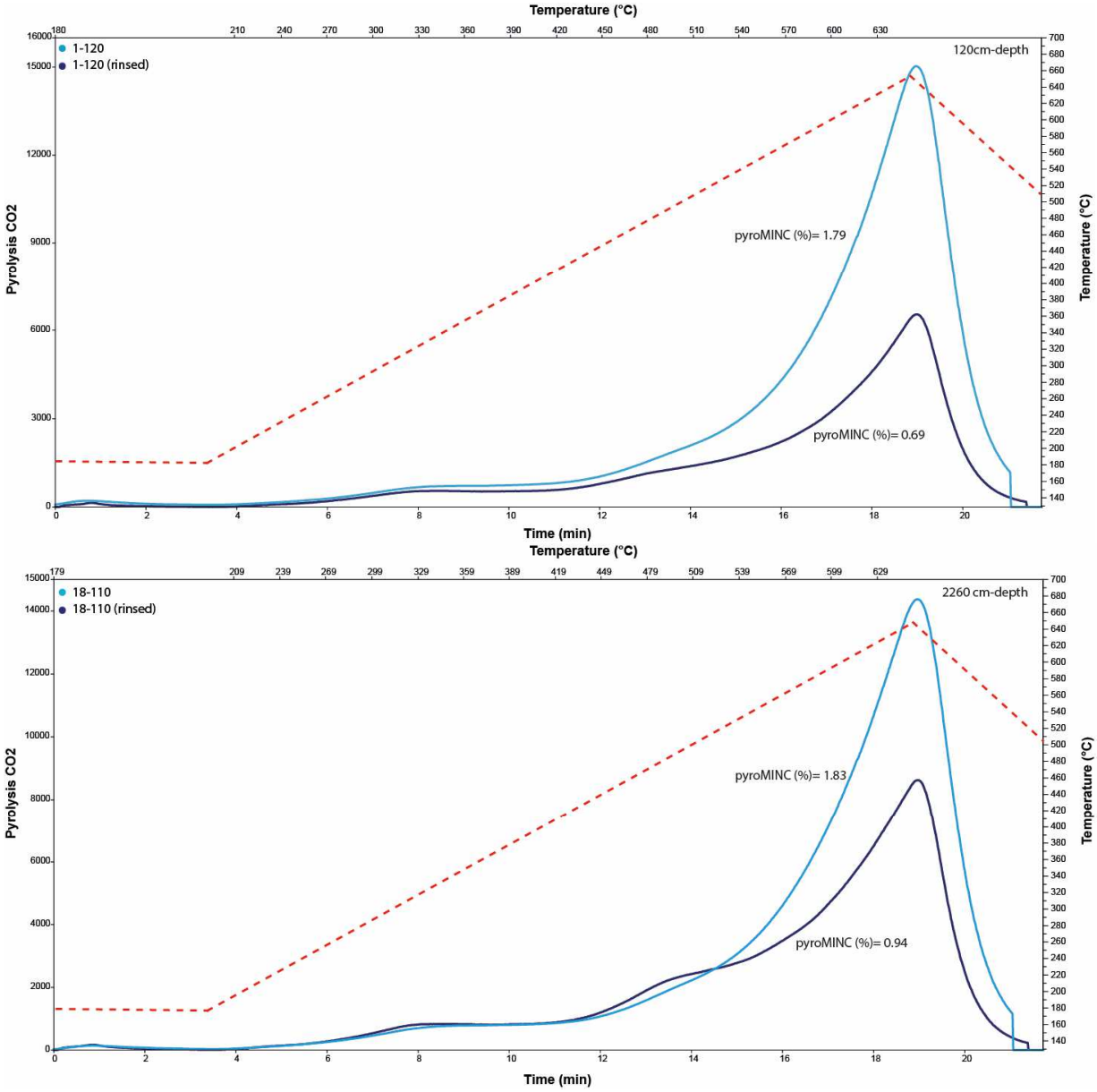

Fig. 6 – Pyrograms of two core samples (at 120 cm and 2260 cm-depth respectively) highlighting the onset of decomposition of carbonates in bulk sediments during Rock-Eval pyrolysis. COLOR FIGURE.

The phenomenon of early decomposition of carbonates in some recent sediments can be explained as follows. The clays have a layered structure that can contain water. Clay minerals consist of silicon, aluminum, oxygen and hydroxyl (OH) ions, organized in layers of two types depending on whether the oxygen atoms or hydroxyl groups are associated in tetrahedra or octahedra. The octahedral and tetrahedral layers coalesce along planes, pooling O and OH, so the sheets are separated by interfoliar spaces. Positive charge deficit can occur due to possible partial substitutions of Si^{4+} by Al^{3+} in the tetrahedra, Al^{3+} by Mg^{2+}, Fe^{2+} or Fe^{3+}, in the octahedra. This is then offset by the insertion of cations or water in the interfoliar spaces. Water molecules are in fact no longer present in the structure but have been expelled as a result of thermal decomposition [36]. When a sediment containing clay minerals is heated, dehydration takes place around 100 °C, releasing water from the clay interlayers. Given the fact that the clay fraction of hemipelagic oozes consists mainly of smectites (Fig. 3), dehydration had to provide a significant amount of water vapor. At higher temperatures around 500 °C, depending on the nature of the clay minerals, dehydroxylation occurs [37, 38, 39, 40, 41, 42] Moreover Du et al. [43] measured melting temperature of chloride salt (NaCl) at 420 °C. These temperatures coincide perfectly with the early decomposition temperatures of calcite observed in our experiments.

Dehydroxylation is significant notably in chlorite and kaolinite, two clay minerals that occur in significant quantities in the samples of hemipelagic oozes collected from the Timor Sea and analysed in the present study. Consequently, and when salted pore water is also present in the sediment, released gaseous water (H_2O) and/or hydroxide anions react with it to form acid vapor (such as hypochlorous acid (HClO) or hydrochloric acid (HCl)). In turn, this acid vapor, reacts with the carbonates ($CaCO_3$) present in the sediment causing chemical decarbonatation, which manifests itself as the release of CO_2. In this case, the phenomenon of carbonate destruction is therefore chemical and non-thermal, giving rise to early release of CO_2 and hence to artificial peaks during Rock-Eval analysis. The CO_2 peak corresponding to the destruction of the carbonate phase of the sediment (S5) thus shifts on the temperature scale, leading to overestimation of mineral carbon and underestimation of organic carbon (Fig. 7).

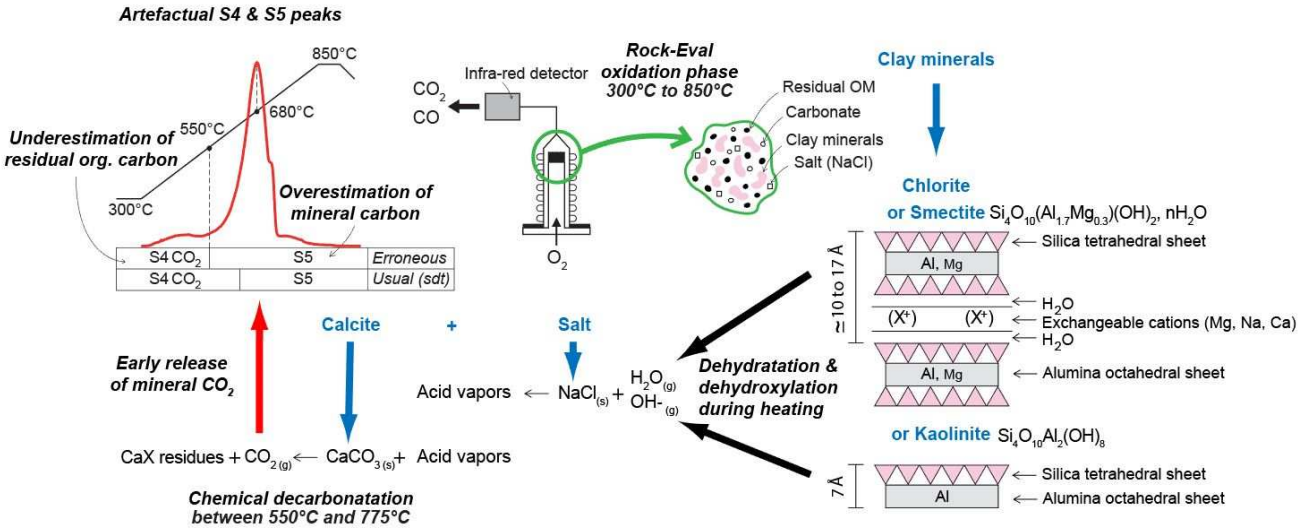

Fig. 7 – Plausible origin of the artefactual S5 peak that appears during Rock-Eval analysis (oxidation phase) of recent marine sediment containing hydrated clay minerals, salt and carbonates. An acid reaction between NaCl and water provided by the dehydration/dihydroxylation of clay minerals causes the dissolution of calcite, with the resulting generation of CO_2 at temperatures ranging between 550 °C and 775 °C. COLOR FIGURE.

However, it is important to really understand the shift of this oxidation CO_2 peak. It would be easy to think that the entire peak of CO_2 shifts which would lead to a reverse observation, i.e. an overestimation of the TOC and underestimation of the MinC since part of the peak associated with the mineral carbon would be included in signal integrated as organic carbon. It is in fact only the mineral part of the oxidation CO_2 peak which is shifted, the formation of acid vapors having no influence on the decomposition temperatures of the organic carbon. Thus, when the mineral part of the CO_2 peak shifts to lower temperatures, the Rock-Eval cursor defining the boundary between the portions of the curve integrated as organic and the one integrated as mineral seeks a new minimum on the curve (Fig. 8). As this minimum is most often located at much lower temperatures, the software integrates a large part of the organic signal as mineral carbon against a small part of the mineral signal as an organic carbon thus explaining the phenomenon of overestimation/underestimation observed.

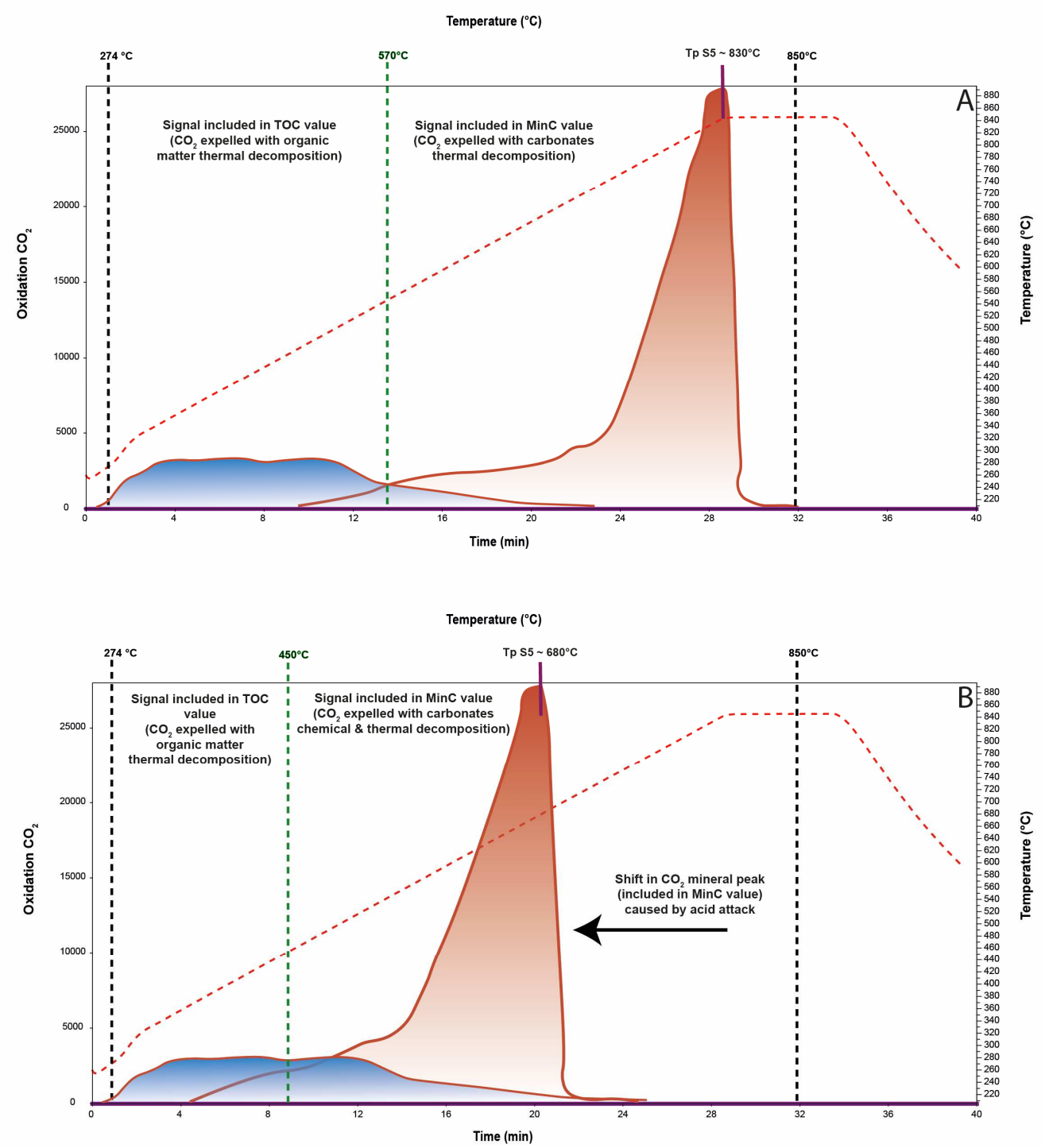

Fig. 8 – Illustration of the position of the cursor separating the organic carbon from the mineral carbon on the CO_2 signal in oxidation for a classical analysis (A) versus an analysis showing the shift of the mineral part of the CO_2 (B) following an early decomposition of the carbonates by chemical attack. COLOR FIGURE.

4. Application

An example of application is presented below to highlight the importance of rinsing recent carbonate sediment samples before analysis. Figure 9 shows four curves representing the percentage of $CaCO_3$ obtained with different methods (calcimetry, Rock-Eval, XRD and XRF) along a core of hemipelagic sediments collected from the Timor Sea. The curve obtained with XRF analyses (light grey line) is a reference curve, since it is not influenced by any other factors than the carbonate content.

Rock-Eval analyses of the bulk sediment (solid line) overestimate carbonate contents while those obtained using calcimetry (dotted line) underestimate them. Indeed, as seen above, the presence of water in the clays and salt in the sediment causes early chemical degradation of the carbonates during the Rock-Eval analysis, inducing a shift of the CO_2 peak emitted and hence overestimation of mineral carbon. When calcimetry is used, this phenomenon does not occur because the sample is not heated. However with calcimetry, there is also an error in the estimation of the percentage of $CaCO_3$. Indeed, the presence of salt in the sample during weighing results in overestimation of the weight of the sample and hence to an underestimation of the carbonate content. During Rock-Eval of the rinsed sediments, the analyzed sample no longer contains salt, and its carbonate contents are consequently much closer to those obtained with XRF (black dots). This observation confirms the results of our study and highlights the importance of using properly processed samples before analysis and interpretation of the results.

It is also interesting to note the variation in these shifts between the different methods and along the core. We observed indeed that the gap between the $CaCO_3$ percentages produced by Rock-Eval for the bulk sediment and the XRF analyses is much larger in the top part of the core but narrows towards the deeper part. This observation can be explained by simple geological phenomena. Indeed, the upper part of the core (close to the surface) is comprised of highly porous sediments and consequently contain a lot of interstitial marine water, resulting in a large quantity of salt when the sediment is oven dried. Towards the deeper parts, when compaction takes effect, the porosity of the sediment decreases and consequently contains less water and fewer salt crystals after drying, thereby limiting errors caused by their presence.

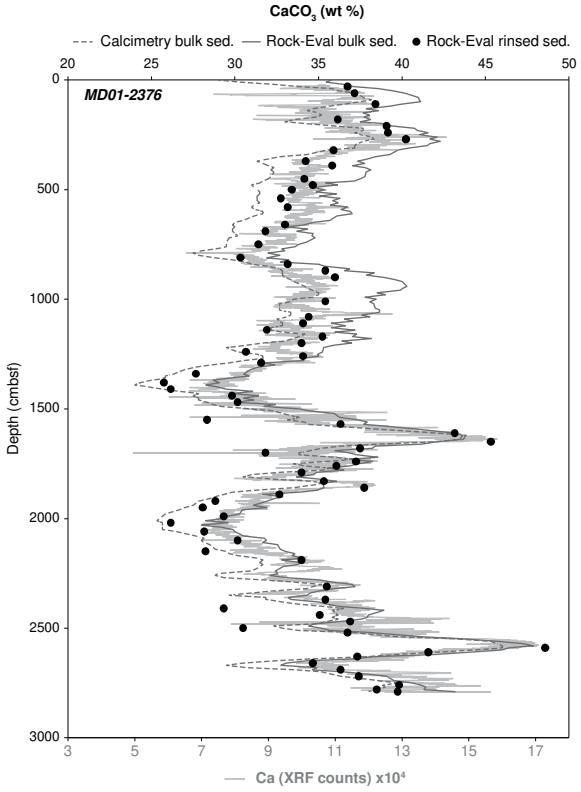

Fig. 9 – Changes (5 point-smoothing) in $CaCO_3$ contents along a 27.9 m-long core of hemipelagic sediments from the Timor Sea. The data were acquired using a calcimetric bomb (dotted line) or were derived from the MinC of Rock-Eval (solid line) of the bulk sediment. Selected samples were rinsed using deionized water and re-analyzed using Rock-Eval (black dots). Variations in the Ca content (light grey line) derived from XRF are shown for the sake of comparison. The latter are in good agreement with $CaCO_3$ determined in rinsed sediments.

Beyond overestimation of mineral carbon and underestimation of organic carbon, the analysis of recent bulk sediments may lead to other misinterpretations. In fact, a certain number of parameters such as the oxygen index (OI) used to define the origin of organic matter are calculated from the CO_2 emission curves obtained during the Rock-Eval analysis. Thus, if this analysis is distorted by a phenomenon such as the early destruction

of carbonates through a chemical reaction, the CO_2 emission curves shift and the parameters based on them are no longer reliable. This is highlighted in figure 10 below, where the OI reaches 1400mg CO_2/g TOC for bulk sediment whereas it does not exceed 600 in the rinsed sediment, a drastic difference for an interpretation based on the pseudo van Krevelen diagram, for example.

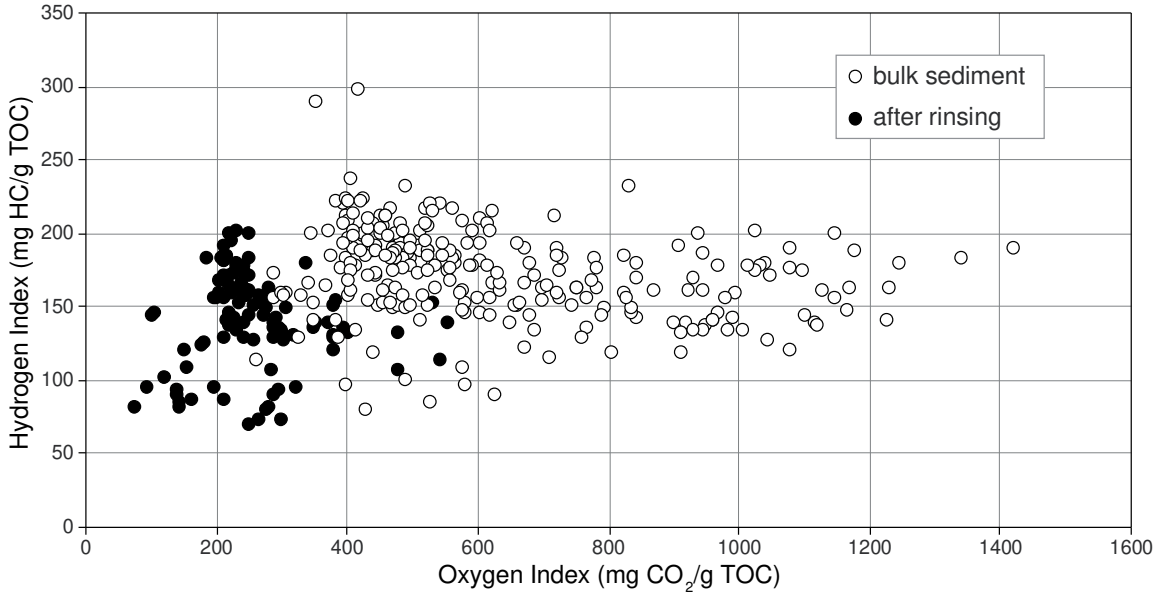

Fig. 10 – Comparison of organic matter typing using a modified van Krevelen diagram (HI-OI) for bulk and rinsed samples of recent hemipelagic sediment from the Timor Sea. The extremely high OI values for bulk sediment are artefactual (see Fig. 5 for explanation).

Finally, an important point when comparing bulk and rinsed sediments that has not yet been discussed in this paper is the mass effect. Indeed, the weight of a bulk sample is not the same as that of a rinsed sample because the salt disappears along with part (soluble) of the organic carbon. This effect must of course be taken into account but accounts for a minimum part of the observed differences between the bulk and rinsed samples. Figure 8 shows that the OI of the average bulk samples is around 600 mg CO_2/g TOC versus 300mg CO_2/g TOC for rinsed samples. If the cause of this very large difference was only linked to the loss of mass, this would imply a factor of 2 between TOC values of the bulk and rinsed samples. However it is very unlikely that rinsing causes such a difference in TOC between the bulk and the rinsed sample, let alone that the mass loss due to the removing of salt and the loss of part of the organic carbon is entirely responsible for such a difference. Moreover, core analyses allow us to definitely disregard the impact of this phenomenon in this study. Indeed, the TOC of sample 1-120 (120 cm from the top of the core) was 0.6% for the bulk sample versus 1.15 for the rinsed sample. This result confirms the underestimation of organic carbon discussed previously in this article but also make it possible to hold the mass effect responsible for this difference. However, sample 18-110 (taken deeper in the core at 2260 cm) was much more compacted than sample 1-120 and therefore did not contain enough water to cause the early chemical dissolution reaction of the carbonates. The TOC values for the rinsed and non-rinsed samples were almost identical (~ 1.11%), thereby confirming the negligible effect of mass loss in this situation.

Conclusion

Rock-Eval analyzes, widely used in the oil industry, were recently found to be appropriate for inferring the $CaCO_3$ content of a sample and identifying the type of carbonates it contains [1]. However, the relevance of the CO_2 production curve shape and temperature ranges obtained during thermal destabilization of carbonates is called into question by the transposition of this method to recent clayey sediments. Indeed, calcite (and probably all carbonates in recent sediments) becomes unstable at temperatures much lower than those of the fossil sedimentary rocks on which the mineral recognition records in the literature are based. Our study allowed us to highlight a shift in peak CO_2 temperatures observed with Rock-Eval and corresponding to the destruction of the carbonate phase within a sediment. This phenomenon is due to the combined presence of salt and water

and/or hydroxide anions expelled from clay minerals that leads to an acid reaction and early decomposition of carbonates itself leading to overestimation of mineral carbon and underestimation of organic carbon. Moreover, this CO_2 curve can also be misinterpreted if one relies on the CO_2 peaks obtained with Rock-Eval to identify the type of carbonate present in the sample according to the method of Pillot *et al.* [1]. The same goes for the OI that is overestimated due to underestimation of organic carbon. Care should thus be taken when analyzing recent hemipelagic samples and the samples should be thoroughly rinsed before analysis and interpretation to avoid any misinterpretation of the results.

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