

Thermal maturity and hydrocarbons potential generation in the Tumaco and San Juan-Atrato Basins as revealed by TOC, RE-Py and petrographic analysis

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Tables 1 and 2 are available in the supplementary files section

Thermal maturity and hydrocarbons potential generation in the Tumaco and San Juan-Atrato Basins as revealed by TOC, RE-Py and petrographic analysis

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ABSTRACT

A total of 763 rock samples from the Tumaco and San Juan-Atrato basins, located along the Colombian Pacific continental margin, were evaluated for total organic carbon (TOC), rock-eval pyrolysis (RE-Py), and vitrinite reflectance (Ro) to determine the type, origin, paleodepositional environment, and thermal maturity of the organic matter (O.M.). In both basins, the TOC content ranges from 0.77 and 2.43%, considered to be within the “acceptable” range. Rock-Eval pyrolysis results indicate that S1 peak (free hydrocarbons) ranges between 0.02 and 1.09 mg HC/g rock, while S2 peak varies between 1.10 and 1.29 mg HC/g rock. The average Tmax ranging between 398 and 417°C, classify the organic matter in its early maturity to thermally immature, which is confirmed by the petrographic measurements with values ranging between 0.1978 to 0.5418%. Geochemical indices derived from the TOC and RE-Py data show hydrogen index (HI) values between 300 and 600 mg HC/g TOC, classifying the organic O.M. as predominantly Type III and/or mixed Type II/III kerogen. This suggests that the primary generated products are gas and/or oil–gas mixtures, particularly within the deeper intervals of the column, reflecting a transitional composition derived from mixtures of marine and terrestrial organic matter. The maturity indices calculated from screening parameters suggest that the O.M. did not originate from a single kerogen source, but rather reflects significant variations in paleodepositional environments and maturity stages.

Keywords: TOC, Rock-Eval Pyrolysis, Vitrinite reflectance, Organic Geochemistry, Tumaco Basin, San Juan-Atrato Basin

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INTRODUCTION

Subduction zones serve as conduits for recycling materials from the crust into and through the trenches. The mass balance over time between the input and output of these material inventories raises fundamental questions about the evolution of the atmosphere, crust, and mantle, as well as their relationship with organic matter processes (Hilton *et al.*, 2002; Brims, 2021). The subduction events in these zones significantly influence both superficial and deep earth processes. Due to their occurrence and the rate at which materials subduct, conditions arise that contribute to continental accretion or the generation of magmatic events (Lutz *et al.*, 2000). The high bioproductivity often associated with near-shore areas and the high sedimentation rates—including the deposition and re-sedimentation of terrestrial matter—creates substantial potential for organic matter to be subducted. (Phujareanchaiwon *et al.*, 2024).

These coastal margins generally have a low potential for conventional oil accumulation (Kroeger *et al.*, 2015; Hessler and Sharman, 2018). However, these zones host significant quantities of the global methane hydrate inventory (Kastner, 2001). While preserving conventional hydrocarbon accumulations in these environments tends to be limited, biogenic methane gas accumulation systems at shallow depths are common. However, quantitative investigations of methane hydrate deposits with a microbial signature suggest that a significant portion of these methane hydrates is released from deep sediments, challenging the perception of low hydrocarbon potential in such environments (Henrys, 2009).

The continental margin in the Colombian Pacific exhibits a complex geological and tectonic framework characterized by varying evolutionary histories that reveal contrasting geodynamics, morphologies, and processes (Idárraga, 2014). The Pacific's active, erosive continental margin is characterized by a continental shelf that transitions into a deep trench zone, marking the subduction of the Nazca Plate beneath the South American continent (Vargas & Mann, 2013; Idárraga, 2016).

Most studies on subduction basins in Central and South America have focused on the Cocos Plate's subduction under the Central American Plate (Costa Rica-Nicaragua) (Peacock *et al.*, 2005; Zhao *et al.*, 2022) and the Nazca Plate's subduction beneath Chilean and Ecuadorian territory (Marcaillou and Collot, 2008; Baudino and Hermosa, 2014; Errazuriz *et al.*, 2024). However, a review of available literature reveals a lack of research on the dynamics of organic matter and sediments in these subduction zones, which could enhance our understanding of the hydrocarbon-generating potential of the Colombian Pacific margin (Borrero *et al.*, 2012; Lopez-Ramos, 2015)

Furthermore, there is limited information regarding the origin, depositional environment, thermal maturity, and biodegradation processes of organic matter in these subduction zones, all of which are essential for assessing the potential for hydrocarbon generation (Cediel *et al.*, 2009; Barbosa, 2012; Echeverry *et al.*, 2015). These circumstances highlight the need for further investigation into the oil potential of frontier basins, particularly those located in subduction zones. It requires exploring the relationship between the evolution of these basins and the types of organic matter. Such research poses an intriguing challenge for understanding the origin and conditions required for hydrocarbon emplacement in fore-arc and back-arc basins. (Marcaillou and Collot, 2008). The acquisition of new data from the active margins of the Colombian Pacific supports the development of new concepts that could guide exploration efforts. This research could provide

insights into generation conditions, migration routes, thermal maturity mechanisms, and potential degradation conditions (Cortes *et al.*, 2019). The main objective of this study is to integrate the geochemical characterization of the organic matter on rock samples from the Tumaco and San Juan-Atrato basins to evaluate the thermal maturity and generation potential of hydrocarbons of the petroleum systems within the fore-arc and back-arc basins on the Pacific continental margin, using geochemical (TOC & RE-Py) and organic petrographic (Ro) results.

2. Geological Assessment

2.1 Tumaco Basin

The onshore Tumaco Basin is located in southwestern Colombia. The Garrapatas Fault system bounds it to the north, the Republic of Ecuador to the south, the Western Cordillera (uplift) to the east, and the Pacific Ocean to the west (Barrero *et al.*, 2007; Cediél *et al.*, 2009; ANH-Universidad de Caldas, 2011; Borrero *et al.*, 2012; Cortes *et al.*, 2019; Grajales *et al.*, 2024). The Tumaco Forearc Basin contains a pre-Miocene mega-sequence and three post-Lower Miocene sequences deposited in shelf-to-bathyal environments. The basement of the basin consists of Cretaceous meta-sedimentary and volcanic rocks (Cediél *et al.*, 2009). The study area maps and detailed stratigraphy columns for both the Tumaco and San Juan Atrato Basins are shown in Figures 1 and 2 (Aguilera *et al.*, 2010; ANH-Antek S.A.S., 2013; Cortes *et al.*, 2019).

The basement of the Tumaco-1 ST-P well is interpreted as an allochthonous block composed of fragments of an oceanic plateau and the Santonian-Campanian island arc, accreted to the continent during the Late Cretaceous and Early Paleocene (Figure 2-A) (ANH-Universidad de Caldas, 2011; ANH-Antek S.A.S., 2013; Cortes *et al.*, 2019). The Tumaco Formation (Chatiense-Early Tortonian) consists of interbedded mudstones, arenites, and occasional conglomerates covering the bottom of the well (interval 3651.5–1640.1 m), with a thickness greater than 2011.4 m. The rocks of this unit can be grouped into eight facies associations, representing bar and estuarine channels, mouth bars, coastal lagoons, proximal front deltaic deposits, prodelta, and platform deposits (Barbosa, 2012; ANH-Antek S.A.S., 2013; Cortes *et al.*, 2019; Grajales *et al.*, 2024).

The Tangareal del Mira Formation (Middle Tortonian-Zanclean) rests unconformably on the Tumaco Formation, covering an interval of 437.9 to 1640.1 m, with a total thickness of 1202.1 m. This unit generally consists of interbedded lithic sandstones and mudstones, with conglomerates at the base. These can be grouped into five facies associations, representing river channels, bar and fluvial channels, bay estuaries, prodelta, and front deltaic deposits (ANH-Antek S.A.S., 2013).

This geological unit indicates the presence of abundant marine fossils and evidence of continental contributions, supporting the existence of a deltaic complex dominated by waves and tides. This complex is associated with the northward migration of the Mira River in the late Miocene, leading to the current position of the Patía River delta (Cediél *et al.*, 2013; Echeverry *et al.*, 2015). The development of fluvial facies at the unit's base suggests a relative sea-level fall, followed by two major transgressive-regressive cycles, showing a significant volcanic influence (ANH-Antek S.A.S., 2013).

The Cascajal Formation (Zanclean) consists of interbedded mudstones, lithoarenites, and conglomerates, which are locally bioturbated. It rests unconformably on the Tangareal del Mira Formation. This formation is characterized by five facies associations, representing the proximal deltaic front, distal deltaic front, channels and estuarine bars, mouth bar, and prodelta deposits (ANH-Universidad de Caldas, 2011; ANH-Antek S.A.S., 2013). The facies associations of the Cascajal Formation indicate bioturbated segments and an abundance of marine and continental fossils, supporting the existence of a deltaic complex dominated by waves and tides during the Late Pliocene, associated with the progradation of the Mira River delta (ANH-Antek S.A.S., 2013).

2.2 San Juan- Atrato Basin (Choco Basin)

The San Juan–Atrato Basin, historically referred to as the Chocó Basin, is physiographically bounded by the Baudó Range to the west, the Western Cordillera to the east, the Pacific Ocean coastline to the southwest, and Panama to the north. (ANH-EAFIT, 2007; Bedoya *et al.*, 2009; Grajales *et al.*, 2024). These sub-basins are two sedimentary structures with distinct geological origins, sharing a partially common evolution and featuring different structural styles (Figure 2-B) (Grajales *et al.*, 2024).

These sub-basins are characterized by a Cenozoic deposit with marine to continental environments, resting on a Cretaceous igneous and sedimentary basement. The Atrato sub-basin comprises six lithostratigraphic units, ranging from the Lower Eocene to the Pliocene, which are arranged from bottom to top as follows: Clavo, Salaqui, Uva, Napipi, Sierra, and Quibdo units. In this sub-basin, five exploratory wells have been drilled: Buchadó-1, Urodó-1, Opogadó-1, Pacurita-1, and Necora-1. (Bedoya *et al.*, 2009; Cediél *et al.*, 2009, ANH-UNAL, 2022).

Several exploration companies and researchers have reported the presence of active hydrocarbon seeps in both Atrato and San Juan Basin, which evidences the present-day generation and migration of crude oil, suggesting the existence of at least two as yet untested oil systems (Mera and Piragua, 2000; ANH-UNAL, 2022).

In the Atrato sub-basin, although with scarce geochemical data, some sedimentological characteristics suggest the Clavo Formation as the hypothetical source rock, which consists of very compact, black claystone with thin interbeds of calcareous limonite and limestone sedimentation (Suarez, 1990). Thermal maturity has been reported to be low, with TOC values in the range from 0.23% to 0.94%, Tmax values in the range of 417°C to 435°C, Ro values ranging between 0.34 to 0.46%, and poor generation potential based on data provided by Robertson Research (1988a) and Compania Petrolera Latina (Cediél *et al.*, 2009).

In the San Juan sub-basin, the sedimentary succession comprises five lithostratigraphic units, ranging in age from Paleocene to Pliocene (ANH-EAFIT, 2007). Most of the succession was deposited in marine environments with strong continental influence (Cediél *et al.*, 2009). Tambora-1 well was drilled in the offshore portion of this basin, while no wells were drilled onshore. Thus, the San Juan Basin comprises five units: Iró, Istmina, Conglomerados de la Mojarra, Condoto, and Raposo/Mayorquin Formations (Bedoya *et al.*, 2009; Cediél *et al.*, 2009).

Based on samples collected in the Iró Formation, it was reported Tmax values of 435°C indicating an immature O.M. entering the oil-generating window, which showed a TOC ranging of 2.55% to 7.55%, suggesting a good to excellent O.M. quality and excellent generating potential from a kerogen II/III based on hydrogen index in the range between 405 mg HC/g TOC (kerogen type II) and 201 mg HC/g TOC (kerogen type III) with the producing potential of oil-prone and oil/gas prone kerogens, respectability (Mera and Piragua, 2000). Additionally, organic geochemical analysis based on biomarkers in the saturate fraction showed that the O.M. in the Iró Formation was deposited in a suboxic marine carbonate environment and derived from plankton O.M. (Cediel *et al.*, 2009; Aguilera *et al.*, 2010, ANH-UNAL, 2022). Thus, it is concluded that the best source rock at the Basin, with good to excellent oil generation potential intervals, is the Paleogene Iró Formation. (Aguilera *et al.*, 2010).

3. Materials and Methods

3.1 Samples

Representative rock samples were collected and analyzed from various depths in cores obtained from the Tumaco-1-ST-P and Buenaventura-1-ST-P stratigraphic wells between years 2013-2014. Additional data were collected from the Buchadó-1, Opogadó-1, Necora-1, Urodó-1, and Pacurita-1 exploratory wells in 2022 (ANH-UNAL, 2022). Older data from the Buchado-1 well, as well as the Majagua-1, Sandi-1, and Tambora-1 wells were sampled and analyzed for Robertson Research between 1981 to 1988 and outcrops from the Chocó area, were sourced from publicly available data (Robertson Research, 1981 & 1988a & 1988b; Gems, 2022; ANH-UNAL, 2022). Of the 763 samples evaluated in this study, 457 were collected and analyzed by the authors at the Organic Geochemical Laboratory of Petromarkers, Inc. in Houston, Tx and at Antek S.A.S. in Bogota, Colombia. The remaining 306 samples were obtained from databases available at the National Hydrocarbons Agency (ANH).

The rock samples were cleaned using hot water, distilled water, and a mixture of dichloromethane and methanol (1:1) to remove contaminants from drilling mud, plastic materials, and related handling processes. The samples were then oven-dried at 60°C and crushed to a 62-mesh size (250 µm) using an agate mortar (Petromarkers, 2024).

3.2 Total Organic Carbon (TOC)

Approximately 1 gram of sample was digested with 10% hydrochloric acid (HCl) to remove inorganic carbon (carbonates). The samples were washed with organic-free water, dried in a vacuum oven at 60 °C for 24 hours, and then transferred to Leco ceramic cells. Before analysis, a mixture of copper and iron (catalyst mixture) was added to the sample. TOC measurements were performed using a Leco CS-200 carbon analyzer, which operates with a high-temperature combustion program in the presence of excess oxygen. Under these conditions, organic carbon is converted to carbon dioxide (CO₂), which is measured by an infrared detector. The CO₂ concentration is then converted into TOC percentage values (ISO 10694:1995; Weiss *et al.*, 2000; Petromarkers, 2024).

3.3 Rock-Eval Pyrolysis

Rock-Eval Pyrolysis for Tumaco-1-ST-P and Buenaventura-1-ST-P wells were conducted using a Vinci-VI, while samples from the exploratory wells in San Juan-Atrato Basin were analyzed using a Hawk source rock analyzer. The analytical conditions were similar for both instruments. Thus, the temperature program was 30°C to 600°C at a rate of 30°C/min. Helium was used as the carrier gas at a flow rate of 60 mL/min. The resulting pyrogram consisted of three peaks: The first peak (S1), representing free hydrocarbons (methane to n-C32), was analyzed between 30°C and 330°C. The second peak (S2), indicating the thermal decomposition of kerogen, was analyzed between 330°C and 600°C. The S1 and S2 peaks were measured using a flame ionization detector (FID), with the maximum elution temperature of the S2 peak recorded as the Tmax value. A third peak (S3), representing CO₂ content in the sample, was analyzed using a thermal conductivity detector (TCD) (Espitalie et al., 1985).

3.4 Organic Petrography (Vitrinite Reflectance)

Vitrinite reflectance (Ro,%) was measured using resin caps containing dispersed organic matter, following the methodologies of Cardott et al. (1988) and Jaramillo (2015). Approximately 10 grams of rock sample were crushed to an 18-mesh size (1000 µm). A mixture of epoxy resin and hardener (5:1) was centrifuged to remove air bubbles and then poured halfway into a plastic cup. The crushed rock sample was mixed with the epoxy resin to ensure all grains were covered and evenly distributed at the bottom of the plastic block. Finally, the plug was completed by adding more bubble-free epoxy resin and allowed to harden at room temperature for 12 hours. The cap containing the dispersed organic matter was polished using #320, #400, and #600 grit sandpapers with a Leco polisher.

Vitrinite reflectance measurements were performed following ASTM D7708-23 standard using a Carl Zeiss Axio-Imager-100 microscope equipped with reflected light and UV fluorescence (spectral range 200–3000 nm). The microscope was coupled to a Craic CoalPro spectrophotometer and a high-speed camera for imaging. Synthetic standards with relative standard deviations (RSDs) of 0.4%, 0.9%, and 1.7% were used to calibrate the system. The immersion oil had a refractive index of 1.5180 at 23°C under sodium light at a wavelength of 589.3 nm. Reflectance was measured under monochromatic light with a wavelength of 546 nm.

4. Results

4.1 Total Organic Carbon (TOC)

Table 1 presents the average values for the geochemical and organic petrographic parameters studied. In the Tumaco Basin, the average TOC value for 250 samples analyzed from the Tumaco-1-ST-P well was 0.95% ± 0.43. The exploratory wells in this basin reported TOC values of 1.50% ± 2.06 for Majagua-1, 0.82% ± 0.41 for Sandi-1, and 0.47% ± 0.18 for Tambora-1. The highest TOC contents in the Tumaco-1-ST-P stratigraphic wells were found in the middle and deeper sections of the stratigraphic column, deposited over siltstones, calcarenites, and calcareous claystones of the Middle-Late Oligocene Tumaco Formation. In the Tangareal del Mira Formation,

relatively high TOC values (0.7-1.0%) are observed in the shallow interval between 51.8 and 213 m, likely associated with buried plant matter undergoing diagenetic transformation.

In the San Juan-Atrato Basin, TOC average values for 105 samples analyzed in the Buenaventura-1-ST-P well was $0.85\% \pm 0.30$, while the exploratory wells were found as $1.85\% \pm 1.75$ in Opogado-1, $0.76\% \pm 0.68$ in Buchado-1 (older data, 1988), $0.94\% \pm 0.51$ in Buchado-1 (new data) $0.77\% \pm 0.29$ in Necora-1, $0.90\% \pm 0.24$ in Urodo-1, and $1.03\% \pm 0.22$ in Pacurita-1 (ANH-Unal, 2022). The highest TOC values in this basin were recorded at depths greater than 3048 m in the Opogado-1 well, characterizing the O.M. as good to excellent quality. Outcrop samples analyzed in the San Juan-Atrato Basin (Gems, 2015) presented average TOC values of $0.85\% \pm 0.10$ for the Itsmina Formation, $0.83\% \pm 0.61$ for the Iró Formation, and $0.61\% \pm 0.02$ for the Conglomerados de la Mojarra Formation. Mean TOC values determined on outcrop samples across these formations were $0.80\% \pm 0.66$, indicating an "acceptable" amount of organic matter.

4.2 Rock-Eval Pyrolysis

Figure 3-A presents the pyrogram of a sample collected at 3010.8 m (Tumaco Fm.) in the Tumaco-1-ST-P well analyzed using a Vinci Technologies Rock-Eval, while Figure 3-B corresponds to Opogado-1 well sample collected at a depth of 3322.3 m (Clavo Fm.) in the San Juan-Atrato Basin obtained in a Hawk source rock analyzer. Both instruments provide comparables results.

In the Tumaco basin, The Tumaco-1-ST-P well shows an average value for S2 peak of 1.1 ± 1.36 mg HC/g rock and a Tmax value of $417^{\circ}\text{C} \pm 26.23$. The exploratory Majagua-1 well presents an average S2 peak of 1.17 ± 1.68 mg HC/g rock and a Tmax value of $429^{\circ}\text{C} \pm 4.14$. The data for the exploratory wells of Remolino Grande-1, Sandy-1, and Tambora-1 was extracted from publication of the public domain where only the TOC, Tmax, HI, OI, IP, Ro experimental and Ro equivalente were reported but S1, S2, and S3 were missing.

In San Juan-Atrato Basin, the Buenaventura-1-ST-P well shows an average value of S2 of 1.29 mg HC/g rock, while Tmax is $399^{\circ}\text{C} \pm 36.3$. These values indicate that the rocks in Tumaco and San Juan-Atrato Basins are in the early maturity stage, still within the diagenetic phase, with organic matter generated from Type III kerogen. The consistency of Tmax results suggests the absence of migrated or trapped hydrocarbons. For the rest of exploratory wells, the S2 peak values range from $0.26\% \pm 0.06$ in Pacurita-1 to $5.09\% \pm 5.39$ mg HC/g rock in Opogado-1. The kerogen quality with characteristics ranging from "good to excellent", although with a low TOC percentage and thermal maturity. Additionally, the Tmax values for the outcrop samples range between $406^{\circ}\text{C} \pm 35$ and $430^{\circ}\text{C} \pm 11$, indicating that the rocks are entering the peak hydrocarbon generation stage.

4.3 Vitrinite Reflectance

Vitrinite reflectance was experimentally measured in 50 representative rock samples from the Tumaco-1-ST-P well. Due to the poor dispersion of organic matter, it was necessary to concentrate the samples using a dense liquid of zinc chloride (ZnCl_2) solution with a density of approximately 2 g/mL. Table 1 shows the average for the experimental Ro results in the Tumaco-1-ST-P and some exploratory wells in Tumaco Basin. Table 2 presents the experimental Ro results for each sample in Tumaco-1-ST-P well whose Ro values ranging from 0.1978% to 0.5418% at depths of

1679.1 to 2569.7 m, with an average of $0.4046\% \pm 0.06$. These values indicate an immature organic matter, still at its diagenetic phase. Table 1 also shows the Ro equivalent for all samples in Tumaco and San Juan-Atrato Basins, based on its Tmax values using the equation $Ro\ equiv. = 0.018 * Tmax - 7.16$. The average values for Ro equivalente vary between 0.3843 ± 0.11 in Opogadó-1 and 0.6571 ± 0.10 in Sandi-1.

5. Discussion

The amount of organic carbon in sedimentary rocks is crucial for assessing their potential for hydrocarbon generation (Volk, 2000). TOC measures the quantity of organic matter but does not indicate its quality, which evolves with thermal maturity (Tissot & Welte, 1984; Peters et al., 2005). TOC content in sedimentary rocks is influenced mainly by the type of OM, input and preservation of organic matter, depositional sedimentary environment, and sediment type (Littke et al., 1993; Volk, 2000).

Based on the relatively narrow TOC content and its standard deviation for the 763 samples analyzed, the organic matter was classified as "poor to acceptable" in terms of hydrocarbon generation potential according to Peters and Casas (1994). The TOC values correlate positively with vitrinite reflectance and Tmax values, confirming a low organic richness and potential for generating oil and natural gas hydrocarbons.

Figure 4 shows the modified Van Krevelen diagram illustrating the kerogen type for rock samples of the Colombian Pacific basins, showing a range of kerogens varying from oil-prone Type II and II/III to carbon-rich inert organic matter (non-generative Type IV) signature. A significant concentration of the samples (Opogado-1 and deepest samples in Tumaco-1 ST/P and Buenaventura-1-ST-P wells) corresponds to Type III kerogen, which is typically gas-generative. According to experimental results and the literature, Type III kerogen is characterized by low hydrogen indices (HI: 50-200 mg HC/g TOC), low atomic H/C ratios (0.7-1.0), and high O/C ratios (greater than 0.3). This type of OM is commonly found in Tertiary sediments, derived mainly from terrigenous organic matter, which is dominated by vitrinite macerals with smaller amounts of inertinite (Bordenave, 1993; Hunt, 1996).

Many samples in these basins correspond to Type II/III kerogen, characterized by HI values of 300-600 mg HC/g TOC, high H/C ratios (1.2-1.5), and lower O/C ratios compared to Type III and IV kerogens. This kerogen type reflects a transitional composition with a mixture of marine and terrestrial OM (continental inputs). A smaller proportion of the samples (Necora-1 well) are classified as Type IV kerogen, often considered "dead" kerogen or residual organic matter. This type of kerogen has very low HI values (<50 mg HC/g TOC), low atomic H/C ratios (<0.7), and medium to high O/C ratios (>0.3). Type IV kerogen generates negligible amounts of hydrocarbons and is characterized by the predominance of inertinite macerals (Hunt, 1996).

Figure 5 shows the HI vs. Tmax values used to indicate thermal maturity and kerogen types (Espitalie et al., 1985). Most samples are classified as Type II/III kerogen, with $Ro < 0.6\%$, indicating that they are immature. A smaller subset of samples from the Tumaco Basin exhibits better oil-generating potential, with Tmax values above 430°C, originated from Type II kerogen. However, these samples show low hydrogen indices, suggesting limited hydrocarbon generation

potential. Overall, the Tmax values in both basins are low to moderate, indicating that all samples are in the immature to early stage of the oil window as shown in Figure 6.

Since HI vs. OI values are often inaccurate in samples with poor OM, Langford & Blanc-Valleron (1990) recommend using an S2 vs. TOC plot to determine HI values more accurately as shown in Figure 7. The slope of the linear regression curve provides more reliable HI values (Volk, 2000). Similar recommendations have been made by Katz (1984) and Katz & Elrod (1983) for Tertiary rocks in the Gulf of Mexico and offshore sediments in California (Volk, 2000). The rocks and cuttings from the Tumaco and San Juan-Atrato Basins show oil potential between 0.1-3 mg HC/g rock, with TOC values ranging from 0.3 to 3.36%, placing the samples between Type II and IV kerogens, indicating a multi-origin OM, with contributions from both marine and terrestrial sources.

S2/S3 is an indicator of hydrogen richness in the kerogen. Thus, values of S2/S3 between 0.28 and 1.77 in the Tumaco and San Juan-Atrato rock samples suggest oxygen-rich O.M., which is indicative of gas-prone type III kerogen or oxidized material. Therefore, the S2/S3 vs TOC relationship for samples in the study indicates poor source rock quality or oxidized/degraded kerogen as is shown in Figure 8.

The relationship between the Production Index (PI) and Tmax is frequently used to indicate the potential for hydrocarbon expulsion (Mansour et al., 2022). Figura 9 shows the Tmax vs. PI plot showing that most of the Tumaco and San Juan-Atrato Basins samples are thermally immature to marginally mature (early window; Tmax <440°C, Table 1). Some samples from Opogado-1 and outcrops from the Choco area show higher Tmax values. Specifically, samples from the Iró Formation will generate gas. Iró Formation has been suggested as a possible source rock for the San Juan Basin, while its equivalent unit in Atrato, the Clavo Formation, is considered the likely source rock.

Vitrinite reflectance (Ro%) remains the most reliable indicator for evaluating the thermal maturity of source rocks (Bordenave, 1993; Hunt, 1996; Volk, 2000). Ro increases with thermal maturity, which correlates with the aromatization of vitrinite (Bordenave, 1993). It should be used in conjunction with other organic petrographic parameters (Tmax, TAI, fluorescence), petrophysical, and high-resolution geochemical parameters such as biomarker (terpanes, steranes, and aromatic hydrocarbons) by GC, GC/MS, and GCMSMS, to reduce the many inconsistencies between values of different thermal maturity indicators, which constrain thermal history models. (Wilkins, 1999; (Carvajal-Ortiz & Gentzis, 2015; Mansour et al., 2022).

Figure 10 shows the photomicrography under reflected white light and fluorescent light (50X) for sample T-7723, showing A) cutinites and pyrite in the vitrinite matrix. B) Sporinites in vitrinite matrix, and C) Collothelinite. Figure 11 shows the photomicrography of sample T-8431, which displays A) funginite, collothelinite, and minerals. B) Cracked colotelinite grain. C) Cracked vitrinite grain with pyrite.

Due to the poor dispersion of organic matter in all samples, it was necessary to concentrate the OM using a dense liquid (zinc chloride, ZnCl₂). The recovery was good, and a vitrinite population was identified. Pyrite, inertinites, sporinite, cutinite, collodetrinite, collothelinite, carbonates and

grains of mixed mineral matter with clayey organic matter were also identified. The organic petrographic analysis indicates that the analyzed sample represents rocks in an immature state.

Vitrinite reflectance profiles have been used to interpret some of the sedimentary and tectonic history of the basins and to identify unconformities using plots of R_o vs depth (Unomah and Ekweozor, 1993; Hunt, 1996). The variation of vitrinite reflectance measurements with depth (m) in the selected samples from Tumaco-1-ST-P well is displayed in Figure 12. In general, all the samples classify as immature based on R_o values. Samples from the Cascajal and Tangareal del Mira formations showing less maturity, while samples from the Tumaco formation show a progressive increase in thermal maturity with depth. The sequence shows a maturity peak around 8500 meters which correlated very well with T_{max} results and consequently with vitrinite reflectance calculated (R_o -equiv).

Conclusions

The organic geochemistry results of the Tumaco and San Juan-Atrato Basins located in the Pacific subduction zone in Colombia were evaluated based on their screening and organic petrography parameters. Based on geochemical indices from Rock-Eval pyrolysis and TOC parameters suggest that OM ranges between oil-gas-prone type II/III to carbon-rich inert organic matter (non-generative type IV) signature. Most samples are classified as Type II/III kerogen, with $R_o < 0.6\%$, indicating that they are immature. A smaller subset of samples from the Tumaco Basin exhibits better oil-generating potential, with T_{max} values above 430°C , originating from Type II kerogen. Overall, the T_{max} values in both basins are low to moderate, suggesting that all samples are in the immature to early stage of the oil window. Values of S_2/S_3 in the Tumaco and San Juan-Atrato rock samples suggest oxygen-rich O.M. indicative of gas-prone type III kerogen or oxidized material.

Vitrinite reflectance measurements indicate that the organic matter in these basins is generally immature, with samples from the Tumaco Formation showing increased maturity at greater depths. The thermal maturity data, including T_{max} and R_o -equiv values, suggest that the organic matter in these frontier Basins has not yet reached the threshold for significant hydrocarbon generation.

In conclusion, while the Tumaco and San Juan-Atrato Basins contain organic matter of poor to acceptable quality, the overall hydrocarbon generation potential appears to be limited. Type III kerogen indicates gas-prone organic matter, while Type II/III kerogen reflects a transitional environment with marine and terrestrial influences. Further exploration and detailed geochemical analysis are required to assess the full potential of these frontier basins.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Funding Declaration

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Data availability

Part of this article's geological and screening data is kept under a confidential agreement between the National University of Colombia and the National Hydrocarbons Agency-Colombia.

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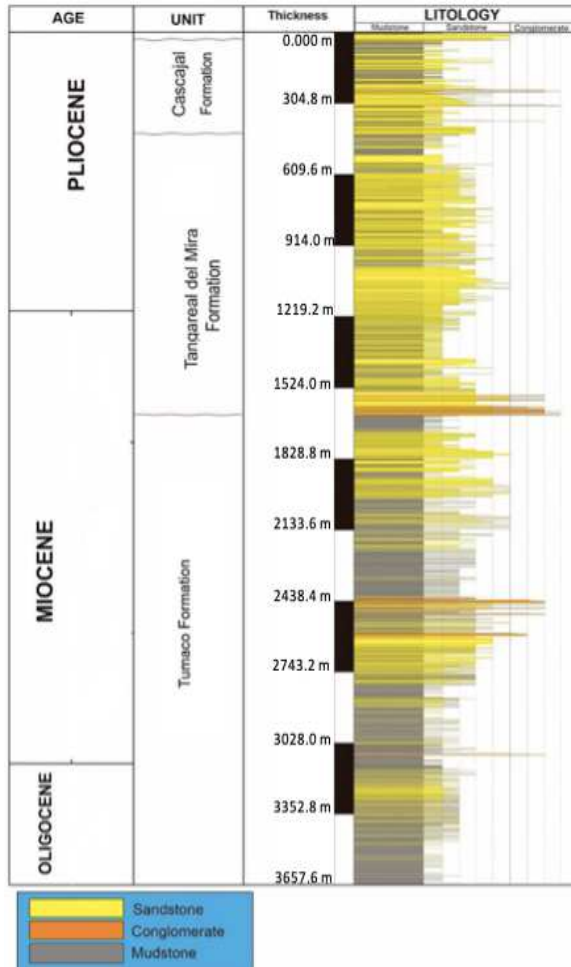
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A. Tumaco Basin



B. San Juan-Atrato Basin

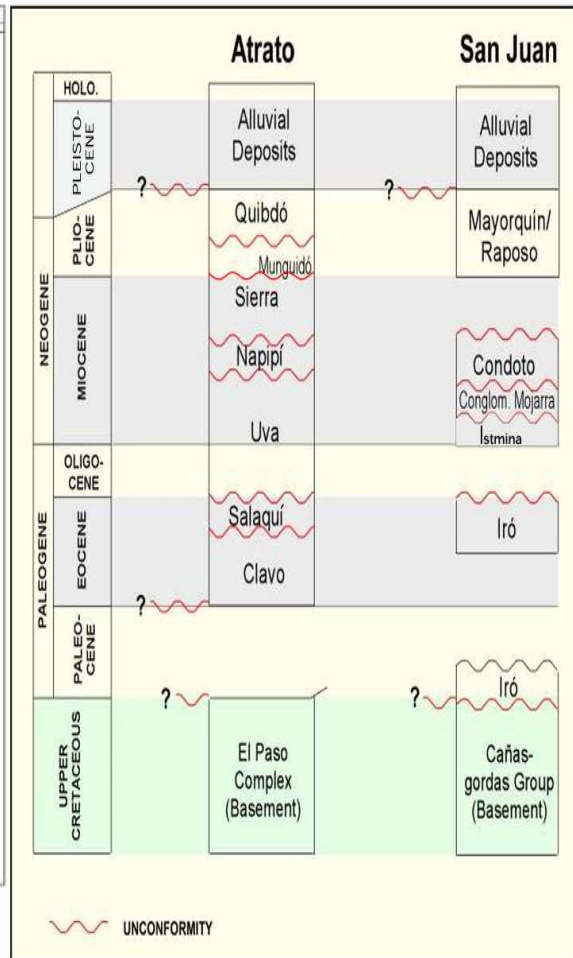
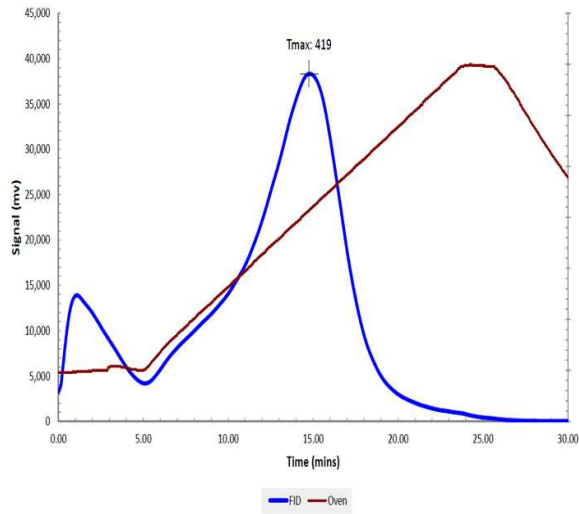


Figure 2. Stratigraphic columns for Tumaco (A) and San Juan-Atrato (B) Basins (Cortes et al., 2019; Cediél et al., 2009)

A. Vinci-VI pyrolyzer



B. Hawk pyrolyzer

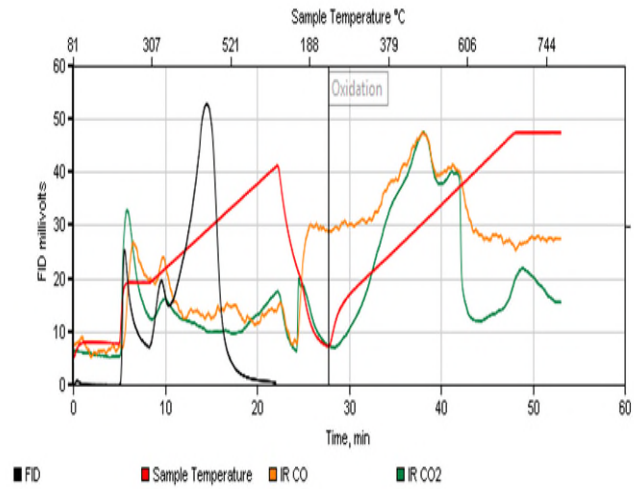


Figure 3. Pyrograms in the rock samples from Tumaco-1-ST-P at 3010.8 m depth (Tumaco Fm.) from Tumaco Basin and Opogado-1 well at 3322.3 m depth (Clavo Fm.) from San Juan-Atrato Basin ([ANH-Antek SAS, 2013](#), [ANH-UNAL, 2022](#))

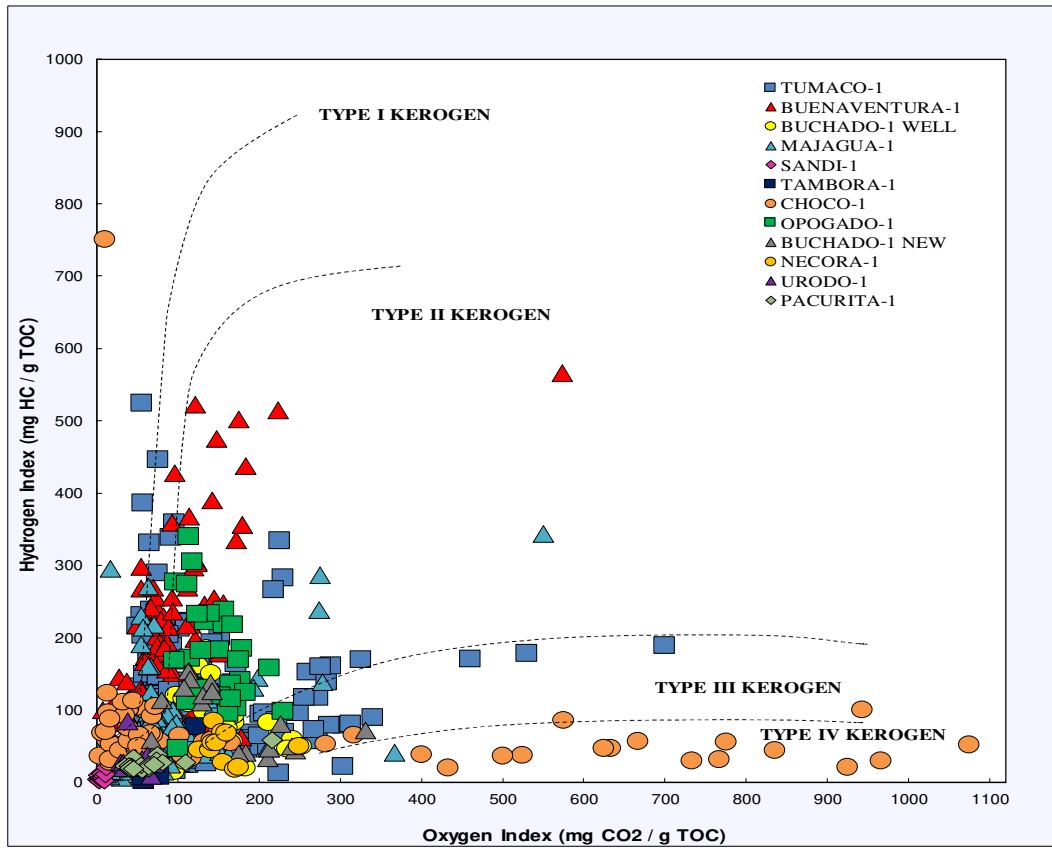


Figure 4. Kerogen type based on HI (mg HC/g TOC) vs. OI (mg CO₂/g TOC) in the rock samples from Tumaco and San Juan-Atrato Basins ([Robertson Research Inc., 1981,1988](#), [ANH-Antek SAS, 2013](#), [ANH-UNAL, 2022](#))

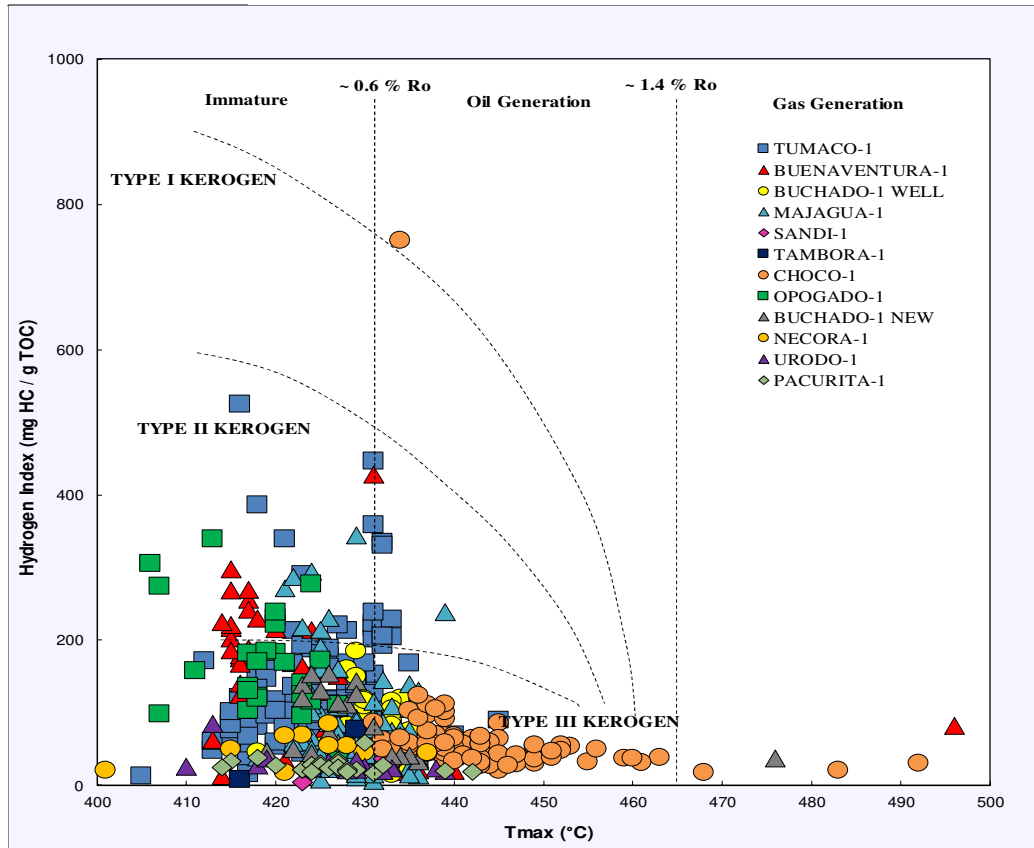


Figure 5. Kerogen type and thermal maturity and hydrocarbon generation using HI (mgHC/g TOC) vs. Tmax (°C) showing the evolution of kerogen composition with thermal maturity in the rock samples from Tumaco and San Juan-Atrato Basins ([Robertson Research Inc., 1981,1988a](#), [Antek SAS-ANH., 2013](#), [ANH-UNAL, 2022](#))

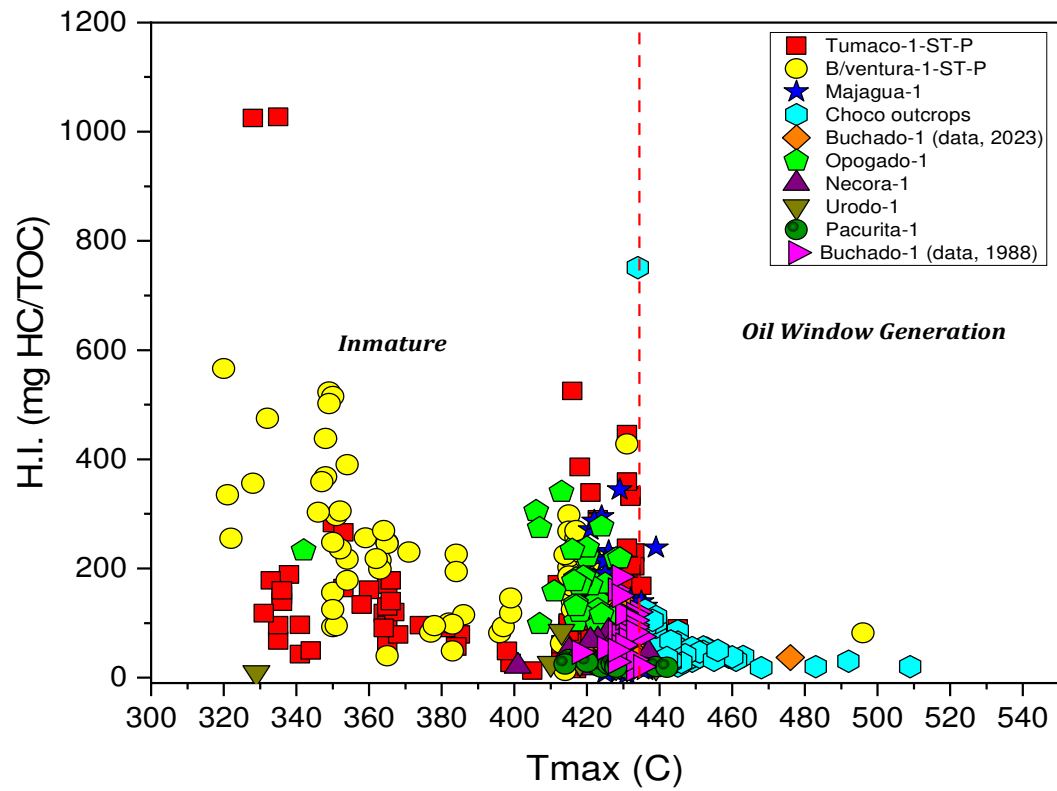


Figure 6. Thermal maturity using HI (mgHC/g TOC) vs Tmax (°C) in the rock samples from Tumaco and San Juan-Atrato Basins. The dashed red line indicates separation between immature and early/oil window generation. ([Robertson Research Inc., 1981,1988a](#), [Antek SAS-ANH. 2013](#), [GEMS, 2020](#), [ANH-UNAL, 2022](#))

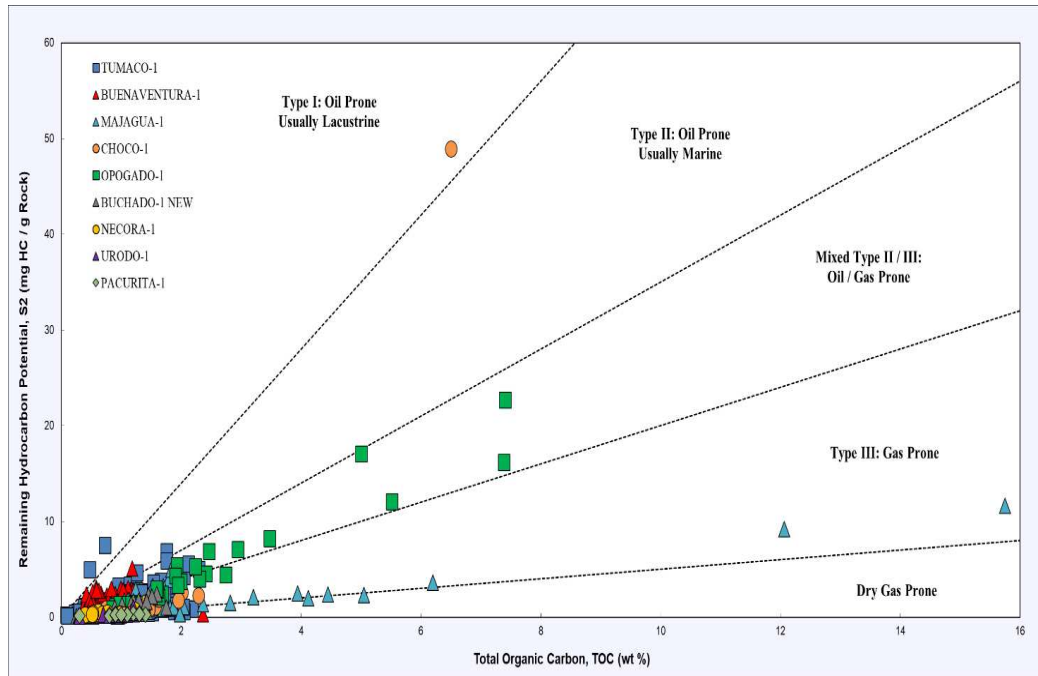


Figure 7. Kerogen quality using S_2 (mg HC/g rock) vs %TOC from Tumaco and San Juan-Atrato Basins (Antek SAS-ANH., 2013, ANH-UNAL, 2022)

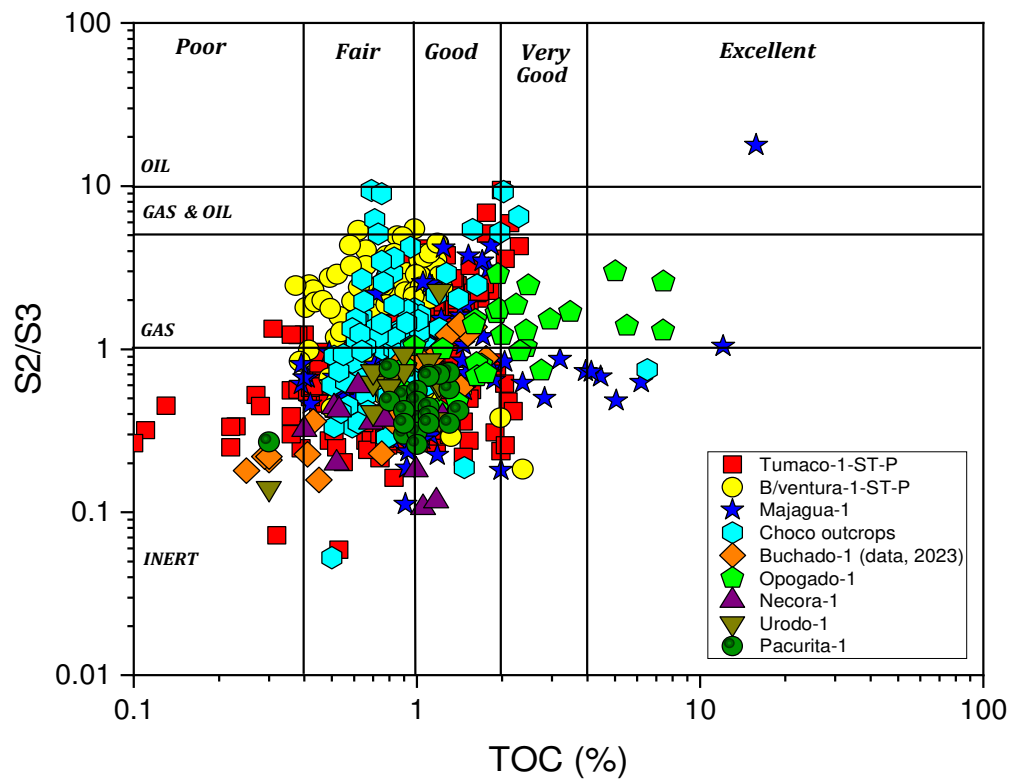


Figure 8. Organic matter quality and generation products using S2/S3 vs TOC (%) in the rock samples from Tumaco and San-Juan Atrato Basins ([Antek SAS-ANH, 2013](#), [GEMS, 2020](#), [ANH-UNAL, 2022](#))

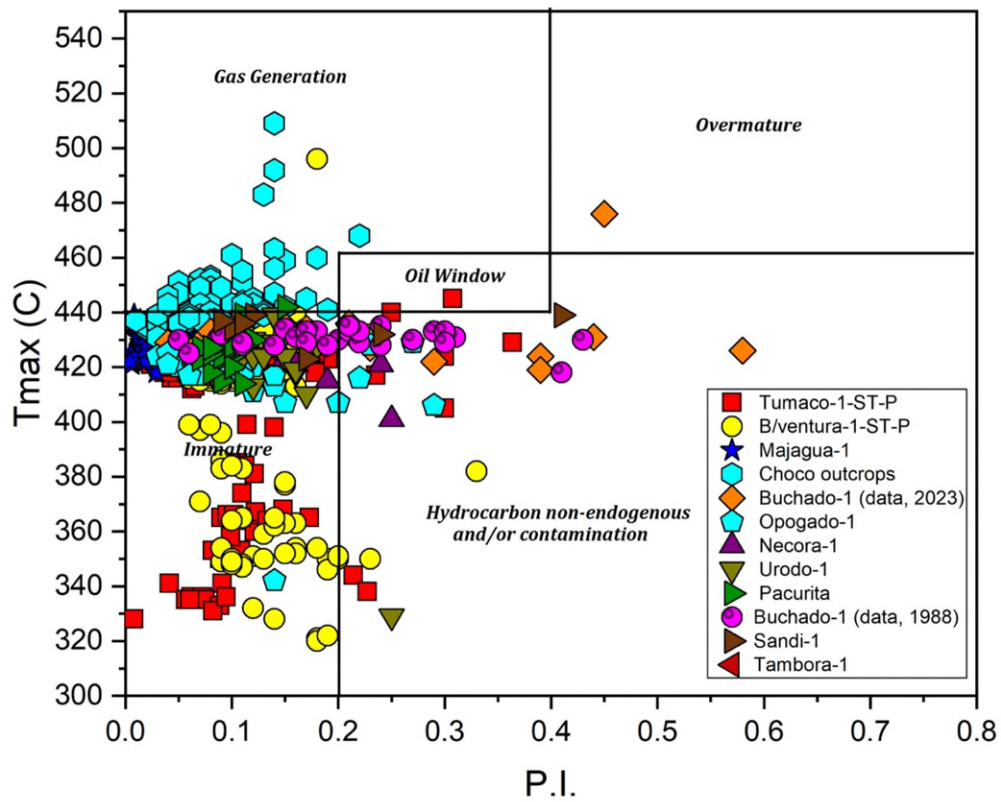


Figure 9. Thermal maturity using T_{max} (°C) vs PI in the rock samples from Tumaco and San Juan-Atrato Basins (Robertson Research Inc., 1981,1988, Antek SAS-ANH. 2013, ANH-UNAL, 2022)

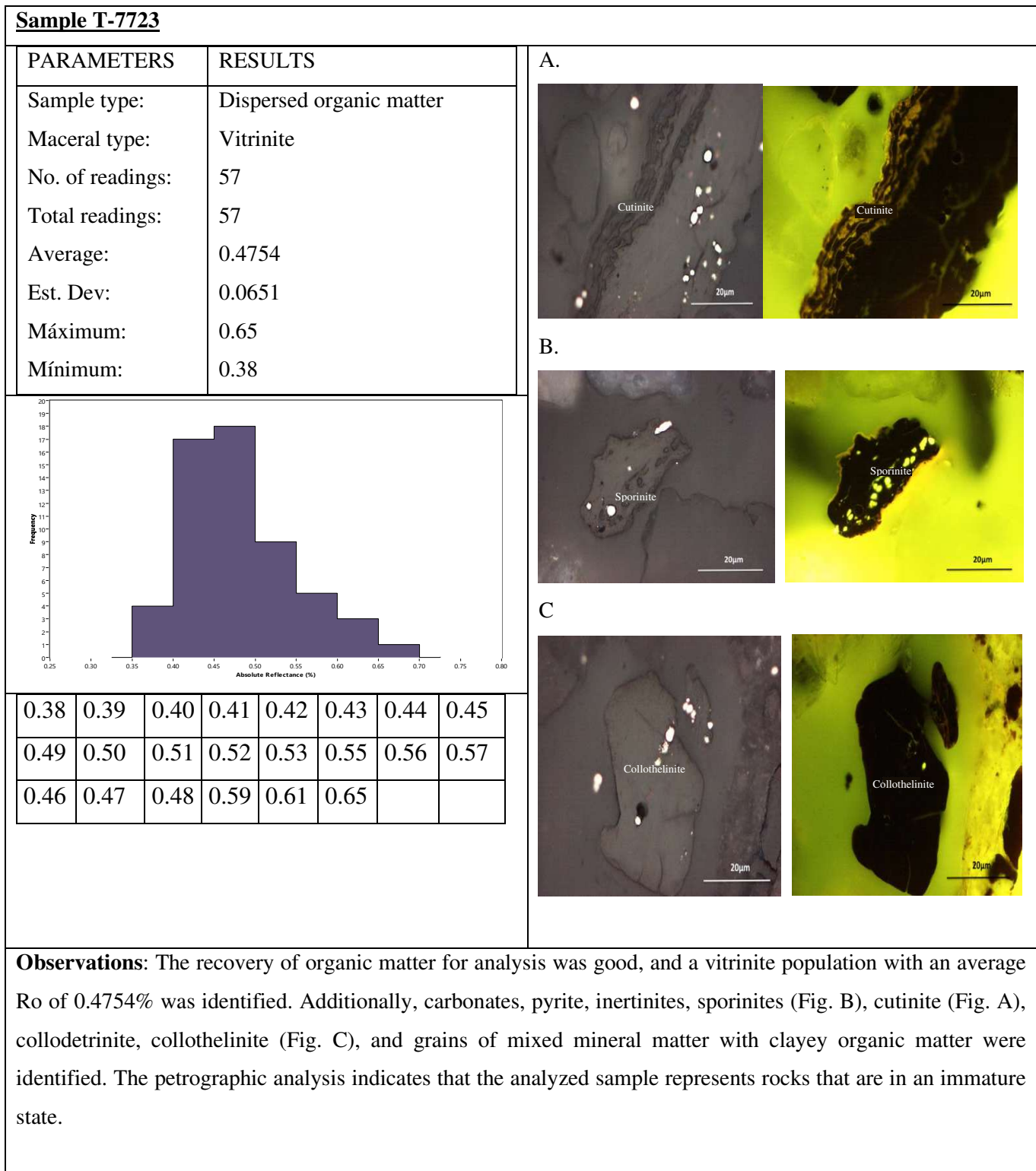
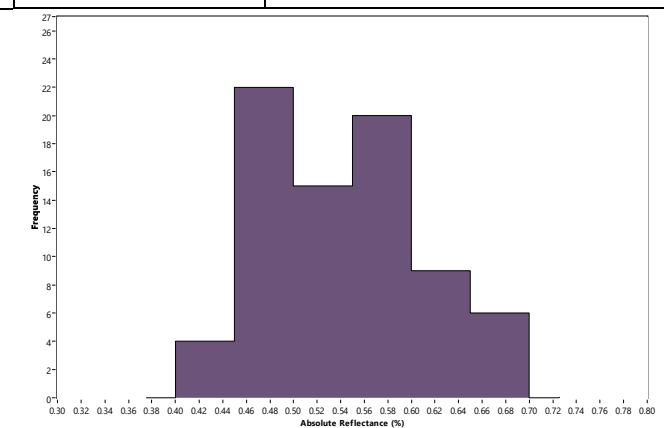


Figure 10. Photomicrography under reflected white-light and fluorescent light (50X) for sample T-7723. A) cutinites and pyrite in vitrinite matrix. B) Sporinites in vitrinite matrix. C) Collothelinite ([Antek SAS-ANH, 2013](#))

Sample T-8431

PARAMETERS	RESULTS
Sample type:	Dispersed organic matter
Maceral type:	Vitrinite
No. of readings:	76
Total readings:	76
Average:	0.5418
Est. Dev:	0.0682
Máximum:	0.69
Mínimum:	0.44

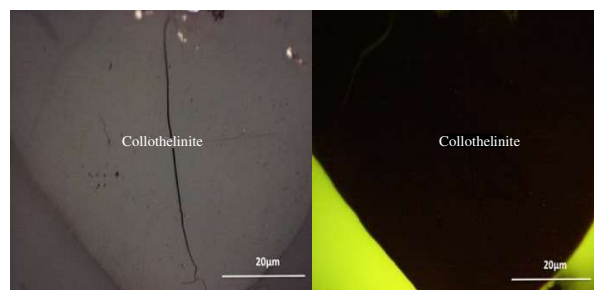


0.44	0.45	0.46	0.47	0.48	0.49	0.51	0.52
0.57	0.58	0.59	0.60	0.61	0.62	0.63	0.64
0.53	0.54	0.55	0.56	0.65	0.66	0.68	0.69

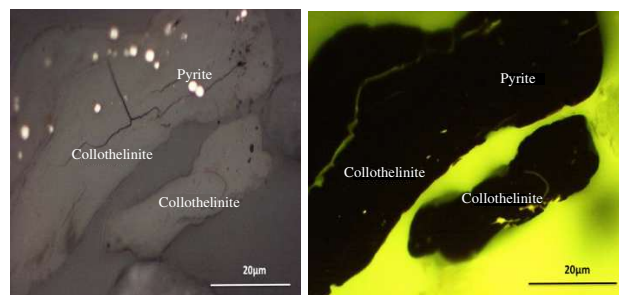
A.



B.



C.



Observations: The recovery of organic matter for analysis was very good, and a vitrinite population with an average Ro of 0.5418% was identified. Additionally, pyrite (Fig. C), cutinite, suberinite, carbonates, and inertinite were identified. Petrographic analysis indicates that the analyzed sample represents rocks that are in an immature state.

Figure 11. Photomicrography under reflected white-light and fluorescent light (50X) for sample T-8431. A) funginite, collothelinite and minerals. B) Cracked colotelinite grain. C) Cracked vitrinite grain with pyrite. ([Antek SAS-ANH, 2013](#))

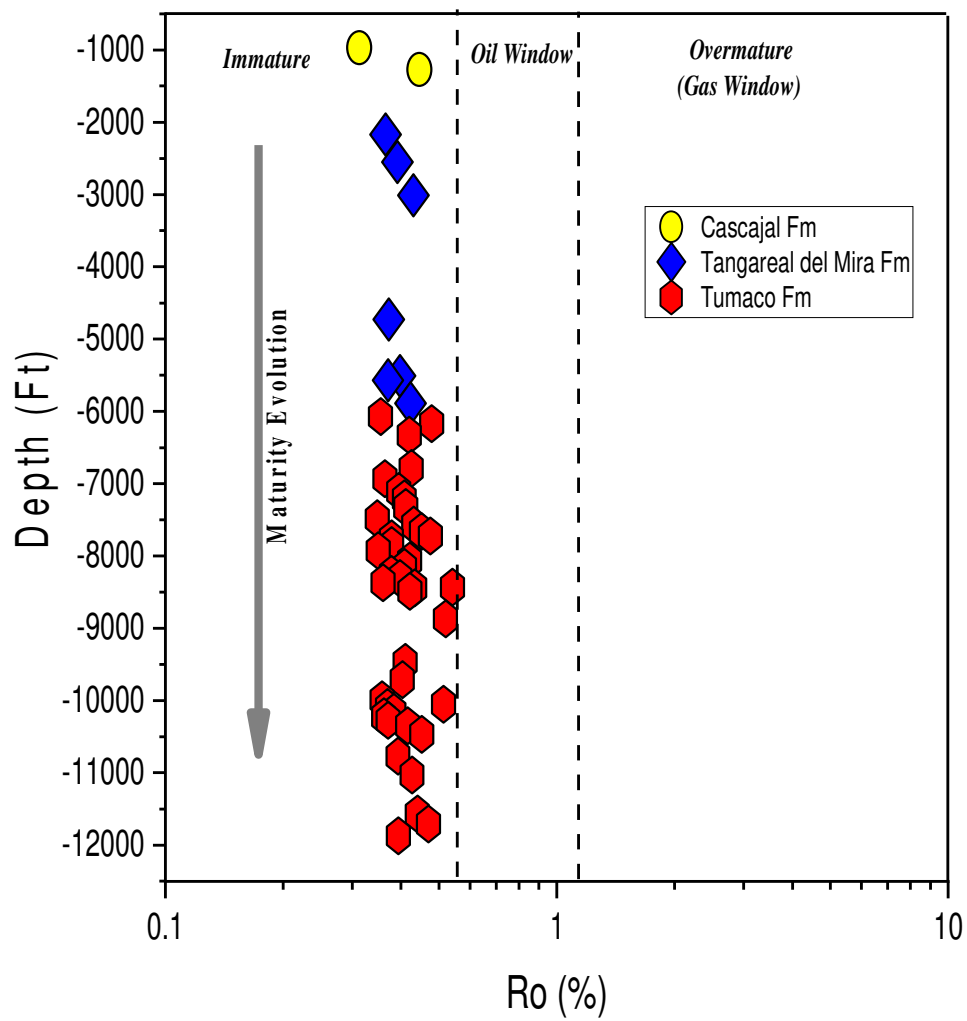


Figure 12. Ro, % vs. depth (meters) and maturity of the OM in the Tumaco-1-ST-P well, Tumaco Basin, Colombia (ANH-Antek SAS, 2013)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [TABLE1.xlsx](#)
- [TABLE2meters.xlsx](#)