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## Nacre biocrystal thermal behavior

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*Nacre is a biocrystal containing 2.4 wt% of organic matter which is made up of aragonite nanograins. The question which is raised in this paper concerns the behaviour of such a composite structure during thermal treatment.*

### Summary

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The thermal behaviour of *Pinctada margaritifera* nacre was studied at different temperatures by means of thermal gravimetric, thermo-mechanical and Rock-Eval analyses. From the mechanical point of view nacre exhibited a complete reversible behaviour up to 230 °C. The bio-aragonite allotrope was seen to be as stable as the abiotic aragonite up to 470–500 °C. It was also evidenced that the organic phase was keeping cracking oxygen functions at temperatures as high as 650 °C.

Nacre thermal behaviour could be described following four distinctive stages and discussed in comparison with previous data obtained in oxidative conditions.

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## **Introduction**

The thermal stability of nacre is of potential interest in different fields as crystallography, biomineralisation, geochemistry, exobiology<sup>1</sup> but also in biomaterials, biomimetism and chemistry.<sup>2</sup> The reason is that nacre is not a pure mineral but a biomineral or biogenic aragonite; the nacre crystal contains organic compounds long believed to be organic inclusions.<sup>3</sup> It was recently shown that a nacre biocrystal is in fact, made up of aragonite nanograins encapsulated into the intracrystalline organic matrix.<sup>4</sup> Despite this nano-composite structure the biocrystal (tablet) presents a perfect coherent diffraction pattern.<sup>5,6</sup> This was asserted by AFM (atomic force microscopy) in tapping mode (Fig. 1) evidencing the nanograins and TEM SAD single crystal-like pattern at the same scale (transmission electron microscopy selected area diffraction).

So the questions raised in this paper are: how nacre behaves during thermal treatment? What is the evolution of the organic matrix with regards to the mineral phase in such a composite crystal? And what is the thermal stability of aragonite under the form of nanograins intimately encapsulated within the intracrystalline organic matrix?

Some of these questions were investigated in oxidative conditions in the case of the same nacre by our group<sup>7</sup> as well as in coral by Dauphin et al.<sup>8</sup> These papers have shown that the organic matrix is not fully destroyed after an oxidation heat-treatment up to more than 500 °C. At the same time aragonite had already transformed into calcite.

## **Results**

The thermal gravimetric analysis (TGA) plots of *Pinctada maxima* nacre showed a good thermal stability up to 230 °C or showed a faint mass loss in the case of fresh nacre due to dehydration (less than 1%). Blocks contained more humidity and lost more weight. Above this temperature, nacre degraded with a two-step mass loss. The first one is minor and corresponds to the degradation of the most labile organic matter between 250 and 450 °C (500 °C for blocks, Fig. 2). The second, between 585 °C and 915 °C (550 °C and 890 °C for the powder), is an important mass loss which occurred due to the transformation of calcite into lime. Finally, at 1000 °C, the mass loss is stabilized (45% of the initial mass).

TMA records any volumetric change with temperature under argon. Two situations were systematically compared: elongation of nacre block parallel (1) and perpendicular (2) to the nacre tablets (see schematic in Fig. 3). First runs were conducted below 200 °C. Expansion of both samples was systematically reversible (not shown). It was possible to measure the two coefficients of thermal expansion:  $\varepsilon = 5 \times 10^{-8} \text{ K}^{-1}$  in the plane and  $\varepsilon = 24.5 \times 10^{-8} \text{ K}^{-1}$  perpendicular to the planes. Thus, as expected, nacre exhibits a good reversible anisotropy below 200 °C: expansion is 5 times higher perpendicularly to the tablets.

As a summary, from room temperature up to 230 °C nacre was stable when heated under argon. A small mass loss was attributed to dehydration. No hydrocarbon nor CO<sub>2</sub> were detected by means of the Rock-Eval technique. A first stage can be pointed out as that of *'nacre reversible expansion from room temperature up to 230 °C'*.

TMA was also conducted up to 1000 °C under argon. An example is given in Fig. 3. A small expansion of 3.5% was seen to occur at 250 °C, solely visible in the stacking direction. It is attributed to a 'puffing' due to the onset of gas departure. This is asserted by the temperature-programmed desorption technique Rock-Eval which is used for detecting hydrocarbons, CO and CO<sub>2</sub>. The TGA 'puffing' at 250 °C occurs as hydrocarbons (Fig. 4(a)) but also CO<sub>2</sub> (Fig. 5(a)) start being released from the structure.

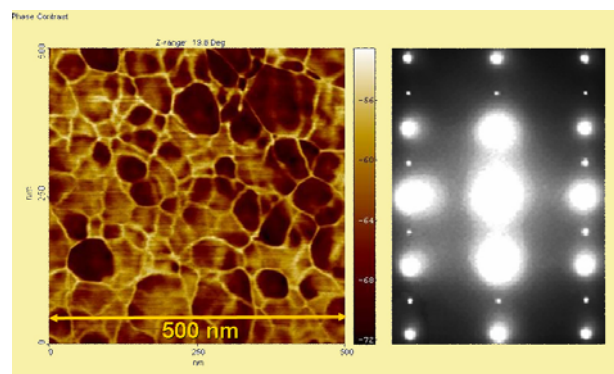
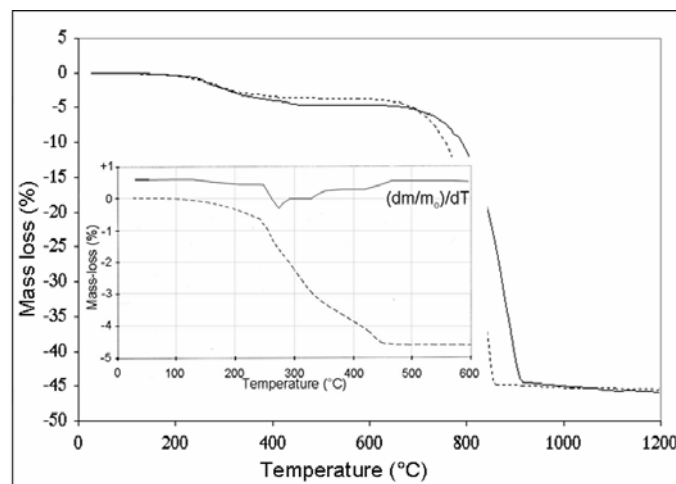


Fig. 1 Nanostructure of nacre biocrystal : nanograins as seen by AFM and TEM electron diffraction showing a single crystal-like pattern at the same scale (Ref 4).

So, a second stage can be defined which extends between 250 and 450 °C when the TGA curve gets back to zero characterized by the *'organic matrix cracking under the form of*

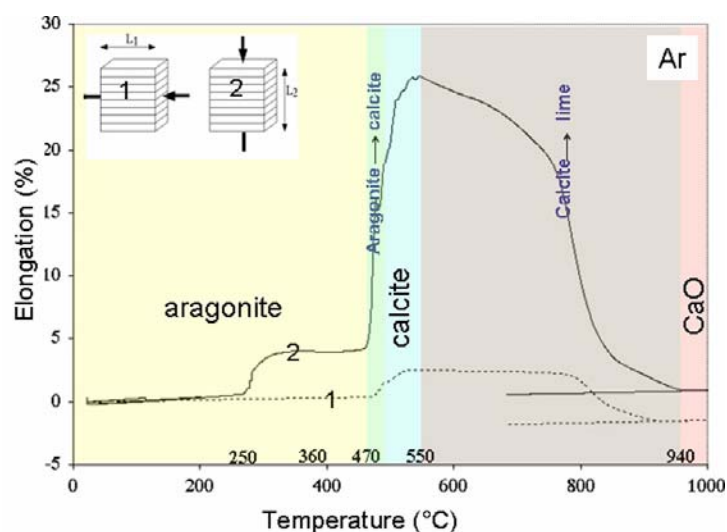
*hydrocarbons*'. Indeed, most of the hydrocarbons are released during this second stage. At the same time, the CO<sub>2</sub> signal exhibits a broad massif between 250 and 500 °C with exclusively C and O of organic origin. The abiotic aragonite crystal—purely mineral—only shows a negligible CO<sub>2</sub> departure below 500 °C. At the same time, decalcified nacre demonstrates that 75% of the organic CO<sub>2</sub> is still to come at the end of the second stage. It is to note that during this second stage the strong cracking of the organic matrix occurs without allotropic transformation of the bio-aragonite: it is stable up to 470 °C as deduced from TMA. The nanocomposite structure of the biocrystal does not change the thermal stability of aragonite.



**Fig. 2 Nacre thermal gravimetric analysis (under nitrogen). Dotted line : powder; full line : block. The inset is a zoom of the thermal behaviour from 20 to 600°C with the derivative of the signal for nacre powder.**

The third stage started at 470 °C with a large ‘swelling’ in the TMA plots in both stacking and in plane directions. This expansion is produced by the allotropic transformation of aragonite to calcite. It was occurring at lower temperature under an isothermal oxidation treatment (300 to 400 °C, see ref. 7). The aragonite–calcite lattice expansion is known in the literature to be +2.8% and occurring between 420 and 520 °C for natural aragonite.<sup>9</sup> Our results are coherent in plane (+2.1%) but much higher in the stacking direction (+21.6%). This lattice expansion is supposedly amplified by a ‘puffing’ effect due to the cracking of the

intracrystalline matrix encapsulating the aragonite nanograins (see Fig. 1). Indeed, the Rock-Eval plots exhibit a peak of hydrocarbon and a peak of organic CO<sub>2</sub> at the same time. As the mechanical resistance of nacre is less in the stacking direction, all the additional expansion occurs in this direction. At the same time, the abiotic aragonite did not show any extra degassing (continuous and very faint) during the allotropic transformation. Also these peaks disappear in the case of decalcified nacre (Fig. 4(b) and 5(b)).



**Fig. 3** A TMA plot of nacre blocks up to 1000°C under argon : (1) sensor parallel to the plane and (2) perpendicular to the tablet stack.

As a summary, the third stage can be considered as the ‘*allotropic transformation of bio-aragonite into calcite between 470 and 550 °C*’. A comparison of nacre with decalcified nacre showed that most of the organic oxygen functions are still stable at the end of this process.

Finally, a fourth and last stage relates to a strong shrinkage between 550 and 940 °C (910 °C in the plane, Fig. 3) and the main weight loss, 40% as asserted by TGA. The Rock-Eval plots showed at the same time that the organic matrix continues to produce mainly CO<sub>2</sub> and CO molecules up to 650 °C. Above this temperature, all the mass loss is due to the calcination of calcite. The end of this fourth stage occurred at 940 °C beyond which, the sample is supposed to be composed of lime, residual calcite and a small fraction of refractive

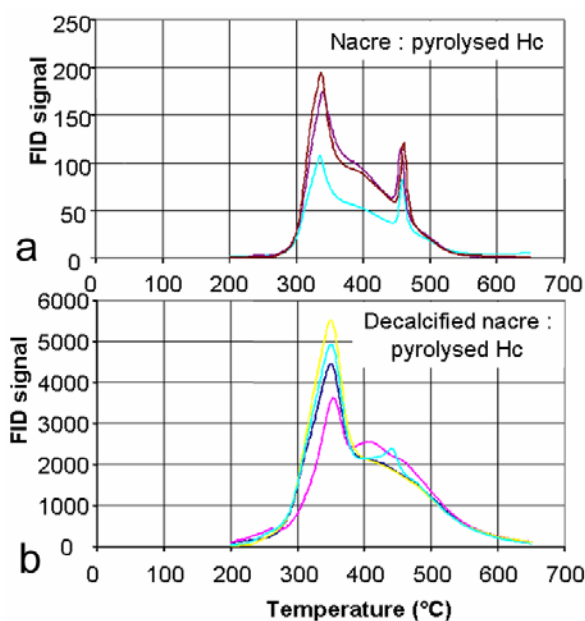
carbon. This phenomenon happened at lower temperature under isothermal oxidation treatment: a blend of calcite and lime was observed already at 550 °C up to 900 °C where a tiny amount of calcite is still visible in the powder.<sup>7</sup> The mineral CO<sub>2</sub> departure can be calibrated with the abiotic aragonite. It really starts above 630 °C with limited amplitudes anyway. It fits with the TMA shrinkage due to the chemical transformation of calcite into lime by departure of CO<sub>2</sub>. The amplitude is meanwhile very limited and one could think that *'CO<sub>2</sub> released by nacre before 650 °C is produced quasi exclusively by the organic fraction'*.

## Discussion and conclusions

The presence of organic matrix in nacre was seen to change the well known transformation of abiotic aragonite to calcite and then calcite into lime with temperature. In nacre, the organic matter is stable up to 250 °C. Then cracking of the organic content occurs two times, between 250–550 °C (comprising all the hydrocarbons) and then between 550–650 °C (oxygen functions). What is noticeable here, is the very high temperature for which the insoluble organic fraction is still active at producing CO<sub>2</sub>: the highest peak is centred at approximately 650 °C. Above 650 °C, only a small residue of refractive organic carbon remains. Refractive organic carbon is quantified by a subsequent oxidation heat treatment by means of the Rock-Eval method up to 850 °C (Fig. 6(b)) measuring the related CO and CO<sub>2</sub> at low temperature (Fig. 6(a)): 20% of the total organic carbon remains as refractive carbon in nacre. Refractive carbon increases up to 50% in the decalcified samples (AIM).

The Rock-Eval technique provides also the total organic carbon balance (TOC). Decalcified nacre (AIM) gave a TOC value of 45 wt% of the mass of the sample. This value was calculated following the standard IFP (Institut Francais du Petrole) method for isolated organic matter, adding high temperature peaks as S3', S3'<sub>CO</sub> as well as S5. As expected the abiotic aragonite did not give any TOC. Nacre provided 2 sets of values: nacre powders gave a TOC value of 1.2%, while blocks gave 0.9%. The organic matrix content of nacre is thereafter 2.7 wt% if measured in the powder and 2.0% in the blocks. The order of magnitude is good since the estimated value by the chemical extraction protocol gives 2.4%.

The experiments conducted on the powder (TGA or Rock-Eval) have shown that the 4 thermal stages looked the same but shifted at lower temperature. The TGA were also conducted under air. There were no changes with this technique when oxidizing at  $5\text{ }^{\circ}\text{C min}^{-1}$ . The reason is that nacre has no porosity so the oxygen diffusion inside the material is limited. At  $5\text{ }^{\circ}\text{C min}^{-1}$  under air, oxidation remained limited even for powder and is much similar to pyrolysis. A comparison of the oxidation conditions of our previous work<sup>7</sup> to the present ones also reveals that the ‘oxidation’ effect is negligible regarding the ‘thermal’ one.



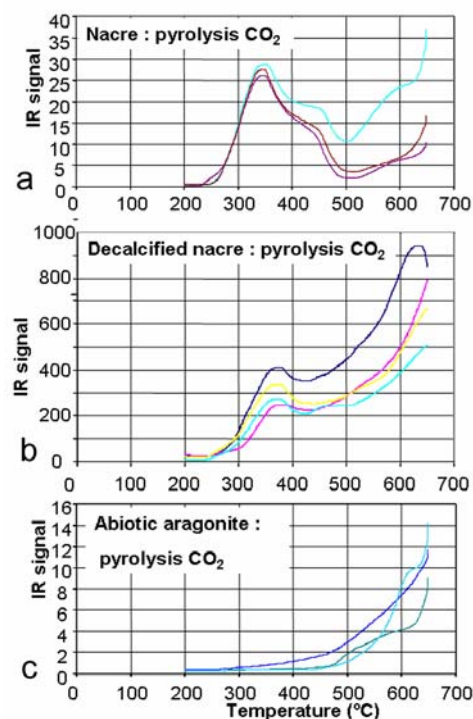
*Fig. 4 Rock-Eval hydrocarbon departure ( $S_{2_{Hc}}$ ) during the pyrolysis: (a) nacre blocks comparison of 3 same samples; (b) insoluble organic matrix (freeze-dry powder of AIM, 4 runs)*

The third stage started at  $470^{\circ}\text{C}$  with a large ‘swelling’ in the TMA plots in both stacking and in-plane directions. This expansion is produced by the allotropic transformation of aragonite to calcite. It was occurring at lower temperature under isothermal oxidation treatment ( $300$  to  $400^{\circ}\text{C}$ , see ref 7). The aragonite/calcite lattice expansion is known in the literature to be  $+2.8\%$  and occurring in-between  $420$  and  $520^{\circ}\text{C}$  for natural aragonite<sup>1</sup>. Our results are



coherent in plane (+2.1%) but much higher in the stacking direction (+21.6%). This lattice expansion is supposedly amplified by a ‘puffing’ effect due to the cracking of the intracrystalline matrix encapsulating the aragonite nanograins (see Fig.1). Indeed, Rock-Eval exhibits a peak of hydrocarbon and a peak of organic CO<sub>2</sub> at the same time. As the mechanical resistance of nacre is less in the stacking direction, all the additional expansion occurs in this direction. In the same time, the abiotic aragonite did not show any extra degassing (continuous and very faint) during the allotropic transformation. Also these peaks disappear in the case of decalcified nacre (Figs 4b and 5b).

As a summary, third stage can be considered as the ‘*allotropic transformation of bio-aragonite into calcite between 470 up to 550°C*’. Comparison of nacre with decalcified nacre showed that most of the organic oxygen functions are still stable at the end of this process.



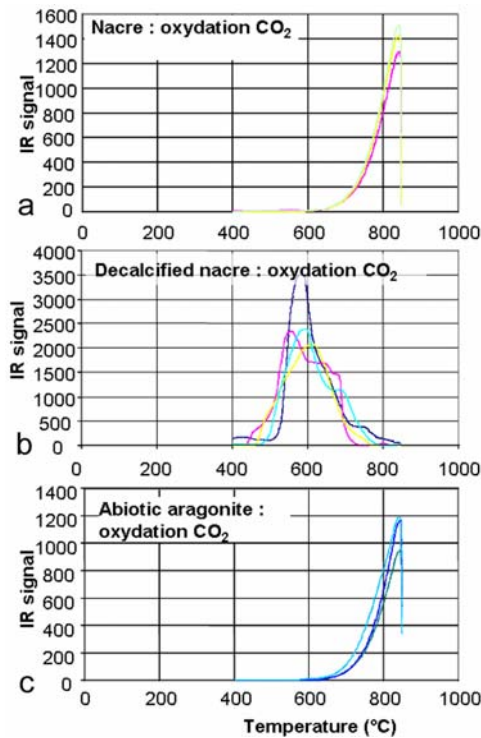
**Fig. 5** Rock-Eval CO<sub>2</sub> pyrolysis plots (S3 and S3’); a) in nacre (3 runs); b) insoluble organic matrix (AIM, 4 runs); c) abiotic aragonite : very weak release (compare the scales, 3 runs).

Finally, a fourth and last stage relates to a strong shrinkage in between 550°C and 940°C (910°C in the plane, Fig. 3) and the main weight loss, 40% as asserted by TGA. Rock-Eval showed in the same time that the organic matrix continues to produce mainly CO<sub>2</sub> and CO molecules up to 650°C. Above, all the mass loss is due to the calcination of calcite. The end of this fourth stage occurred at 940°C. Above, the sample is supposed to be composed of lime, residual calcite and a small fraction of refractive carbon. This phenomena happened at lower temperature under isothermal oxidation treatment : a blend of calcite and lime was observed already at 550°C up to 900°C where a tiny amount of calcite is still visible in the powder<sup>7</sup>.

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*Fig. 6 Rock-Eval oxidation CO<sub>2</sub> plots (S5). (a) nacre: mineral CO<sub>2</sub> released by calcination (3 samples); (b) decalcified nacre : organic CO<sub>2</sub> released by oxidation of refractive carbon (4 samples); (c) abiotic aragonite: mineral CO<sub>2</sub> (3 samples).*

Rock Eval provides also the total organic carbon balance (TOC). Decalcified nacre (AIM) gave a **TOC value of 45 wt%** of the mass of the sample. This value was calculated following the standard IFP method (Institut Francais du Petrole) for isolated organic matter, adding high temperature peaks as S3', S3'<sub>CO</sub> as well as S5. As expected the abiotic aragonite did not give any TOC. Nacre provided 2 sets of values : nacre powders gave a TOC value of 1.2 %, while blocks gave 0.9%. The organic matrix content of nacre is thereafter 2.7 weight % if measured in the powder and 2.0% in the blocks. The order of magnitude is good since the estimated value by the chemical extraction protocol gives : 2.4%.

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## Experimental

Densities were obtained on nacre powder with a helium pycnometer (AccuPyc 1330 from Micrometrics) and a mean value of ten successive tests. The *Pinctada maxima* nacre used in this work was found to have a specific mass of  $2.836 \pm 2.10^{-3} \text{ g cm}^{-3}$  by helium picnometry. This value is to be compared with that of geologic crystals which varies between 2.920 and  $2.995 \text{ g cm}^{-3}$  or with the calculated value of  $2.920 \text{ g cm}^{-3}$  for a reference crystal (JCPDS no. 41-1475). This lower experimental density can be simply related to the fact that nacre is not pure aragonite. The lower density of the organic matrix fraction makes the difference (2.4 wt% as measured by the biochemical extractions or approximately 6% in volume).

Thermogravimetric analyses (TGA) were conducted with a TAG 24 from Setaram with a ramp of  $5^{\circ}\text{C min}^{-1}$  on pristine powder and block of nacre under argon (or under air, with no difference).

The thermal behaviour was also characterized by means of thermo-mechanical analysis (TMA) conducted with a Dilatometer Sestys 24 from Setaram, France. The first measure concerns the anisotropy of the reversible expansion of nacre between  $20^{\circ}\text{C}$  and  $230^{\circ}\text{C}$ . The ramp used for this purpose is  $1^{\circ}\text{C min}^{-1}$  up to  $200^{\circ}\text{C}$  and back to room temperature at  $1^{\circ}\text{C min}^{-1}$ . The second series of tests concerns the thermo-mechanical characterization of nacre in the range of  $1000^{\circ}\text{C}$  (ramp up to  $1000^{\circ}\text{C}$  at  $5^{\circ}\text{C min}^{-1}$  and back to room temperature at the same speed). For that purpose, two blocks of nacre were cut with a diamond saw ( $L1 = 4.474 \pm 0.005 \text{ mm}$  and  $L2 = 3.320 \pm 0.005 \text{ mm}$ ). All the runs were performed along the two main directions, say parallel and perpendicular to the anisotropy plane of nacre.

The Rock-Eval analysis (Vinci Technologies, Rock-Eval 6 Turbo, France) was developed for estimating the petroleum potential of sedimentary rocks (IH, OH and Tmax), the total organic carbon content (TOC), the total mineral carbon content (CMin) by heating samples in an open pyrolysis system under argon.<sup>10-12</sup> An analysis takes place in 2 steps. First, during a pyrolysis under nitrogen a desorption of hydrocarbon is maintained at 200 °C for 5 min. Then a cracking occurs between 200 and 650 °C at 30 °C min<sup>-1</sup>. Hydrocarbons are monitored by a flame ionization detector (FID), forming the so-called peak S1 (mgHc (g<sub>sample</sub>)<sup>-1</sup>, ‘volatilized hydrocarbons’), S2 (mgHc (g<sub>sample</sub>)<sup>-1</sup>, ‘pyrolyzed hydrocarbons’). At the same time infrared cells detect CO and CO<sub>2</sub> (Rock-Eval gives 2 values: S3<sub>CO</sub> (mgCO (g<sub>sample</sub>)<sup>-1</sup>) and S3<sub>CO<sub>2</sub></sub> (mgCO<sub>2</sub> (g<sub>sample</sub>)<sup>-1</sup>) corresponding to the release of functions linked to organic molecules. At higher temperature it records also the S3’<sub>CO</sub> which is organic and mineral CO and S3’ generally attributed to mineral CO<sub>2</sub>. In the present work, it was evidenced that organic CO<sub>2</sub> can be easily integrated up to 650 °C for nacre. Second, the residue recovered after pyrolysis undergoes a combustion from 400 °C up to 850 °C, under artificial air (N<sub>2</sub> : O<sub>2</sub>, 80 : 20) in a second oven. CO and CO<sub>2</sub> released are monitored on line by means of infrared cells. The Rock-Eval method then gives S4<sub>CO</sub> and S4<sub>CO<sub>2</sub></sub> (respectively mgCO (g<sub>sample</sub>)<sup>-1</sup> and mgCO<sub>2</sub> (g<sub>sample</sub>)<sup>-1</sup>) of organic origin in this work. Finally, S5 measure the CO<sub>2</sub> provided by the mineral source above 400 °C. The initial weight was measured with a precision over 0.5 mg in order to obtain reliable Rock-Eval parameters (*i.e.* S2 ± 0.5 mg (g<sub>rock</sub>)<sup>-1</sup>, TOC and C<sub>Min</sub> ± 0.1 wt%). The organic matrix extracted using the acetic acid protocol was also tested (insoluble fraction: AIM).

## Acknowledgements

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