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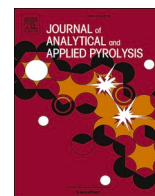
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The effect of the mineral matrix during thermal analysis of polymers: Implications for microplastics characterization

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ABSTRACT

The exponential growth of global plastic production complicates waste management, leading to the accumulation of microplastics in the environment. Currently, the identification and quantification of microplastics rely on various analytical methods that often require sample pretreatments, which can introduce errors. The Rock-Eval® thermal method, through the total quantity of hydrocarbon (*Total HC* parameter) and the temperature of their maximum release (T_{peak}), identifies and quantifies polymers when individually analyzed. However, mineral matrices in natural sediments can influence these parameters. In this study, synthetic mixtures of various mineral matrices and polymers were analyzed using the thermal Rock-Eval® method. Three effects of mineral matrices on the thermal degradation of polymers have been identified: (1) catalysis, which accelerates the polymer degradation; (2) multimodal inhibition, characterized by a fractionated release of hydrocarbons, first at expected pyrolysis temperatures and then at higher temperatures; and (3) retention, which reduces total HC released. The same mineral matrix can produce different effects depending on the type of polymer with which it is mixed. For instance, illite catalyzes the degradation of polyethylene (PE), but inhibits that of polyethylene terephthalate (PET). Despite these effects, linear regressions between the Total HC and polymer content in synthetic mixtures provide a coefficient of determination (r^2) of 0.99, confirming that matrix effects do not hinder polymer quantification. Furthermore, mixtures with natural matrices show effects comparable to those observed with synthetic matrices. These findings represent a first step towards understanding the effects of the matrix and confirm the possibility of using the thermal Rock-Eval® method as a simple tool to identify and quantify microplastic pollution in natural sediments.

1. Introduction

Global plastic production has been increasing since the middle of the twentieth century. In 1950, production amounted to only 2 million tons (Mt), but this figure has risen to 450 Mt in 2024 [16]. Among the most commonly produced polymers are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET), each suited to specific applications, including food packaging, electronic devices, medical equipment, and synthetic textiles.

However, the rapid growth of plastic production has outpaced the

ability to manage the resulting waste. A significant portion of plastic waste escapes recycling or treatment and is ultimately released into the environment. Rainwater often transports these plastics into rivers, which serve as primary conduits to the oceans [1,29,32]. Jambeck et al. [21] estimate that 8–12 million tons of plastic enter the oceans each year, threatening marine ecosystems.

In aquatic environments, plastic debris takes various forms, including primary microplastics (MPs), which are intentionally manufactured at a small size, such as plastic beads or microfibers, and secondary microplastics generated by the breakdown of larger plastic

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products or textile fibers [1,2]. Microplastics are particles ranging in size from 1 μm to 5 mm, with shapes and densities varying depending on degradation mechanisms and polymer types. These factors influence the processes of microplastic deposition and sedimentation in aquatic environments. It is important to be able to identify microplastics in sediments in order to better understand the fate of this waste.

To assess the risks posed by microplastics, standardized methodologies are essential to compare results between studies. Currently, there is no universal method and the diversity of techniques introduces complexities in data comparison [19,3]. This challenge is compounded by the extensive sample pretreatments often required to isolate microplastic particles from environmental samples, introducing biases in both identification and quantification [18]. Today, a consensus on how to analyze microplastics control data has not been yet established [9]. For instance, the Fourier transform infrared (FTIR) spectroscopy technique is widely employed to identify chemical species, characterize composition, and quantify microplastic abundances. However, as shown by Munno et al. [30], steps like organic matter degradation and mineral matrix separation can affect accuracy. The phenomenon of 'missing plastics' exemplifies the challenge: a large proportion of plastic waste remains unaccounted for, highlighting the need for simpler and more reliable methods.

Thermal methods are increasingly recognized as suitable for microplastic analysis. These include pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) [31]. However, these techniques often require the prior separation of microplastics from the sample matrices to ensure accurate results. For example, Salter et al. [36] conducted tests using clay and iron oxide matrices and demonstrated that the composition of the matrix significantly influences the Py-GC/MS signals and their intensities, particularly when analyzing PE alone versus PE combined with these matrices. These matrix effects prevent the accurate identification and quantification of polymers in sediments [24,26].

In this context, the thermal Rock-Eval® apparatus has emerged as a promising alternative to identify and quantify polymers in environmental samples [33]. This method involves a two-step temperature-programmed analysis. In the first step (pyrolysis phase), the sample is heated under an inert atmosphere, and the release of hydrocarbons (HC), carbon monoxide (CO), and carbon dioxide (CO₂) is measured as pyrolysis temperature increases. In the second step (oxidation phase), the residual carbon is combusted under an oxidative atmosphere, and the CO and CO₂ released are again quantified.

From these thermal signals, several parameters are derived, including total organic carbon (TOC), pyrolyzable carbon (PC), residual carbon (RC), and total hydrocarbon yield (Total HC). The temperature of maximum hydrocarbon release (*Tpeak*) is specific to each polymer and thus provides a key metric for polymer differentiation.

Compared to the most widely used techniques— μFTIR and Py-GC/MS—Rock-Eval® addresses several limitations. While μFTIR is limited by its detection threshold ($\sim 20\ \mu\text{m}$), difficulties with black particles and synthetic fibers, and geometric approximations for mass estimation, Py-GC/MS requires complex calibration, is sensitive to polymer aging, and can be affected by matrix residues that mimic polymer signatures [7].

A recent study successfully applied Rock-Eval® method to quantify textile microfibers in laundry wastewater, further validating its applicability to environmental samples containing microplastics [34].

For soil samples, a key advantage of Rock-Eval® lies in its intended use with minimally pretreated samples, in contrast to μFTIR and Py-GC/MS which necessitate thorough sample preparation. Although matrix effects have been observed, Romero-Sarmiento et al. [33] demonstrated that quantification remains possible if the composition of the natural matrix is known.

Despite this progress, further research is required to understand how mineral matrices specifically influence the pyrolysis and oxidation products of polymers as thermal degradation proceeds. Although

previous studies have investigated matrix effects during the artificial thermal maturation of the sedimentary organic matter [10,13], their impact on synthetic polymers has not been explored yet. The objective of this research is to evaluate the influence of various mineral matrices on the degradation of selected polymers during thermal analyses. This work aims to establish a straightforward Rock-Eval® protocol based on the identification and quantification of microplastics in sediments, thus advancing the field of environmental plastic analysis and understanding of matrix effects.

2. Materials and methods

2.1. Materials: selected mineral matrices and polymer samples

Three pure polymers were selected for this study as follows:

1. Polyethylene (PE), which represents nearly one-third of the world's plastic production and is one of the most prevalent polymers in marine environments [38]. It is mainly used for plastic packaging and its chemical formula is $(\text{C}_2\text{H}_4)_n$.
2. Polyethylene terephthalate (PET), the primary polymer used for bottles. It is commonly found in oceans as bottle fragments, with the chemical formula $(\text{C}_{10}\text{H}_8\text{O}_4)_n$.
3. Polylactic acid (PLA), a biodegradable polymer with the chemical formula $(\text{C}_3\text{H}_4\text{O}_2)_n$.

The polymers used in this study were provided by Sigma-Aldrich for PE and Goodfellow for PET and PLA.

To compare interactions between polymers and mineral matrices, an inert matrix was selected, consisting of sand primarily composed of silica (SiO₂). The sand was sourced from the Fontainebleau sandstone formation, located in the southern Île-de-France region, approximately 60 km southeast of Paris, France. It corresponds to the same sandy matrix previously used in Romero-Sarmiento et al. [33] and Romero-Sarmiento et al. [34]. To ensure that the sand contained no natural organic matter or traces of carbonate, it was heated to 850°C before use. Table S1 Supplementary data from Romero-Sarmiento et al. [34] present the detailed chemical composition of the natural sand sample used as the reference inert mineral matrix in this study.

In addition, five synthetic mineral matrices were chosen, as detailed in Table 1, in order to ensure the absence of natural organic matter and to allow for a controlled assessment of plastic–mineral interactions.

1. Calcite (CaCO₃), a major component of carbonated rocks,
2. Illite ((K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂(H₂O)]),
3. Kaolinite (Al₂Si₂O₅(OH)₄), both clay minerals, are commonly found not only in marine sediments, but also in fine-grained detrital rocks and on continental surfaces,
4. Sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O), a hydrated fibrous clay mineral, is a good representative of the fibrous phyllosilicate group, and
5. Goethite (FeOOH), an iron oxide, is a representative of iron (oxyhydr)oxides frequently encountered in surface environments, particularly in soils and weathering profiles.

All pure mineral matrices were acquired in dry powder form from Sigma-Aldrich®, except for calcite, which was obtained from CARLO ELBA.

In order to compare the effects generated by an interaction-free synthetic mineral matrix and a natural mineral matrix, three natural matrices were also selected:

1. Chalk (CaCO₃): A sample sourced from the upper Cretaceous chalk succession, characteristic of the eastern part of the Paris Basin (France), with a calcitic mineralogical composition.
2. Kaolinitic claystone (Al₂Si₂O₅(OH)₄): A natural sample obtained from a deposit of kaolinite.

Table 1
Properties of mineral matrices tested.

Mineral	Density (g/cm ³)	Specific Surface Area (m ² /g)	Cation Exchange Capacity (CEC) (meq/100 g)	Clay Type	Dehydration Temperature (°C)	Decomposition Temperature (°C)	References
Sand	2.65	Very low	Very low		100–200	> 1700	[20]
Calcite	2.71	Very low	Very low		100–200	600–900	[27]
Illite	2.6–2.9	20–40	10–40	2:1 Clay	100–150 (surface) 350 – 400 (interfoliar)	800–900	[22]
Kaolinite	2.6	10–20	3–15	1:1 Clay	100–200	500–600	[14,35]
Sepiolite	2.0–2.5	100–300	20–30	Fibrous Clay	70 – 90 (surface) 210–320 (channel)	350–500	[15,39]
Goethite	3.3–4.3	10–132	Low		100–200	250–300	[24,28]

3. Illitic claystone, composed of a mixture of illite (80 %) and quartz (20 %).

These three mineral matrices were analyzed by X-ray diffraction to confirm their mineralogical composition and by Rock-Eval® to assess their total organic carbon (TOC) content. Chalk and kaolinitic claystone have a negligible TOC content (TOC ≤ 0.01 wt%), whereas illitic claystone contains a small amount (TOC ≈ 0.1 wt%).

This selection of mineral matrices and polymers represents a diverse range of sediment types that cover various physicochemical characteristics, closely resembling samples found in the environment. Artificial composite samples were prepared by mixing a given mineral matrix (100 %) with a polymer, following the procedures described in Romero-Sarmiento et al. [33].

2.2. Methods: Rock-Eval® device and procedures

The samples were analyzed using a Rock-Eval®7S apparatus operated at Sorbonne Université (commercialized by Vinci Technologies). During pyrolysis, all hydrocarbon compounds generated were monitored by a flame ionization detector (FID), while nonhydrocarbon compounds, such as CO₂ and CO released during pyrolysis and oxidation, were monitored by an infrared detector [12,25,33,4,6].

A modified 'Basic / Bulk-Rock' method was applied for the analyzes, characterized by an initial pyrolysis step at 200 °C for 3 min, followed by a temperature ramp of 25 °C / min to 650 °C. The oxidation conditions ranged from 200 °C to 850 °C with a temperature increase of 20 °C / min [6,11,12,25,33].

The Rock-Eval® analysis protocol was performed as follows:

1. The sand was analyzed successively with each polymer to characterize their thermal properties. Polymer samples were prepared with a concentration of 3 %, corresponding to 1.8 mg of polymer for a total sample weight of approximately 60 mg. This concentration is higher than typical environmental levels, but was intentionally increased to enhance the detection of matrix effects. It was also optimized to remain within the linear response range of the FID detector, avoiding saturation while ensuring sufficient signal even in cases of strong retention or thermal desorption effect.
2. For synthetic and natural mineral matrices, polymer mixtures were prepared with the same polymer concentration of 3 %. For calcium carbonate, the sample weight was set at 40 mg to avoid detector saturation, following the recommendations of Baudin et al. [5]. Sepiolite was also weighed at 40 mg due to its lower density, while a weight of 60 mg was used for all other matrices. The impact of polymer concentration on results was studied by preparing mixtures with varying PE concentrations (0.2–4.2 %, in increments of 1 %) combined with different mineral matrices.

All analyzes were conducted in triplicate to ensure the reproducibility of the results. The instrument was calibrated using the IFPEN 160,000 reference sample, and the accuracy of the measurements was verified with this reference sample every ten analyzes. Rock-Eval®

thermograms were visualized using Geoworks-Geochemical software provided by Vinci Technologies (France). Rock-Eval® parameters previously defined to characterize polymer families (e.g. *Total HC*, *Tpeak*, among others) were then calculated following procedures already published in Romero-Sarmiento et al. [33]. Furthermore, Rock-Eval® FID/IR signal deconvolutions were integrated using Python accordingly.

3. Results

3.1. Synthetic mineral matrices

Fig. 1 presents the FID pyrolysis thermograms of PE, PET, and PLA (3 wt%) mixed with different mineral matrices, illustrating the significant impact of the mineral matrices on the thermal degradation of these polymers.

Table 2 summarizes the Rock-Eval® pyrolysis parameters for each composite polymer-mineral matrix sample, providing insights into variations in T_{peak} and Total HC release.

3.1.1. Polyethylene

Sand, used as the reference inert matrix, exhibits a T_{peak} of 507 ± 2 °C with a Total HC release of 32.21 ± 0.71 mg/g, reflecting the thermal behavior of PE in the absence of matrix interactions.

Calcite has a negligible effect on PE pyrolysis, showing similar T_{peak} and Total HC values to those observed with sand.

Clay minerals induce a significant change in the thermal degradation profile of PE. The presence of illite, kaolinite, and sepiolite reduces T_{peak} to 422 ± 2 °C, 486 ± 1 °C, and 455 ± 5 °C, respectively, accompanied by a decrease in Total HC release to approximately 27 mg/g for all three mixtures.

Goethite exerts the most pronounced effect on Total HC, reducing hydrocarbon release to 5.81 ± 0.55 mg/g and slightly altering the thermal degradation temperature.

Fig. 2 provides a detailed view of the release of hydrocarbons for PE in various mineral matrices at different concentrations. Table S1 (Supplementary Material) quantifies the Total HC values, highlighting a gradual decrease in HC release in the presence of clays, with goethite showing the most significant reduction. Regardless of the mineral matrix, increasing the concentration of PE in the sample leads to higher Total HC values.

Clays exhibit a stronger influence on PET degradation. Illite increases T_{peak} to 517 ± 2 °C while reducing Total HC to 7.36 ± 0.16 mg/g. Sepiolite leads to a significant shift, raising T_{peak} to 583 ± 2 °C.

Kaolinite behaves similarly to sand, showing a T_{peak} of 459 ± 2 °C and a Total HC release of 9.51 ± 0.16 mg/g. However, like calcite, the release of HC continues after this initial liberation.

Goethite exerts the strongest effect, reducing the Total HC release to 4.08 ± 0.25 mg/g while increasing T_{peak} to 537 ± 4 °C.

3.1.2. Polylactic acid (PLA)

Sand, as a reference matrix, exhibits a T_{peak} of 378 ± 4 °C and a Total HC release of 7.47 ± 0.73 mg/g, representing PLA degradation in the absence of matrix effects. Calcite shows a slightly lower T_{peak} ($367 \pm$

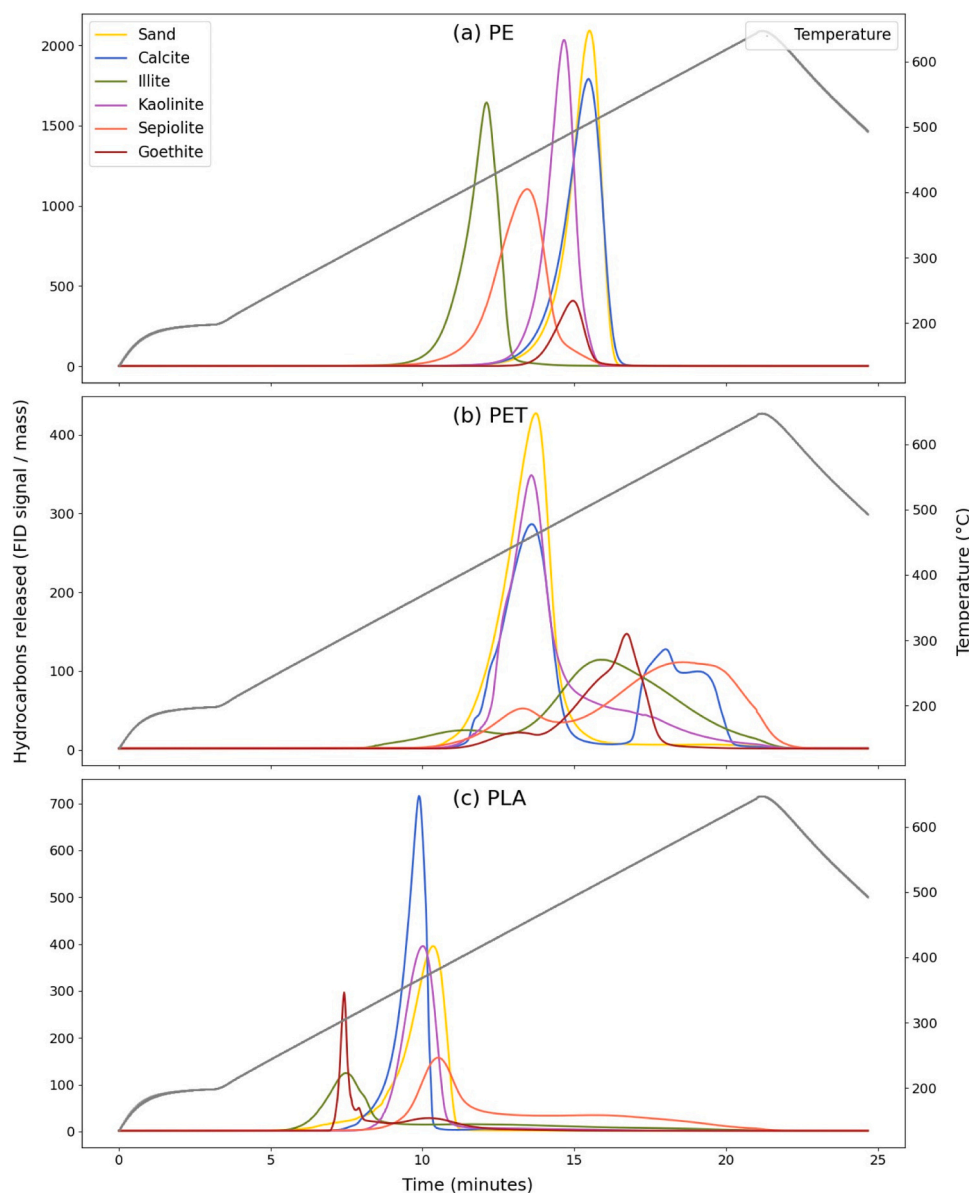


Fig. 1. Rock-Eval® FID thermograms showing the *Total HC* released during the thermal degradation of (a) polyethylene (PE), (b) polyethylene terephthalate (PET), and (c) polylactic acid (PLA) mixed with different mineral matrices.

Table 2

Total HC and T_{peak} parameters for polyethylene (PE), polyethylene terephthalate (PET) and polylactic acid (PLA) with 3% polymer concentration in different mineral matrices.

Matrix	PE		PET		PLA	
	T_{peak} (°C)	Total HC (mg/g)	T_{peak} (°C)	Total HC (mg/g)	T_{peak} (°C)	Total HC (mg/g)
Sand	507 ± 2	32.21 ± 0.71	463 ± 2	9.71 ± 0.24	378 ± 4	7.47 ± 0.73
	506 ± 5	32.06 ± 0.18	460 ± 7	10.13 ± 0.19	367 ± 2	8.01 ± 0.15
Calcite	422 ± 2	25.9 ± 0.2	517 ± 2	7.36 ± 0.16	310 ± 10	3.71 ± 0.02
	486 ± 1	27.87 ± 0.14	459 ± 2	9.51 ± 0.16	370 ± 2	6.30 ± 0.03
Illite	455 ± 5	27.14 ± 0.06	583 ± 2	8.07 ± 0.25	382 ± 3	6.04 ± 0.01
	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
Kaolinite	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
Sepiolite	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
Goethite	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36
	493 ± 4	5.81 ± 0.55	537 ± 4	4.08 ± 0.25	304 ± 2	2.32 ± 0.36

2°C) while maintaining a similar Total HC value (8.01 ± 0.15 mg/g).

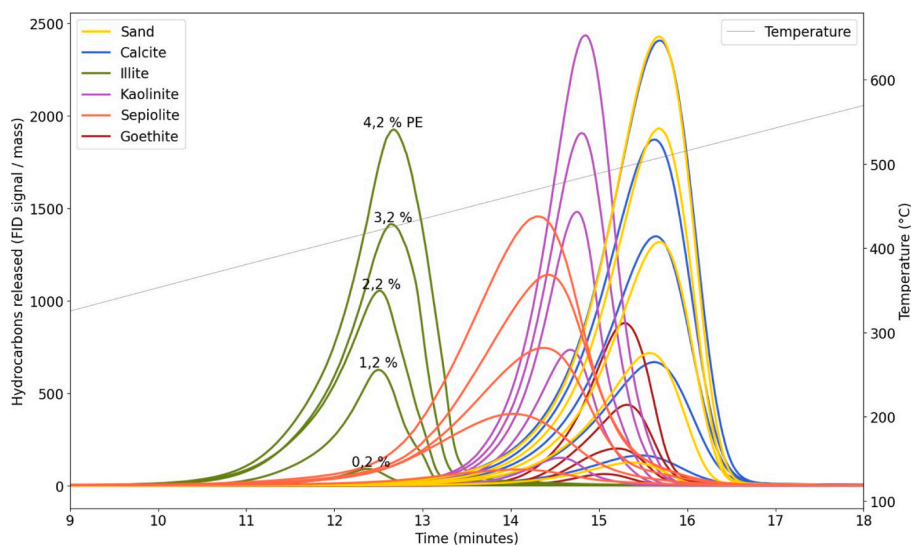
Clay minerals significantly modify the thermal degradation of the PLA polymer. Illite reduces T_{peak} to 310 ± 10 °C and decreases Total HC to 3.71 ± 0.02 mg/g. Kaolinite shows values comparable to those obtained with sand, while sepiolite increases T_{peak} to 382 ± 3 °C, exceeding the reference of sand, with prolonged HC release.

Goethite significantly alters PLA degradation, reducing Total HC release to 2.32 ± 0.36 mg/g and shifting T_{peak} to 304 ± 2 °C.

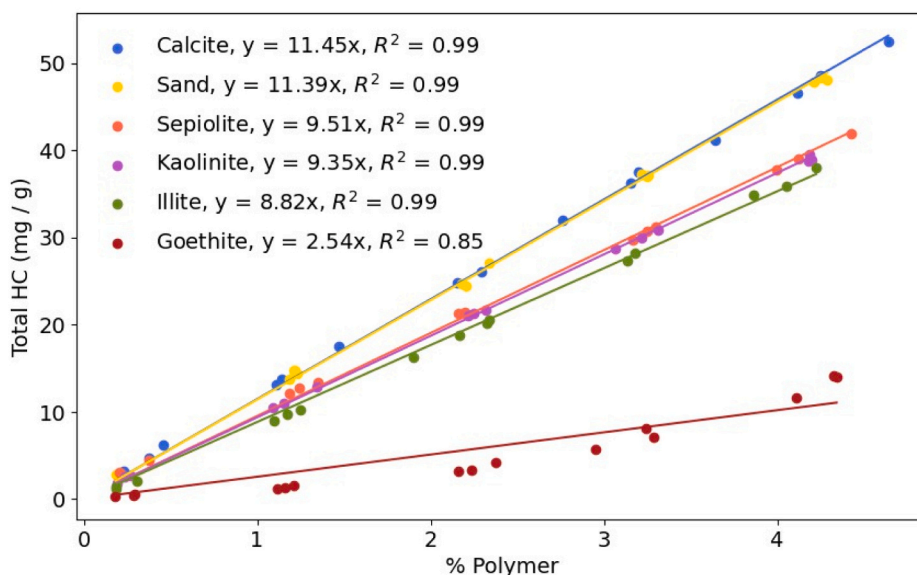
These findings emphasize the role of mineral matrices in modulating the thermal degradation pathways of PE, PET, and PLA, with goethite and clay minerals inducing the most significant variations in degradation temperatures and hydrocarbons release (T_{peak} and *Total HC* parameters, respectively).

3.2. Natural mineral matrices

Fig. 3 presents the thermograms comparison of sand (inert matrix) with three synthetic and natural mineral matrices mixed with different polymers. The natural matrices studied here include chalk, kaolinitic



(a) Rock-Eval® FID thermograms for PE at various proportions within different mineral matrices

(b) Linear regressions of the *Total HC* parameter as a function of PE content for different mineral matrices**Fig. 2.** Comparison of (a) Rock-Eval® FID thermograms and (b) Total HC linear regressions for polyethylene (PE) at various proportions in different mineral matrices.

claystone, and illitic claystone, which are compared with synthetic matrices equivalent. Table 3 provides T_{peak} and Total HC for each polymer with each natural matrix. These values can be compared with the value in Table 2 to compare with the inert matrix and the corresponding synthetic matrices.

3.2.1. Polyethylene (PE)

For PE, the T_{peak} values obtained with natural matrices of chalk and kaolinitic clay are comparable to those observed with synthetic matrices. In particular, chalk exhibits a T_{peak} of approximately $507 \pm 1^\circ\text{C}$, which is closely aligned with the values recorded for PE in calcite and sand ($507 \pm 2^\circ\text{C}$). A slight decrease in T_{peak} is observed for both

synthetic kaolinite and kaolinitic claystone, although the value remains slightly higher for kaolinitic clay ($475 \pm 2^\circ\text{C}$). However, this trend does not hold for illitic clay, where T_{peak} ($503 \pm 5^\circ\text{C}$) is similar to that of sand.

Regarding Total HC values in natural matrices, similar reductions are observed for both synthetic and natural clays. Chalk exhibits a Total HC value of $31.33 \pm 0.87\text{ mg/g}$, comparable to those of sand and calcite. In contrast, a decrease is observed with kaolinitic argillite ($27.58 \pm 0.22\text{ mg/g}$), and a more pronounced reduction is observed with illitic argillite ($23.02 \pm 0.56\text{ mg/g}$).

3.2.2. Polyethylene terephthalate (PET)

For PET, as for PE, the natural matrices of chalk and kaolinitic

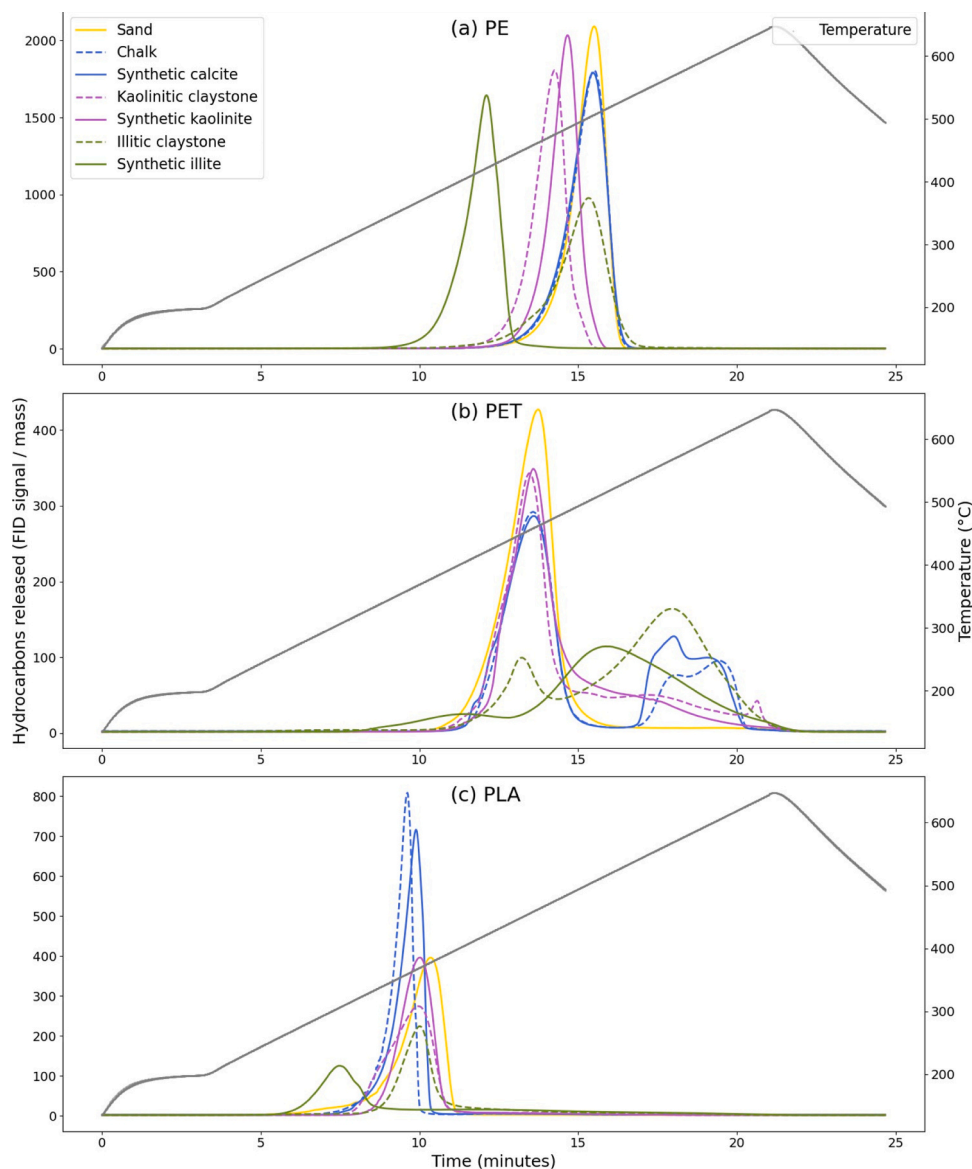


Fig. 3. Rock-Eval® FID thermograms showing the Total HC released during the thermal degradation of (a) polyethylene (PE), (b) polyethylene terephthalate (PET), and (c) polylactic acid (PLA) mixed with synthetic and sedimentary mineral matrices.

Table 3

Total HC and T_{peak} parameters for PE, PET, and PLA with different mineral matrices.

Matrix	T_{peak} (°C)	PE Total HC (mg/g)	T_{peak} (°C)	PET Total HC (mg/g)	T_{peak} (°C)	PLA Total HC (mg/g)
Chalk	507 ± 1	31.33 ± 0.87	459 ± 1	9.24 ± 0.37	361 ± 3	7.47 ± 0.22
Kaolinitic claystone	475 ± 2	27.58 ± 0.22	456 ± 3	9.83 ± 0.48	369 ± 5	6.04 ± 0.12
Illitic claystone	503 ± 5	23.02 ± 0.56	568 ± 1	9.6 ± 0.27	370 ± 1	4.17 ± 0.09

claystone exhibit variations similar to those observed with their corresponding synthetic matrices. The T_{peak} values measured for chalk ($459 \pm 1^\circ\text{C}$) and kaolinitic claystone ($456 \pm 3^\circ\text{C}$) are comparable to those obtained for PET in the presence of sand ($463 \pm 2^\circ\text{C}$), calcite ($460 \pm 7^\circ\text{C}$), and kaolinite ($459 \pm 2^\circ\text{C}$). The FID thermograms display similar multilobed curves. However, illitic clay induces a significant increase in

T_{peak} up to $568 \pm 1^\circ\text{C}$, whereas the T_{peak} value for synthetic illite is $517 \pm 2^\circ\text{C}$.

Regarding the Total HC, natural matrices exhibit a behavior similar to that of synthetic matrices. Chalk and kaolinitic clay produce 9.24 ± 0.37 mg/g and 9.83 ± 0.48 mg/g of hydrocarbons, respectively, while illitic clay yields 9.6 ± 0.27 mg/g. These values are comparable to those obtained with synthetic matrices, except for illitic clay, where the decrease observed in the synthetic matrix is not apparent in the natural one.

3.2.3. Polylactic acid (PLA)

For PLA, the T_{peak} values obtained with natural mineral matrices follow trends similar to those observed for their synthetic counterparts. Chalk exhibits a T_{peak} of $361 \pm 3^\circ\text{C}$, slightly lower than that of sand ($378 \pm 4^\circ\text{C}$) and calcite ($367 \pm 2^\circ\text{C}$). Kaolinitic claystone presents a T_{peak} of $369 \pm 5^\circ\text{C}$, comparable to that of synthetic kaolinite ($370 \pm 2^\circ\text{C}$). In contrast, illitic claystone shows a T_{peak} of $370 \pm 1^\circ\text{C}$, whereas synthetic illite lowers the T_{peak} to $310 \pm 10^\circ\text{C}$.

Regarding Total HC release, chalk exhibits a value of 7.47 ± 0.22 mg/g, similar to sand (7.47 ± 0.73 mg/g) and calcite ($8.01 \pm$

0.15 mg/g). Kaolinitic claystone leads to a moderate reduction in Total HC (6.04 ± 0.12 mg/g), closely resembling the behavior of synthetic kaolinite (6.30 ± 0.03 mg/g). The most pronounced effect is observed for illitic claystone, which reduces Total HC to 4.17 ± 0.09 mg/g, though this decrease is less significant than that observed for synthetic illite (3.71 ± 0.02 mg/g).

4. Discussion

The results presented above highlight the significant influence of the mineral matrix on the Rock-Eval® parameters obtained by each investigated polymer. This effect is primarily evaluated based on T_{peak} and the Total HC parameters.

As shown in Fig. 4, each polymer exhibits a characteristic T_{peak} , in agreement with the findings of Romero-Sarmiento et al. [33], who demonstrated that Rock-Eval® parameters can be used for polymer identification. Moreover, the results highlight the contrasting effects of mineral matrices on the thermal degradation of different polymers (PE, PET, and PLA). These observations are consistent with previous studies [10,13,4], which reported that mineral matrices can accelerate or slow the artificial thermal decomposition of organic matter, depending on their composition, structure and adsorption / cation exchange capacities. However, these authors never precisely described these effects, nor named them all, nor demonstrated that the effects could be antagonistic; which we do here for the first time on selected polymers.

4.1. Catalytic effect

For PE, compared to sand (an inert matrix), a decrease in the T_{peak} values was observed for various synthetic matrices, suggesting an accelerated thermal degradation of the polymer. This reduction in T_{peak} values in mixtures mainly containing clay and goethite points to a catalytic effect induced by the mineral matrices, which accelerates the degradation of the polymer. Espitalié et al. [13] demonstrated that specific clays promote the breakdown of C-C hydrocarbon bonds at moderate temperatures, which could explain the observed reduction in the cracking temperature of PE in our samples. The catalytic effect, reflected by the lower T_{peak} , is indicative of a faster polymer degradation process facilitated by these mineral matrices. Similar T_{peak} reductions were also observed for polypropylene and polystyrene—two polymers mainly composed by carbon and hydrogen—when they were combined with the same mineral matrices, suggesting that such catalytic effects may be broadly relevant to these type of polymers (unpublished data).

This phenomenon is possibly attributed to the presence of active sites, such as Lewis and Brønsted acids in clays and iron oxides, which act as catalysts by generating reactive sites that facilitate the degradation of PE [8]. A similar effect is observed for some PLA mixtures, specifically those with calcite and kaolinite. However, not all PLA-mineral matrix interactions result in a catalytic effect, suggesting that the mineral structure and chemical surface play a key role in determining its

catalytic activity. In contrast, no catalytic effect is observed for PET.

4.2. Thermal desorption effect

Unlike PE, PET exhibits a different thermal behavior in the presence of mineral matrices, with T_{peak} increasing rather than decreasing. This suggests that the mechanisms governing its degradation are distinct from those observed for PE. However, T_{peak} corresponds to the temperature at which hydrocarbon release is maximal, but additional, lower-intensity hydrocarbon emissions can occur at different temperatures. Indeed, for mineral matrices other than sand, the presence of multimodal curves suggests a stepwise hydrocarbon release, with an initial peak similar to that of PET in sand, followed by matrix-specific secondary releases characteristic of a thermal desorption effect.

This behavior likely results from interactions between polymer degradation products and the active sites of mineral matrices, leading to the formation of heavier compounds that require higher temperatures to be released. According to Lauschke et al. [26], PET mixed with calcite favors the formation of benzophenone, which may explain the delayed release of hydrocarbons. Similar effects are observed with clays and goethite. This observation was made using flash pyrolysis at 600°C for 20 seconds.

Differences in thermal degradation behavior can be attributed to the rigid chemical structure of PET, particularly its ester bonds, which are less susceptible to catalytic degradation by clays and metal oxides [23]. A similar thermal desorption effect is observed in one PLA-mineral matrix mixture, specifically with sepiolite, potentially resulting from interactions between sepiolite and PLA degradation products, with PLA being characterized by ester bonds.

4.3. Combined catalytic and thermal desorption effects

As demonstrated by the results on PLA, catalytic and thermal desorption effects can coexist. Specifically, illite exhibit a catalytic effect, where the majority of hydrocarbons are released before the T_{peak} observed for PLA in sand. However, a second release is detected at higher temperatures. This suggests that while these minerals accelerate initial polymer degradation, subsequent interactions between pyrolysis products and mineral active sites lead to the formation of heavier compounds requiring higher temperatures to break down.

These findings highlight the complex interplay between the thermal polymer degradation mechanisms and mineral matrix interactions. The combined catalytic and thermal desorption effects observed with certain PLA mixtures underscore the importance of considering both primary and secondary degradation pathways when analyzing polymer-mineral interactions.

4.4. Retention effect

Fig. 5 presents the proportions of Total HC released for different

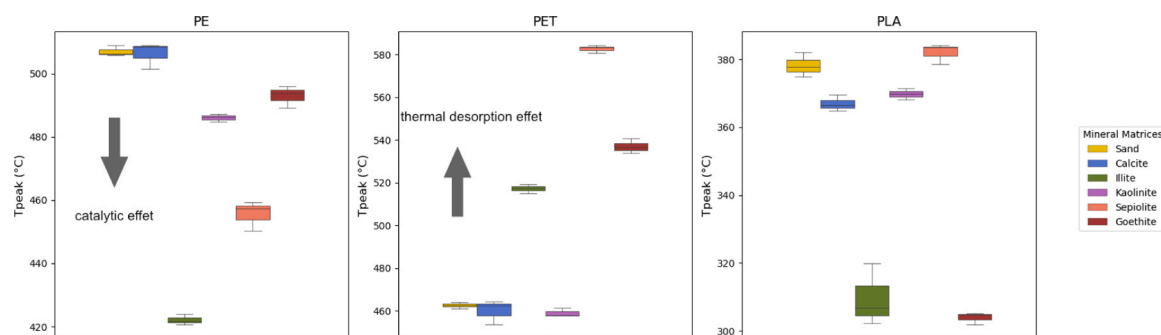


Fig. 4. T_{peak} for different polymers (PE: polyethylene; PET: polyethylene terephthalate; PLA: polylactic acid) mixed with reference (quartz) and various mineral matrices.

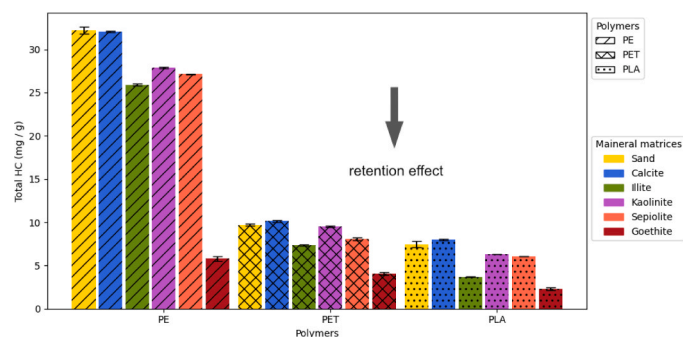


Fig. 5. Effect of mineral matrices on Total HC parameter from PE, PET, and PLA.

polymers mixed with various mineral matrices. The quantity of the Total HC is influenced by both the type of polymer and the mineral matrix. The reduction in Total HC observed in mixtures containing clays and, particularly, goethite, as shown in the previous figures, can be attributed to the retention of the pyrolysis products. According to Espitalié et al. [13], certain clays, such as illite, exhibit high retention capacities, which hinder the complete release of heavy hydrocarbons generated during pyrolysis. Another key observation is that the importance order of the retention effect remains consistent across the three investigated polymers. Specifically, for a given polymer, sand and calcite exhibit similar Total HC values. Kaolinite consistently contributes to release the highest amount of hydrocarbons among clays, followed by sepiolite, and finally illite, which shows the strongest retention capacity among clays. However, in all mineral matrices, goethite exhibits the highest retention effect. This suggests that while the retention effect varies with the type of polymer, it is primarily governed by the retention capacity of the mineral matrix.

Even if this work has been mainly focused on the evaluation of HC signatures, in line with the findings of Romero-Sarmiento et al. [33] on PET pyrolysis with different mineral matrices, an increase in CO and CO₂ signals release has been also observed depending on the nature of the mineral matrix. In some cases, interactions between the mineral matrix and the polymer appear to enhance the formation of oxidized products during pyrolysis. In other cases, retained compounds are released in residual form during the oxidation stage of the thermal Rock-Eval® method. These retained compounds may undergo further oxidation at higher temperatures, leading to an increase in residual carbon or coke deposition on the matrix surface.

4.5. Comparison with Py-GC/MS method

The matrix effects detected in this study are also relevant for other thermal analysis techniques, such as Py-GC/MS. Previous research has demonstrated that mineral matrices significantly influence the composition and intensity of pyrolysis products in Py-GC/MS analysis. For example, Salter et al. [37] observed that when PE is pyrolyzed in the presence of kaolinite, the characteristic peaks of n-alkene and alkane remain detectable; however, alkenes disappear and there is a shift towards shorter-chain and branched aliphatic hydrocarbons. These observations were made using a furnace-type pyrolysis unit (CDS Analytical 2000 Pyroprobe coupled via a CDS 1500 valve interface). Similarly, in mixtures containing illite, pyrolysis products exhibit an increase in aromatic compounds, such as toluene and alkylbenzenes, while alkene and alkane signals decrease in intensity. In contrast, when PE is associated with goethite, the resulting pyrolysate is predominantly composed of aromatic compounds, including benzene, toluene, and naphthalene, with a significant reduction in aliphatic hydrocarbons. These findings confirm that each mineral matrix induces specific changes in the composition and abundance of the pyrolysis products.

A similar trend has been reported for PET. Lauschke et al. [26]

demonstrated that the influence of mineral matrices on PET pyrolysis is also evident in Py-GC/MS analyses conducted using furnace-type pyrolyzers, including a CDS Pyroprobe 6200 and a Frontier Labs Multi-Shot Pyrolyzer 3030D. In the presence of calcite, a prominent benzophenone peak was observed, a feature absent in the other blend. Instead, pyrolysis in the presence of montmorillonite, a clay from the smectite group, led to a reduction in the peaks of aliphatic hydrocarbons and an increase in the peaks of aromatic compounds. In particular, in the case of goethite, pyrolysis yielded almost no detectable organic products, apart from CO₂ and minor amounts of benzene, suggesting extensive oxidation of the polymer. These results further illustrate that different mineral matrices not only alter the intensity of pyrolysis peaks, but also induce specific chemical transformations.

The observations of the Rock-Eval® analysis in this study align with these findings, strengthening the impact of mineral matrices on the thermal degradation of synthetic polymers. In addition to hydrocarbon retention, Rock-Eval® allows the quantification of CO and CO₂, which can provide further insight into the nature of polymer-matrix interactions. If increased amounts of CO and CO₂ are detected, this may indicate oxidative interactions between the polymer and the mineral matrix. Understanding these matrix-induced modifications is essential for refining thermal analysis methodologies and improving the identification and quantification of microplastics in complex environmental samples.

4.6. Consequence for microplastics quantification

Fig. 2b summarizes the Total HC obtained for polyethylene mixed in varying proportions with different mineral matrices. The retention effect previously described for clay matrices and goethite is also observed. However, while this retention effect remains stable for clay matrices and is independent of the proportion of PE in the sample ($r^2 > 0.99$), it appears to depend on the proportion of PE in mixtures with goethite.

For sand, calcite and clays, the retention effect independent of the polymer proportion is consistent with the findings of Romero-Sarmiento et al. [33], who reported similar results for PET mixed with sand, carbonates, shales and marls.

For all investigated mineral matrices, good correlation coefficients were observed between the Total HC parameter and the amount of polymer at different concentrations, indicating that this Rock-Eval® parameter can be also used to quantify the polymer content. This suggests that, despite the observed mineral effects, this thermal degradation method holds promise for the characterization and quantification of microplastic content in sediment samples, at least under controlled laboratory conditions (Fig. 2b).

4.7. Implications for natural matrices

The effects previously described for synthetic matrices are also observed for mixtures with natural mineral matrices. Rock-Eval® analyses conducted on three natural mineral matrices—chalk, kaolinitic claystone, and illitic claystone—reveal that the same thermal behaviors occur regardless of whether the mineral matrix is synthetic or natural for two mineral matrices (chalk and kaolinitic claystone). This observation holds for all identified effects: catalysis, thermal desorption, and retention.

Specifically, for PE, chalk exhibits no significant effect, while kaolinitic claystone induces a comparable catalytic effect in both synthetic and natural contexts. For PET, the initial release occurs at approximately the same temperature as that of sand, followed by a thermal desorption effect that varies depending on the mineral matrix. With respect to PLA, the results for kaolinite are consistent across different matrix types; however, although a catalytic effect is observed with chalk, it is not strictly identical to that observed with synthetic calcite.

On the other hand, for illitic claystone, which contains a small

amount of organic matter, the effect is completely different from that observed for synthetic illite. This observation suggests that active sites may preferentially interact with natural organic matter in cases where a catalytic effect is observed (PE and PLA). In fact, for the catalytic effect, the illitic claystone mixture exhibits an approximately similar T_{peak} to that of the inert matrix. In contrast, in the case of a thermal desorption effect (PET), the same effect is observable but with a different hydrocarbon release temperature. In this case, we can suggest that interactions occur between the mineral matrix and polymer degradation products. Further studies are necessary to investigate this hypothesis.

5. Conclusions and perspectives

The results of this study highlight the complex impact of mineral matrices on polymer pyrolysis, revealing several distinct effects, namely catalytic, thermal desorption, and retention effects. These effects vary depending not only on the nature of the mineral matrix, but also on the type and chemical composition of the polymer Table 4. The catalytic effect was observed through an acceleration of polymer degradation, particularly for polyethylene and polylactic acid, where mineral matrices such as clays and goethite contributed to a significant reduction in degradation temperatures (T_{peak}), thus facilitating the early release of hydrocarbons. This phenomenon, which relies on the active sites of the matrices, showed a direct relationship between the structure of the matrix and its catalytic potential.

However, the thermal desorption effect was primarily observed for PET and some PLA blends, where mineral matrices induced the release of hydrocarbons in multiple stages. This delayed release can be attributed to complex interactions between the polymer degradation products and the active sites of the matrices, which promote the formation of heavier products, requiring higher temperatures for their degradation. This effect is particularly pronounced for matrices such as calcite (for PET), clays, and goethite, which interact with polymers and influence the distribution of pyrolysis products. More studies are needed to better understand these interactions and their impact on hydrocarbon release.

The retention effect, particularly observed with clays and goethite, indicates that the pyrolysis products of the studied polymers can be retained by the mineral matrix, thereby limiting the release of hydrocarbons. However, this retention does not seem to be influenced by the amount of polymer in the sample, except for goethite, where the effect was dependent on the proportion of PE in the mixture. This phenomenon can be explained by the adsorption of degradation products onto the matrix surface, which inhibits their full release during pyrolysis.

Another key observation of this study was the comparison of the effects of synthetic and natural mineral matrices. The results showed that the catalytic, thermal desorption, and retention effects were similar

for both synthetic and natural matrices, in the case of natural matrices with negligible TOC content. This consistency reinforces the robustness of the Rock-Eval® method as a reliable tool for the identification and quantification of microplastics in sediments, demonstrating that natural matrices devoid of organic matter can be studied in the same way as synthetic ones in the context of microplastic pollution.

In conclusion, this study emphasizes the importance of considering the influence of mineral matrices in the study of thermal degradation of polymers, particularly to better understand the underlying mechanisms behind the release of pyrolysis products. A better understanding of these interactions is crucial to developing simplified yet robust methods for analyzing plastic pollution in the environment.

In this regard, further research on the effects of the matrix, including threshold influences, could expand the applicability of the Rock-Eval® method to increasingly complex environmental analyzes, especially in the context of microplastic pollution in marine, lacustrine, and continental sediments.

In parallel, the question of co-pyrolysis deserves special attention. While the present study focused on single-polymer systems, environmental samples often contain mixtures of different polymer types. These mixtures can lead to interactions during the thermal degradation, which may modify both the quantity and nature of the released pyrolysis products. Such effects are already well documented in Py-GC-MS studies and raise the question of whether similar interactions may occur in thermal Rock-Eval® analysis [17]. Recently, Romero-Sarmiento et al. [34] also demonstrated that synthetic textile microfibers show Rock-Eval® pyrolysis temperature overlaps (similar T_{peak} parameters), indicating the impossibility of differentiating the type of synthetic fibers, for example between polyester (PET), viscose and/or nylon (PA) fibers. Additional work is still necessary to addressing co-pyrolysis effects to improve and validate the application of this thermal method to real case studies about microplastic pollution.

CRedit authorship contribution statement

Maria-Fernanda Romero-Sarmiento: Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization. **François Baudin:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Clémentine Ricard:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Victor Lieunard:** Writing – review & editing, Validation, Investigation, Formal analysis. **Lucas Friceau:** Writing – review & editing, Validation, Investigation, Formal analysis. **Yoann Copard:** Writing – review & editing, Validation, Conceptualization. **Nicolas Bouton:** Writing – review & editing, Validation, Software, Investigation,

Table 4
Effects of mineral matrices on polymer thermal behavior.

Polymer Matrix	PE	PET	PLA
Quartz	2	2	2
Calcite	2	4	1
Illite	1 / 3	1 / 3 / 4	1 / 3
Kaolinite	1 / 3	4	1 / 3
Sepiolite	1 / 3	3 / 4	3 / 4
Goethite	1 / 3	3 / 4	1 / 3

Legend:

- 1 = Catalytic effect
- 2 = No matrix effect
- 3 = Retention effect
- 4 = Thermal desorption

Formal analysis. **Rohais Sebastien:** Writing – review & editing, Validation, Methodology, Investigation, Conceptualization. **Wolfgang Ludwig:** Writing – review & editing, Validation.

Declaration of Competing Interest

he authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2025.107219](https://doi.org/10.1016/j.jaap.2025.107219).

Data availability

Data will be made available on request.

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