High-resolution molecular stratigraphy of Oligocene–Miocene sequence of Tumaco-1-ST-P well, Tumaco forearc Basin, Colombia

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Abstract

In the present work, high-resolution molecular stratigraphy technique has been applied to the rock samples from Tumaco-1-ST-P well to investigate vertical variations of the deposited organic matter (O.M.) based on screening parameter and high-resolution biomarkers in both saturate and aromatic fractions in order to establish its origin, organic facies, depositional paleoenvironment, thermal maturity, biodegradation processes and to evaluate the exploratory potential in this frontier forearc basin. The O.M. is immature with a high concentration of biolipids (early diagenesis) and with poor to fair generation potential originated from a type II/III or III kerogen. Original total organic carbon (TOC_o) and original hydrocarbon index (HI_o) values for each formation and lithology are determined to evaluate the hydrocarbons potential in the basin. *n*-alkanes, isoprenoids, and tricyclic terpanes suggest an algal/bacterial and terrestrial input deposited on a marine-deltaic shale under oxic to suboxic conditions. The O.M. was deposited on siliciclastic rocks in a marine-continental (transitional) environment, although carbonate rocks were also deposited in the bottom of the column (late Oligocene). The molecular stratigraphic interpretation allows to conclude that organic facies and lithology in Tumaco-1-ST-P are characterized in Cascajal and Tangareal del Mira Fms. (1000–5000 ft) by a marine-deltaic paleoenvironment with an important terrestrial contribution and varying between deltaic plain and prodelta during the late Miocene. At the top of Tumaco Fm (5000–9000 ft) in the late to medium Miocene, the depositional environment was like the marine delta of the Tangareal del Mira Fm, changing to a marine platform environment at 8000 to 10,000 ft depth in the middle to early Miocene. Toward the bottom of the column (10,000–12,000 ft), Tumaco Fm was deposited in the late Oligocene under a marine shelf environment. In the present paper, we propose a modeling approach, based on the evolution of the thermal maturity through the stratigraphic column, that at 17,000 feet depth could exist rocks with O.M. in the hydrocarbon generation window for Tumaco Basin, Colombia.

Keywords Hydrocarbon source rock · Marine-deltaic environment · Thermal maturity · Saturate–aromatic biomarkers · Frontier basin · Tumaco forearc basin

Introduction

Tumaco basin is a frontier basin under the influence of a subduction zone of the Pacific active margin. Consequently, the importance of both the new stratigraphic and the geochemical data is essential to provide new information for developing new exploration projects in the Colombian Pacific margin. The Tumaco-1-ST-P stratigraphic well gives evidences of the Tumaco basin sedimentation system during the late Oligocene to Pliocene, dominated by the movements of the paleodeltas of the Tumaco and Mira rivers (ANH-Universidad de Caldas 2011, ANH-Antek S.A. 2013). In the late Oligocene-middle Miocene, Tumaco Fm is observed the presence of a large deltaic complex (associated with paleodelta of the Patia River), with sources areas

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that involve, at least partially, the Central Cordillera. For the late Miocene–early Pliocene, the displacement to the north of the Patía River leads to the establishment of the Mira fluvio-deltaic system in the area, represented by deposits of the Tangareal del Mira Fm, which is the only present source areas of the Western Cordillera. Finally, in the late Pliocene, deltaic deposits of Cascajal Fm record a period of intense volcanism (ANH-Antek S.A. 2013).

The application of high-resolution organic geochemical techniques to evaluate the sedimentary sequence on a “layer-by-layer” basis is called “molecular stratigraphy” (Brassell et al. 1986; Farrimond et al. 1990; Keely et al. 1993). In this study, this approach was applied to investigate the evolution of the sedimentary organic matter in the Tumaco-1-ST-P stratigraphic well in the range between 750 and 11,930 ft covering the Miocene–Oligocene sequence in the onshore Tumaco basin, Colombia to characterize the origin and type of organic matter, paleodepositional environment, genetic relation between bitumen, maturity, and possible degradation processes in a sedimentary basin under the subduction influence.

Geological setting

Regional stratigraphy

The onshore Tumaco basin is located in the southwestern of Colombia. The basin is bounded by the Garrapatas fault system in the north, Ecuador country in the south, Western Cordillera (uplift) in the east, and the Pacific Ocean in the west (IGAC-Ingeominas 2001; Barrero et al. 2007; Cediel et al. 2010; ANH-Universidad de Caldas 2011; Borrero et al. 2015). The Tumaco forearc basin contains a pre-Miocene mega-sequence and three post-lower Miocene sequences deposited in shelf to bathyal environments. The basin basement is made up of Cretaceous metasedimentary and volcanic rocks (Cediel et al. 2010). The study area map and detailed stratigraphy column of the Tumaco-1-ST-P well are given in Figs. 1 and 2, respectively (ANH-Antek S.A. 2013).

Previous work including a detailed discussion of the geology of the onshore Tumaco basin is found in the literature derived from recent projects led by National Hydrocarbon Agency, Colombia (Universidad de Caldas 2011; ANH-Antek S.A. 2013). Suárez (2007) studied the Colombian

Fig. 1 Map showing the study area and location of the Tumaco-1-ST-P stratigraphic well (ANH-Antek S.A. 2014)

Fig. 2 Generalized lithostratigraphic column of Tumaco basin (ANH-Antek S.A. 2014)

Pacific provinces using a data set including seismic, gravimetric, and aeromagnetic data. Additional geological and tectonic data can be searched in publications by Suárez (2007), Echeverri et al. (2011), and Echeverri et al. (2015). Stratigraphic studies of the area have been published by Cediél et al. (2010) based on the description of the Chagüi-1, Majagua-1 y Remolino Grande-1 stratigraphic wells.

In brief, the basement of the Tumaco basin is interpreted as an allochthonous block composed of fragments of oceanic plateau (Kerr et al. 2002) and the Santonian–Campanian arc of islands, accreted to the continent during the late Cretaceous and early Paleocene (ANH-Universidad de Caldas 2011). The following discussion about geological setting and regional stratigraphy is taken from the technical report presented by Antek S.A. to the National Hydrocarbon Agency (NHA), Colombia (ANH-Antek S.A. 2013).

The Tumaco formation (Chatiense-early Tortonense) is composed of interbedded mudstones, arenite, and occasionally conglomerates covering the bottom of Tumaco 1-ST-P well (interval 11,980–5381 ft), which has a thickness greater than the 6599 ft (the base is not present). The rocks of this unit can be grouped into eight facies associations represented by bar and estuarine channels, mouth bar, coastal lagoon, proximal front deltaic, prodelta, and platform deposits, respectively.

In the facies associated with the Tumaco Fm, occur occasional mudstones, sandstones and conglomerates, abundant fossils of marine affinity and evidence of rocks associated with deltaic paleoenvironment with the influence from the continent, it allows considering the existence during the late Oligocene and much of the Miocene of an enormous deltaic complex dominated by waves and tides. It seems to correspond to the paleodelta of the Patia River when it disem-bogued in the area now occupied by the Tumaco Bay.

The Tumaco Fm origin indicates an input area that, at least partially, involved sectors of the Central Cordillera that were recorded in the stratigraphic record with the presence of minerals such as garnets and pumpellyite and fragments of metamorphic rocks such as marbles, although there is a clear preponderance of a mafic–intermediate source area and some recycled rocks of the first cycle.

The Tangareal del Mira Fm (middle Tortonense-Zancliense), rests unconformably on the Tumaco Fm covering the interval between 1437 and 5381 ft (thickness 3944 ft). In general, the unit consists of interbedded lithic sandstones and mudstones with a development of conglomerates at the base that can be grouped into five associations of facies representing river channels, bar and fluvial channels, bay estuarine, prodelta, and front deltaic deposits.

As in Tumaco Fm, the set of facies and facies associations of Tangareal del Mira Fm allow us to observe the presence of abundant fossils of marine affinity and evidence of continental contribution that would support the existence of a

deltaic complex dominated by waves and tides occurs with migration north Mira River in the late Miocene, the position left to the Patia River Delta in its movement to its present site mouth. The development of fluvial facies at the base of the unit, showing the relative fall of sea level in the area, which is succeeded by two transgressive–regressive greater cycles, where is evident a high volcanic influence.

The Cascajal formation (Zancliense), which was examined in detailed in Tumaco-1-ST-S well, since in Tumaco-1-ST-P well, only cuttings were available and partially in some outcrops located on the Tumaco Bay; it is composed of interbedded mudstones, litoarenites, and conglomerate facies, locally bioturbated, it reposes unconformably on the Tangareal del Mira Fm. Moreover, it may be characterized in five associations of facies represented by 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. 2013).

The facies associated with Cascajal formation allow to observe the presence of bioturbated segments, abundant fossils of marine affinity and the continental influence that would support the existence during the late Pliocene of a deltaic complex dominated by waves and tides (Fig. 4) which is associated with the progradation of the delta of Mira River. In this unit, the volcanic contribution is even greater than in the Tangareal del Mira.

The Quaternary is represented by the first 110.89 ft of Tumaco 1-ST-S well (ANH-Universidad de Caldas 2011), which corresponds to fluvial deposits of the Mira River. These deposits consist of interbedded litoarenites and sublitoarenites, massive mudstones, and occasional interbedded polymictic conglomerates with a significant contribution of volcanic rocks.

Samples and experimental

Samples

Samples were selected from the stratigraphic column in the interval 750 to 12,000 ft covering the Miocene to the late Oligocene in the Tumaco-1-ST-P well. Two hundred and fifty samples were analyzed for TOC and RE-Py, 25 samples for vitrinite reflectance, and 100 samples for extractable organic matter (EOM), SARA fractionation, GC/FID, and GCMS analyses applying Antek S.A. geochemical validated procedures, which are part of its ONAC-ISO-17025 quality assurance manual (Antek S.A. 2011). All the samples were picked and washed to remove any contaminant. After the samples had been air-dried or oven-dried, they were crushed on porcelain mortar and pestle up to 62 µm for screening analysis, organic matter extraction, and biomarkers analysis.

Total organic carbon (TOC) and Rock–Eval pyrolysis (RE-Py)

For TOC analysis, 1 g of rock and cutting powder were digested overnight with 10% HCl to remove the carbonate, then washed and dried in oven at 60 °C for 24 h. Approximately 100 mg of sample was transferred onto a Leco cell and mixed with copper/iron catalyst. TOC analysis was run on a Leco S-200 carbon analyzer. Rock–Eval pyrolysis analysis was done in a Vinci-VI instrument with temperature programmed from 30 to 600 °C at 30 °C/min rate. Helium was maintained at 60 mL/min. S1, S2 peaks and $T_{\max}$ were detected by FID detector, while S3 peak was quantitated by TCD detector.

Organic petrography (vitrinite reflectance)

All samples presented a relatively poor dispersed organic matter that it was necessary to make a organic matter concentration with zinc chloride (ZnCl₂), a heavy liquid prepared at a density of near 2 g/mL (ICCP 1963; ISO 1985, 1994; Pawlewicz 2013). Vitrinite reflectance analysis was conducted according to ASTM D-7708-11 and ISO-7404 standard methods. The measurements were done using a Carl Zeiss model Axio-Imager-100 petrographic microscope equipped with reflected and fluorescence UV light in the spectral range between 200 and 3000 nm. The microscope was coupling to a Craic model CoalPro spectrophotometer and a high-speed high-resolution photographic camera. The system was calibrated using a 0.4, 0.9, 1.7, and 5.3% synthetic standards. The microphotometer was equipped with an oil immersion objective (X50/0.85). The oil immersion used has a refraction index of 1.5189 at 23 °C over sodium light at 589.3 nm. The reflectance was measured with normal incident monochromatic light at wavelength of 546 nm.

Organic matter extraction and fractionation (EOM and SARA analyses)

Rock powder samples were extracted using a Dionex ASE-200 accelerated extraction equipment. The solvent was 100% DCM. The extraction condition were solvent pressure at 1500 psi, extraction cell temperature of 100 °C, static pressure time of 2 min, solvent flush 75%, and nitrogen purge time of 60 s. After extraction, the solvent was removed until almost dried by rotaevaporation in a Buchi model 130 rotaevaporator and then transferred in a 4 mL pre-weighed vial. Finally, the extracts were dried with a nitrogen stream and the extractable organic matter (EOM) was determined by gravimetry.

Due to the low EOM content, all the bituminous extracts were used for SARA fractionation by microcolumnation on alumina. The bituminous extracts were dissolved in an

excess of *n*-pentane, and the asphaltenes were precipitated overnight at -10 °C into the refrigerator. Asphaltenes were separated from maltene fraction by centrifugation. The maltene was fractionated by liquid chromatography on activated silica gel in saturates, aromatics, and resins. The saturated fraction was eluted with *n*-hexane; the aromatic fraction was eluted with *n*-hexane: dichloromethane (70:30), and the polar (NSO) fraction was eluted with dichloromethane: methanol (98:2). The saturated fraction was analyzed by GC/FID. The branched and cyclic fractions (biomarkers) were separated from *n*-alkanes by silicalite powder S-115 and then analyzed by SIM-GC/MS. The aromatic fractions were analyzed directly by GC/FID, and some selected samples were analyzed for aromatic biomarkers by gas chromatography-mass spectrometry (SIM-GC/MS).

C₁₅⁺ saturated fraction by GC/FID

C₁₅⁺ saturated fractions obtained from SARA analysis were dissolved according to the mass with *n*-hexane (approximately 10 mg/mL) and analyzed using an Agilent 6890 HRGC/FID fitting with a DB-1 60 m × 0.25 mm × 0.25 μm capillary column. Samples were injected in splitless mode. The GC oven temperature was programmed from 60 to 320 °C at 5 °C/min. Helium was used as carrier gas at a linear velocity of 50 cm/s (12 psig). Injector/detector was maintained at 320 °C/350 °C, respectively. Data handling was done with Agilent Chemstation version 10 chromatographic software.

Biomarkers by GC/MS-SIM

SIM-GC/MS of branched and cyclic and aromatic hydrocarbons was analyzed using an Agilent 7890B gas chromatograph coupling to an Agilent 5975C VL MSD mass spectrometer. The separation was carried out using a Restek Rtx-5MS of 60 m × 0.25 mm × 0.25 μm capillary column operated at constant flow (1 mL/min) (initial head column pressure of 8.23 psi) and the linear velocity of 20 cm/s. Column program started at 60 °C (2 min) to 320 °C at 3 °C/min and maintained at 320 °C for 11 °C/min. The ion source was operated in electronic impact (EI) mode at 70 eV at 150 °C. The MS was operated in selective ion monitoring (SIM) for the following saturate ions: internal standard, Squalane (m/z 99 and 113); *n*-alkanes (m/z 99); isoprenoids (m/z 183), terpanes (m/z 191), demethylated hopanes (m/z 177), steranes (m/z 217 and 218) and aromatic ions: alkylnaphthalenes (m/z 128, 142, 156, 170), alkylphenanthrenes (m/z 178), alkylidibenzothiophenes (m/z 184), monoaromatic steroids (m/z 253), and triaromatic steroids (m/z 253). The Agilent ChemStation version A02.00 (2012) was utilized as data acquisition system. Biomarker quantitation was done using the area peaks from the GC/MS traces.

Results and discussions

Total organic carbon (TOC) and Rock–Eval pyrolysis

TOC and Rock–Eval pyrolysis results are summarized in Table 1. TOC content analyzed by Leco carbon analyzer, after removal of carbonate minerals, showed values ranging between 0.09 and 2.30 wt%. The major TOC values were found in the deepest intervals of the Tumaco-1-ST-P well (11,610–11,700 ft), which were deposited on calcareous and siliceous siltstones corresponding to the late Oligocene sequence. 47% of the samples analyzed are grouped in the range between 0.5 and 1.0 wt%, which are considered with fair source rock potential. 38% of the samples are classified as O.M. with good quality. Finally, 13% of the total of 250 rock samples analyzed showed TOC values < 0.5%. Rocks organically poor with TOC < 0.5% are considered, in almost all the cases, like rocks with poor generator potential (Bordenave 1993; Peters and Cassa 1994; Hall et al. 2016) therefore, without economic interest.

Free hydrocarbons (S1 peak) average value was 0.075 mg HC/g rock (ranging between 0.02 and 0.80 mg HC/g rock). The high heterogeneity of S1 through the stratigraphic column is due to the multiple and successive changes of organic facies in the sedimentary strata. Samples collected at 11,570–11,730 ft in the late Oligocene displayed the highest values of S1 ranging between 0.2 and 0.8 mg HC/g rock, while most of the samples had values < 0.25%, which classifies the generation potential as “poor and/or acceptable” (Peters and Cassa 1994). In practical terms, the peak S1 is less than the removable fraction (EOM) for immature sediments; for mature sediments, peak S1 and the content of EOM fraction are fairly comparable (Peter et al. 2005).

S2 values vary between 0.07 and 1 or removal 0.45 mg HC/g rock, with an average of 1.1 ± 1.36 mg HC/g rock. The highest S2 peak values were found in the interval around 11,700 ft in the late Oligocene of the Tumaco Fm. S2 peak at 5570 ft registered a value of 10.45 mg HC/g rock which is inconsistent with the low thermal evolution of the O.M. in the samples, based on the values of TOC, S1 and bitumen extracted (EOM). The value of $T_{\max}$ is proportional to the thermal maturity of the organic matter in a rock (Tissot and Welte 1984). $T_{\max}$ values vary between 328 and 445 °C, with an average value of 417.5 °C ($SD \pm 26.23$ °C), indicating rocks relatively immature or at the start of its early maturity.

Present-day hydrogen index (HI_{pd}) suggests that a significant number of samples from the Tumaco-1-ST-P well corresponds to type II/III kerogen, characterized by HI_{pd} between 300 and 600 mg HC/g TOC. This kind of kerogen is dominated by liptinitic macerals, despite a minor vitrinite and inertinite input. Type II/III kerogen describes mixtures of transitional marine and terrestrial organic matter.

Figure 3 displays the hydrogen index (HI_{pd}) versus oxygen index (OI_{pd}) cross-plot to illustrate the quality and level of maturation of the studied samples. Results cover a broad range of maturity between oil-prone type II kerogen with HI_{pd} of 525 mg HC/g TOC and dry gas-prone type IV kerogen with HI_{pd} of 13 mg HC/g TOC values, indicating that the O.M. in study comes from a single and unique kerogen with a significant variation of the organic facies and paleodepositional environments.

Figure 4 shows the cross-plot HI_{pd} versus $T_{\max}$ to correlate kerogen type and thermal maturity in terms of the degree of kerogen conversion, indicating that most of the samples show a $T_{\max} < 430$ °C and $HI_{pd} < 600$ mg HC/g TOC confirming an immature O.M. and type III kerogen. Some specimens, however, show an O.M. with oil generation potential and type II and II/III kerogen. The pseudo van Krevelen diagram between S2 and TOC_{pd} % indicating the type and quality of the kerogen in the rock samples is shown in Fig. 5 (Langford and Blanc-Valleron 1990). Thus, a large number of rocks and cuttings from Tumaco-1-ST-P well confirm a type III and/or IV kerogen (gas prone and dry gas prone, respectively). About 20 samples showed a transitional type II/III kerogen, which would generate oil/gas, and a smaller number of samples presented a type II kerogen (oil prone, usually marine). Thus, Cascajal and Tangareal del Mira formations show the lower quality due to its terrestrial origin and its diagenetic maturity.

Figure 6 shows the paleoenvironmental evolution based on the lithology and stratigraphic analyses for Tumaco-1-ST-P well (ANH-Antek S.A.S 2013). Since the kerogen type is related to the original type of organic matter and its evolution and preservation over time, which is in turn associated with depositional environment and climate (Hall et al. 2016), the evaluation of depositional environment can be done through the TOC content and RE-pyrolysis data and indexes. Thus, the results discussed in Sect. 4.1 indicate that O.M. was deposited in a fluvio-deltaic and deltaic (upper delta plain/lower delta plain and prodelta) environment on siliciclastic lithofacies with organofacies characterized by input of higher plants, algae, and marine algae on a II/III kerogen type which is consistent with the depositional environment deduced from lithology and stratigraphic analysis.

Vitrinite reflectance and maceral analysis

Organic petrography is used almost systematically as a complement of the screening parameters (TOC, RE-Py, Fluorescence, etc.) to evaluate the O.M. type and the characteristics of the depositional environment, such as redox conditions (oxic/anoxic), energy level, microorganisms type, and additional data that allows the quantification of the thermal evolution of the O.M. Mean random Vitrinite reflectance ($R_{v,r}$) of the dispersed organic matter was measured on immersed

Table 1 Present-day and original TOC and Rock–Eval pyrolysis parameters for Tumaco-1-ST-P well, Tumaco basin, Colombia

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-750	750	Cascajal Fm	Sandstone	0.93	0.95	0.04	0.40	1.54	341	43	47	166	4.30	0.09	9	–	–
T-770	770	Cascajal Fm	Sandstone	0.50	0.51	0.05	0.76	1.3	336	152	171	260	10.0	0.06	6	–	–
T-790	790	Cascajal Fm	Sandstone	0.22	0.23	0.03	0.11	0.44	344	50	63	200	13.6	0.21	21	–	–
T-850	850	Cascajal Fm	Calcareous sandstone	0.09	0.09	0.05	0.17	0.63	338	189	234	700	55.6	0.23	23	–	–
T-970	970	Cascajal Fm	Sandstone	0.53	0.54	0.03	0.07	1.19	405	13	19	225	5.70	0.30	30	0.313	–
T-990	990	Cascajal Fm	Sandstone	0.32	0.33	0.03	0.07	0.97	424	22	31	303	9.40	0.30	30	–	0.472
T-1050	1050	Cascajal Fm	Siltstone	0.74	0.76	0.06	0.34	1.37	417	46	54	185	8.10	0.15	15	–	0.346
T-1130	1130	Cascajal Fm	Siltstone	1.91	1.96	0.08	1.85	2.49	341	97	101	130	4.20	0.04	4	–	–
T-1190	1190	Cascajal Fm	Sandstone	1.29	1.33	0.14	1.79	3.65	336	139	149	283	10.9	0.07	7	–	–
T-1270	1270	Cascajal Fm	Mudstone	0.48	0.6	0.4	4.93	5.33	335	1027	1039	1110	83.3	0.08	8	0.4456	–
T-1290	1290	Cascajal Fm	Siltstone	1.14	1.17	0.04	0.31	1.17	399	27	30	103	3.50	0.11	11	–	–
T-1470	1470	Tangareal de Mira Fm	Siltstone	0.73	0.93	0.06	7.48	7.6	328	1025	1038	1041	100.0	0.09	9	–	–
T-1950	1950	Tangareal de Mira Fm	Siltstone	0.51	0.53	0.08	0.6	1.39	364	118	133	273	15.7	0.12	12	–	–
T-2150	2150	Tangareal de Mira Fm	Siltstone	0.27	0.28	0.06	0.46	0.88	365	170	190	326	22.2	0.12	12	–	–
T-2170	2170	Tangareal de Mira Fm	Siltstone	0.23	0.24	0.04	0.41	1.22	333	178	193	530	17.4	0.09	9	0.3655	–

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-2370	2370	Tangareal de Mira Fm	Calcareous sandstone	0.7	0.72	0.08	1.20	3.22	412	171	180	460	11.4	0.06	6	–	0.256
T-2490	2490	Tangareal de Mira Fm	Sandstone	0.92	0.94	0.06	0.44	1.65	413	48	55	179	6.5	0.12	12	–	0.274
T-2550	2550	Tangareal de Mira Fm	Calcareous siltstone	1.46	1.5	0.06	1	2.78	335	68	71	190	4.1	0.06	6	0.3915	–
T-2570	2570	Tangareal de Mira Fm	Sandstone	1.32	1.36	0.08	0.81	2.38	365	61	67	180	6.1	0.09	9	–	–
T-2590	2590	Tangareal de Mira Fm	Sandstone	1.17	1.2	0.11	0.93	3.56	385	79	89	304	9.4	0.11	11	–	–
T-2610	2610	Tangareal de Mira Fm	Calcareous sandstone	1.11	1.14	0.08	0.63	1.94	384	57	64	175	7.2	0.11	11	–	–
T-2650	2650	Tangareal de Mira Fm	Calcareous sandstone	0.97	1.00	0.06	0.93	2.41	335	96	102	248	6.2	0.06	6	–	–
T-2690	2690	Tangareal de Mira Fm	Calcareous sandstone	0.88	0.90	0.07	0.43	1.64	398	49	57	186	8.0	0.14	14	–	–
T-2710	2710	Tangareal de Mira Fm	Calcareous sandstone	0.74	0.76	0.06	0.43	2.01	415	58	66	272	8.1	0.12	12	–	0.310
T-3010	3010	Tangareal de Mira Fm	Calcareous siltstone	0.66	0.68	0.05	0.52	1.89	426	79	87	286	7.6	0.09	9	0.4305	0.508

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S2	T.R. (%)	Ro (%)	Rc (%)
T-3030	3030	Tangareal de Mira Fm	Sandstone	0.72	0.74	0.05	0.58	2.25	418	81	88	313	6.9	0.08	8	–	0.364
T-3490	3490	Tangareal de Mira Fm	Sandstone	0.49	0.50	0.04	0.36	1.31	431	73	81	267	8.2	0.10	10	–	0.598
T-3770	3770	Tangareal de Mira Fm	Sandstone	0.57	0.59	0.06	0.67	1.46	331	118	128	256	10.5	0.08	8	–	–
T-4090	4090	Tangareal de Mira Fm	Calcareous siltstone	0.92	0.95	0.05	1.00	0.8	426	109	115	87	5.4	0.05	5	–	0.508
T-4130	4130	Tangareal de Mira Fm	Sandstone	0.98	1.01	0.06	1.11	1.28	424	113	119	131	6.1	0.05	5	–	0.472
T-4330	4330	Tangareal de Mira Fm	Calcareous siltstone	1.63	1.68	0.1	3.47	1.67	428	213	218	102	6.1	0.03	3	–	0.544
T-4410	4410	Tangareal de Mira Fm	Calcareous sandstone	1.39	1.43	0.09	2.61	1.28	424	188	193	92	6.5	0.03	3	–	0.472
T-4470	4470	Tangareal de Mira Fm	Calcareous sandstone	1.81	1.86	0.12	3.23	1.42	426	178	185	78	6.6	0.04	4	–	0.508
T-4550	4550	Tangareal de Mira Fm	Calcareous siltstone	0.77	0.79	0.07	0.87	0.95	424	113	121	123	9.1	0.07	7	–	0.472
T-4730	4730	Tangareal de Mira Fm	Sandstone	0.48	0.49	0.06	0.45	0.97	417	94	107	202	12.5	0.12	12	0.3718	0.346

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-4750	4750	Tangareal de Mira Fm	Calcareous sandstone	0.36	0.37	0.08	0.58	1.04	360	161	180	289	22.2	0.12	12	–	–
T-4810	4810	Tangareal de Mira Fm	Calcareous sandstone	0.40	0.41	0.11	1.13	0.92	350	283	304	230	27.5	0.09	9	–	–
T-4830	4830	Tangareal de Mira Fm	Calcareous siltstone	0.38	0.39	0.09	1.01	0.83	353	266	284	218	23.7	0.08	8	–	–
T-5030	5030	Tangareal de Mira Fm	Calcareous sandstone	1.25	1.29	0.18	4.18	2.82	432	334	344	226	14.4	0.04	4	–	0.616
T-5394	5394	Tangareal de Mira Fm	Calcareous mudstone	1.26	1.30	0.09	2.73	1.15	431	217	224	91	7.1	0.03	3	–	0.598
T-5458	5458	Tangareal de Mira Fm	Mudstone	0.44	0.45	0.05	0.44	0.66	415	100	110	150	11.4	0.10	10	–	0.310
T-5475	5475	Tumaco Fm	Mudstone	1.85	1.90	0.07	1.21	1.46	431	65	68	79	3.8	0.05	5	–	0.598
T-5509	5509	Tumaco Fm	Calcareous mudstone	1.25	1.29	0.09	2.51	1.9	431	201	207	152	7.2	0.03	3	0.1978	0.598
T-5526	5526	Tumaco Fm	Calcareous mudstone	0.9	0.93	0.07	1.07	0.97	426	119	126	108	7.8	0.06	6	–	0.508
T-5536	5536	Tumaco Fm	Mudstone	0.94	0.97	0.09	1.46	1.22	429	155	165	130	9.6	0.06	6	–	0.562
T-5543	5543	Tumaco Fm	Calcareous mudstone	1.11	1.14	0.1	2.14	1.58	432	193	201	142	9.0	0.04	4	–	0.616

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/ S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-5560	5560	Tumaco Fm	Calcareous siltstone	1.67	1.72	0.1	3.72	1.82	431	223	229	109	6.0	0.03	3	–	0.598
T-5570	5570	Tumaco Fm	Calcareous sandstone	1.99	2.05	0.47	10.45	1.1	416	525	537	55	23.6	0.04	4	0.3706	0.328
T-5650	5650	Tumaco Fm	Calcareous siltstone	1.29	1.33	0.08	1.43	1.33	425	111	117	103	6.2	0.05	5	–	0.49
T-5730	5730	Tumaco Fm	Sandstone	0.96	0.99	0.08	3.25	0.88	421	339	344	92	8.3	0.02	2	–	0.418
T-5750	5750	Tumaco Fm	Calcareous siltstone	1.53	1.58	0.09	2.39	1.21	418	156	162	79	5.9	0.04	4	–	0.364
T-5810	5810	Tumaco Fm	Siltstone	1.15	1.19	0.09	3.33	0.86	423	290	297	75	7.8	0.03	3	–	0.454
T-5890	5890	Tumaco Fm	Calcareous siltstone	1.14	1.17	0.08	1.92	1.11	428	168	174	97	7.0	0.04	4	0.4227	0.544
T-5910	5910	Tumaco Fm	Siltstone	1.13	1.16	0.07	1.59	0.91	429	141	147	81	6.2	0.04	4	–	0.562
T-5950	5950	Tumaco Fm	Calcareous siltstone	1.15	1.18	0.04	1.46	0.82	429	127	131	71	3.5	0.03	3	–	0.562
T-5990	5990	Tumaco Fm	Calcareous siltstone	1.46	1.50	0.04	1.65	0.81	430	113	115	55	2.7	0.02	2	–	0.580
T-6010	6010	Tumaco Fm	Siltstone	1.19	1.22	0.06	1.46	1.2	422	123	128	101	5.0	0.04	4	–	0.436
T-6070	6070	Tumaco Fm	Calcareous sandstone	1.39	1.43	0.05	2.51	1.02	425	181	185	73	3.6	0.02	2	0.355	0.490

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-6090	6090	Tumaco Fm	Calcareous siltstone	1.44	1.48	0.05	2.12	1.06	431	147	150	74	3.5	0.02	2	–	0.598
T-6110	6110	Tumaco Fm	Calcareous sandstone	1.12	1.15	0.05	1.23	1.23	418	110	115	110	4.5	0.04	4	–	0.364
T-6130	6130	Tumaco Fm	Calcareous sandstone	1.56	1.60	0.07	0.84	1.5	420	54	59	96	4.5	0.08	8	–	0.400
T-6150	6150	Tumaco Fm	Siltstone	1.63	1.67	0.06	2.66	1.21	426	163	166	74	3.7	0.02	2	–	0.508
T-6170	6170	Tumaco Fm	Calcareous sandstone	1.73	1.78	0.06	2.28	0.91	429	132	136	53	3.5	0.03	3	0.4792	0.562
T-6190	6190	Tumaco Fm	Siltstone	1.58	1.63	0.08	2.42	1.09	431	153	158	69	5.1	0.03	3	–	0.598
T-6210	6210	Tumaco Fm	Calcareous siltstone	1.21	1.25	0.1	2.67	1.33	427	221	229	110	8.3	0.04	4	–	0.526
T-6250	6250	Tumaco Fm	Calcareous siltstone	1.48	1.52	0.09	2.14	1.11	429	145	151	75	6.1	0.04	4	–	0.562
T-6310	6310	Tumaco Fm	Calcareous sandstone	1.11	1.14	0.07	0.92	1.26	422	83	89	114	6.3	0.07	7	–	0.436
T-6330	6330	Tumaco Fm	Calcareous siltstone	1.36	1.40	0.07	1.35	0.85	427	99	104	63	5.1	0.05	5	0.4196	0.526
T-6390	6390	Tumaco Fm	Calcareous sandstone	1.22	1.25	0.05	1.17	1.16	422	96	100	95	4.1	0.04	4	–	0.436

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-6430	6430	Tumaco Fm	Sandstone	1.04	1.07	0.06	1.73	0.67	419	166	171	64	5.8	0.03	3	–	0.382
T-6550	6550	Tumaco Fm	Sandstone	1.33	1.37	0.09	1.83	1.14	428	138	145	86	6.8	0.05	5	–	0.544
T-6570	6570	Tumaco Fm	Sandstone	1.17	1.2	0.06	1.64	1.07	429	140	146	91	5.1	0.04	4	–	0.562
T-6590	6590	Tumaco Fm	Siltstone	1.35	1.39	0.06	1.16	1.33	422	86	91	99	4.4	0.05	5	–	0.436
T-6630	6630	Tumaco Fm	Siltstone	1.35	1.39	0.09	1.45	1.22	423	107	114	90	6.7	0.06	6	–	0.454
T-6710	6710	Tumaco Fm	Calcareous siltstone	1.25	1.28	0.05	1.48	0.99	426	118	122	79	4.0	0.03	3	–	0.508
T-6750	6750	Tumaco Fm	Sandstone	1.18	1.21	0.11	1.76	0.89	429	149	158	75	9.3	0.06	6	–	0.562
T-6770	6770	Tumaco Fm	Calcareous siltstone	1.14	1.17	0.05	1.74	0.85	428	153	157	75	4.4	0.03	3	–	0.544
T-6790	6790	Tumaco Fm	Calcareous sandstone	1.36	1.40	0.06	1.90	0.95	428	140	144	70	4.4	0.03	3	0.4248	0.544
T-6810	6810	Tumaco Fm	Calcareous sandstone	1.13	1.16	0.06	1.64	0.78	429	145	151	69	5.3	0.04	4	–	0.562
T-6830	6830	Tumaco Fm	Calcareous sandstone	1.2	1.23	0.05	1.58	0.9	429	132	136	75	4.2	0.03	3	–	0.562
T-6850	6850	Tumaco Fm	Calcareous sandstone	1.18	1.21	0.05	1.76	0.69	429	149	153	58	4.2	0.03	3	–	0.562
T-6890	6890	Tumaco Fm	Siltstone	1.17	1.2	0.07	1.62	0.89	424	138	143	76	6.0	0.04	4	–	0.472

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-6930	6930	Tumaco Fm	Sandstone	0.96	0.99	0.05	1.14	0.77	428	119	123	80	5.2	0.04	4	0.364	0.544
T-6970	6970	Tumaco Fm	Siltstone	0.8	0.82	0.05	0.97	0.56	416	121	126.7	70	6.3	0.05	5	–	0.328
T-7050	7011	Tumaco Fm	Calcareous mudstone	0.45	0.46	0.09	0.43	0.93	365	96	114	207	20.0	0.17	17	–	–
T-7110	7043	Tumaco Fm	Calcareous mudstone	0.76	0.78	0.03	0.25	0.98	417	33	37	129	3.9	0.10	11	–	0.346
T-7011	7050	Tumaco Fm	Calcareous mudstone	1.76	1.82	0.29	6.79	0.99	418	386	397	56	16.5	0.04	4	–	0.364
T-7043	7110	Tumaco Fm	Siltstone	1.18	1.22	0.1	2.51	0.83	422	213	220	70	8.5	0.04	4	0.3946	0.436
T-7130	7130	Tumaco Fm	Calcareous sandstone	1.08	1.11	0.08	2.49	0.6	420	231	237	56	7.4	0.03	3	–	0.400
T-7210	7210	Tumaco Fm	Calcareous sandstone	1.16	1.19	0.12	1.70	0.88	419	147	157	76	10.3	0.07	7	0.4081	0.382
T-7230	7230	Tumaco Fm	Calcareous siltstone	1.09	1.12	0.07	1.82	0.7	422	167	173	64	6.4	0.04	4	–	0.436
T-7290	7290	Tumaco Fm	Calcareous siltstone	1.07	1.1	0.06	1.21	0.77	420	118	119	72	5.6	0.05	5	–	0.400
T-7310	7310	Tumaco Fm	Calcareous Siltstone	1.06	1.09	0.08	0.90	1.02	415	85	92	96	7.5	0.08	8	–	0.310

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-7330	7330	Tumaco Fm	Calcareous siltstone	1.09	1.12	0.05	0.67	1.19	415	61	65	109	4.6	0.07	7	0.4113	0.310
T-7370	7370	Tumaco Fm	Calcareous siltstone	0.94	0.97	0.04	0.57	1.04	413	61	65	111	4.3	0.07	7	–	0.274
T-7450	7450	Tumaco Fm	Calcareous siltstone	1.36	1.4	0.13	2.51	0.97	423	193	195	71	9.6	0.05	5	–	0.454
T-7453	7453	Tumaco Fm	Calcareous siltstone	0.69	0.71	0.02	0.23	0.81	431	33	36	117	2.9	0.08	8	–	0.598
T-7470	7470	Tumaco Fm	Siltstone	1.34	1.38	0.12	2.53	0.93	426	189	197	69	9.0	0.05	5	–	0.508
T-7471	7471	Tumaco Fm	Siltstone	0.91	0.93	0.03	0.33	1.08	426	36	39	119	3.3	0.08	8	–	0.508
T-7476	7476	Tumaco Fm	Siltstone	0.67	0.69	0.03	0.21	0.87	431	31	36	130	4.5	0.13	13	–	0.598
T-7488	7488	Tumaco Fm	Siltstone	0.88	0.9	0.03	0.36	1.05	432	41	44	119	3.4	0.08	8	0.3478	0.616
T-7504	7504	Tumaco Fm	Siltstone	0.92	0.94	0.03	0.29	0.84	433	32	35	91	3.3	0.09	9	–	0.634
T-7522	7522	Tumaco Fm	Siltstone	0.82	0.84	0.03	0.32	0.93	428	39	43	113	3.7	0.09	9	–	0.544
T-7539.5	7540	Tumaco Fm	Siltstone	0.39	0.4	0.04	0.17	0.69	423	44	54	177	10.3	0.19	19	–	0.454
T-7557	7557	Tumaco Fm	Siltstone	0.52	0.53	0.04	0.18	0.72	427	35	42	138	7.7	0.18	18	–	0.526
T-7574	7574	Tumaco Fm	Siltstone	0.82	0.84	0.04	0.31	0.88	425	38	43	107	4.9	0.11	11	0.431	0.49
T-7591	7591	Tumaco Fm	Siltstone	1.25	1.28	0.03	0.37	1.22	429	30	33	98	2.4	0.08	8	–	0.562
T-7609	7609	Tumaco Fm	Siltstone	0.11	0.11	0.04	0.07	0.22	429	64	97	200	36.4	0.36	36	–	0.562

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-7627	7627	Tumaco Fm	Siltstone	0.82	0.84	0.05	0.29	0.87	429	35	41	106	6.1	0.15	15	–	0.562
T-7642.5	7643	Tumaco Fm	Sandstone	0.36	0.37	0.04	0.25	0.83	429	69	79	231	1.1	0.14	14	–	0.562
T-7659	7659	Tumaco Fm	Sandstone	0.59	0.61	0.04	0.23	0.65	432	39	46	110	6.8	0.15	15	0.451	0.616
T-7693	7693	Tumaco Fm	Calcareous mudstone	1.25	1.28	0.04	0.49	1.37	440	39	42	110	3.2	0.08	8	–	0.760
T-7712	7712	Tumaco Fm	Calcareous mudstone	1.08	1.11	0.03	0.38	1.1	435	35	38	102	2.8	0.07	7	–	0.670
T-7723	7723	Tumaco Fm	Calcareous mudstone	0.83	0.85	0.04	0.13	0.8	417	16	21	96	4.8	0.24	24	0.4754	0.346
T-7740	7740	Tumaco Fm	Calcareous mudstone	0.51	0.52	0.05	0.23	0.73	425	45	54	143	9.8	0.18	18	–	0.490
T-7761	7761	Tumaco Fm	Calcareous mudstone	0.85	0.87	0.03	0.30	0.96	429	35	38	113	3.5	0.09	9	0.3782	0.562
T-7777	7777	Tumaco Fm	Calcareous mudstone	1.05	1.08	0.03	0.45	1.06	432	43	46	101	2.9	0.06	6	–	0.616
T-7795	7795	Tumaco Fm	Mudstone	0.92	0.94	0.04	0.28	0.96	429	30	34	104	4.3	0.13	13	–	0.562
T-7828	7828	Tumaco Fm	Siltstone	0.85	0.87	0.05	0.31	0.94	429	36	42	111	5.9	0.14	14	–	0.562
T-7844	7844	Tumaco Fm	Siltstone	0.74	0.76	0.04	0.3	1.00	431	41	46	135	5.4	0.12	12	–	0.598
T-7856	7856	Tumaco Fm	Calcareous siltstone	0.79	0.81	0.03	0.21	0.82	429	27	31	104	3.8	0.13	13	0.3787	0.562

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-7861	7861	Tumaco Fm	Calcareous siltstone	1.11	1.14	0.03	0.37	0.96	431	33	36	86	2.7	0.08	8	–	0.598
T-7878	7878	Tumaco Fm	Calcareous siltstone	0.96	0.99	0.04	0.28	1.01	426	29	32	105	4.2	0.13	13	–	0.508
T-7895	7895	Tumaco Fm	Calcareous siltstone	1.53	1.57	0.04	0.43	1.57	433	28	31	103	2.6	0.09	9	–	0.634
T-7911	7911	Tumaco Fm	Calcareous siltstone	1.98	2	0.04	0.50	2.11	431	25	27	107	2.0	0.07	7	–	0.598
T-7928	7928	Tumaco Fm	Sandstone	2.1	2.16	0.04	0.82	1.72	435	39	41	82	1.9	0.05	5	0.3496	0.670
T-7955	7955	Tumaco Fm	Calcareous mudstone	0.88	0.9	0.03	0.38	0.57	433	43	46	65	3.4	0.07	7	–	0.634
T-7971	7971	Tumaco Fm	Siltstone	2.19	2.25	0.04	0.78	1.87	435	36	38	85	1.8	0.05	5	–	0.670
T-8017.5	8017.5	Tumaco Fm	Sandstone	0.93	0.95	0.03	0.32	0.95	432	34	37	102	3.2	0.09	9	–	0.616
T-8045	8045	Tumaco Fm	Siltstone	0.63	0.65	0.03	0.26	0.50	441	41	45	79	4.8	0.10	10	–	0.778
T-8067	8067	Tumaco Fm	Sandstone	0.92	0.94	0.03	0.4	0.74	432	43	46	80	3.3	0.07	7	0.421	0.616
T-8084	8084	Tumaco Fm	Siltstone	1.04	1.07	0.02	0.37	0.82	433	36	38	79	1.9	0.05	5	–	0.634
T-8107.5	8107.5	Tumaco Fm	Siltstone	0.13	0.13	0.03	0.09	0.2	440	69	90	154	23.1	0.25	25	–	0.760
T-8123.5	8123.5	Tumaco Fm	Sandstone	0.22	0.23	0.02	0.11	0.33	426	50	58	150	9.1	0.15	15	–	0.508
T-8145	8145	Tumaco Fm	Siltstone	1.12	1.15	0.03	0.39	0.79	436	35	38	71	2.7	0.07	7	–	0.688

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S2	T.R. (%)	Ro (%)	Rc (%)
T-8160.5	8160.5	Tumaco Fm	Siltstone	0.28	0.29	0.03	0.17	0.38	431	61	71	136	10.7	0.15	15	0.4083	0.598
T-8194	8194	Tumaco Fm	Siltstone	1.02	1.05	0.03	0.34	1.00	431	33	36	98	2.9	0.08	8	–	0.598
T-8211	8211	Tumaco Fm	Mudstone	1.3	1.33	0.03	0.47	0.95	432	36	38	73	2.3	0.06	6	–	0.616
T-8233	8233	Tumaco Fm	Calcareous mudstone	1.46	1.5	0.03	0.36	1.65	427	25	27	113	2.1	0.08	8	–	0.526
T-8243	8243	Tumaco Fm	Calcareous mudstone	1.19	1.12	0.03	0.4	1.37	433	34	36	115	2.5	0.07	7	–	0.634
T-8255.5	8255.5	Tumaco Fm	Calcareous mudstone	1.89	1.94	0.03	0.54	1.75	433	29	30	93	1.6	0.05	5	0.378	0.634
T-8266	8266	Tumaco Fm	Calcareous siltstone	0.94	0.96	0.03	0.45	1.13	439	48	51	120	3.2	0.06	6	–	0.742
T-8275	8275	Tumaco Fm	Calcareous siltstone	2.05	2.1	0.04	0.54	2.10	433	26	28	102	2.0	0.07	7	–	0.634
T-8302.5	8302.5	Tumaco Fm	Siltstone	1.36	1.4	0.05	0.82	1.24	435	60	64	91	3.7	0.06	6	–	0.67
T-8312.5	8312.5	Tumaco Fm	Siltstone	1.16	1.19	0.04	0.58	1.16	438	50	53	100	3.4	0.06	6	0.3977	0.724
T-8317	8317	Tumaco Fm	Calcareous siltstone	1.19	1.22	0.04	0.59	0.99	434	50	53	83	3.4	0.06	6	–	0.652
T-8332.5	8332.5	Tumaco Fm	Siltstone	1.53	1.57	0.04	0.71	1.43	437	46	48	93	2.6	0.05	5	–	0.706
T-8338	8338	Tumaco Fm	Mudstone	1.2	1.23	0.05	0.43	1.36	433	36	40	113	4.2	0.10	10	–	0.634

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-8354.5	8354.5	Tumaco Fm	Calcareous siltstone	1.31	1.34	0.03	0.43	1.12	434	33	35	85	2.3	0.07	7	–	0.652
T-8370.5	8370.5	Tumaco Fm	Siltstone	1.3	1.33	0.04	0.36	1.21	432	28	31	93	3.1	0.10	10	0.3599	0.616
T-8380	8380	Tumaco Fm	Siltstone	1.2	1.23	0.05	0.38	1.02	433	32	36	85	4.2	0.12	12	–	0.634
T-8388	8388	Tumaco Fm	Sandstone	0.65	0.67	0.03	0.25	0.71	433	38	43	109	4.6	0.11	11	–	0.634
T-8395	8395	Tumaco Fm	Siltstone	0.55	0.56	0.03	0.15	0.74	431	27	32	135	5.5	0.17	17	–	0.598
T-8406.8	8406.8	Tumaco Fm	Sandstone	0.96	0.99	0.04	0.33	0.91	432	34	38	95	4.2	0.11	11	–	0.616
T-8431	8431	Tumaco Fm	Siltstone	1.2	1.23	0.04	0.51	1.16	433	43	46	97	3.3	0.07	7	0.5418	0.634
T-8440	8440	Tumaco Fm	Calcareous siltstone	0.1	0.1	0.04	0.09	0.34	445	90	126	340	40.0	0.31	31	0.4335	0.85
T-8448	8448	Tumaco Fm	Siltstone	0.97	1	0.04	0.34	0.80	436	35	39	82	4.1	0.11	11	–	0.688
T-8457.5	8457.5	Tumaco Fm	Siltstone	0.85	0.87	0.03	0.21	0.77	435	25	29	91	3.5	0.13	13	–	0.670
T-8470	8470	Tumaco Fm	Siltstone	1.00	1.03	0.04	0.54	0.92	431	54	58	92	4.0	0.07	7	–	0.598
T-8487.5	8487.5	Tumaco Fm	Siltstone	0.77	0.79	0.03	0.24	0.85	429	31	35	110	3.9	0.11	11	0.4213	0.562
T-8510	8510	Tumaco Fm	Calcareous sandstone	0.38	0.39	0.03	0.22	0.39	428	58	65	103	7.9	0.12	12	–	0.544
T-8530	8530	Tumaco Fm	Calcareous sandstone	0.65	0.67	0.03	0.39	0.68	420	60	64	105	4.6	0.07	7	–	0.400

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-8550	8550	Tumaco Fm	Calcareous sandstone	0.36	0.37	0.05	0.31	0.80	415	86	99	222	13.9	0.14	14	–	0.310
T-8590	8590	Tumaco Fm	Calcareous sandstone	0.50	0.51	0.06	0.48	0.71	415	96	107	142	12.0	0.11	11	–	0.310
T-8650	8650	Tumaco Fm	Calcareous sandstone	0.42	0.43	0.04	0.32	0.63	415	76	85	150	9.5	0.11	11	–	0.310
T-8710	8710	Tumaco Fm	Calcareous sandstone	0.81	0.83	0.1	0.79	0.95	417	98	109	117	1.3	0.11	11	–	0.346
T-8770	8770	Tumaco Fm	Siltstone	0.78	0.8	0.07	0.58	0.78	425	74	83	100	9.0	0.11	11	–	0.490
T-8850	8850	Tumaco Fm	Siltstone	1.24	1.27	0.03	0.73	0.99	431	59	61	80	2.4	0.04	4	–	0.598
T-8870	8870	Tumaco Fm	Calcareous sandstone	2.04	2.09	0.07	1	1.63	432	49	53	80	3.4	0.07	7	0.5201	0.616
T-8890	8890	Tumaco Fm	Calcareous sandstone	1.58	1.62	0.06	0.95	1.41	431	60	64	89	3.8	0.06	6	–	0.598
T-9050	9050	Tumaco Fm	Calcareous sandstone	0.81	0.83	0.04	0.54	1.04	429	67	72	128	4.9	0.07	7	–	0.562
T-9070	9070	Tumaco Fm	Siltstone	0.77	0.79	0.05	0.68	0.98	429	88	94	127	6.5	0.07	7	–	0.562
T-9150	9150	Tumaco Fm	Calcareous siltstone	1.20	1.23	0.05	0.77	1.11	429	64	68	93	4.2	0.06	6	–	0.562

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-9230	9230	Tumaco Fm	Calcareous siltstone	0.66	0.68	0.08	0.53	0.61	417	80	91	92	12.1	0.13	13	–	0.346
T-9250	9250	Tumaco Fm	Calcareous sandstone	0.66	0.68	0.06	0.44	0.59	417	67	76	89	9.1	0.12	12	–	0.346
T-9310	9310	Tumaco Fm	Calcareous siltstone	0.92	0.94	0.05	0.54	0.90	423	59	64	98	5.4	0.08	8	–	0.562
T-9390	9390	Tumaco Fm	Calcareous sandstone	0.67	0.69	0.09	0.91	0.84	422	136	148	125	13.4	0.09	9	–	0.562
T-9430	9430	Tumaco Fm	Calcareous siltstone	0.74	0.76	0.14	1.32	1.07	366	178	195	145	18.9	0.10	10	–	–
T-9470	9470	Tumaco Fm	Calcareous sandstone	0.68	0.7	0.06	0.68	0.70	424	100	108	103	8.8	0.08	8	0.410	0.472
T-9490	9490	Tumaco Fm	Calcareous siltstone	0.78	0.8	0.07	0.72	0.73	422	92	100	94	9.0	0.09	9	–	0.436
T-9550	9550	Tumaco Fm	Calcareous siltstone	0.89	0.91	0.06	0.79	0.67	427	89	96	75	6.7	0.07	7	–	0.526
T-9610	9610	Tumaco Fm	Calcareous siltstone	0.71	0.73	0.07	0.61	0.57	428	86	95	80	9.9	0.10	10	–	0.544
T-9630	9630	Tumaco Fm	Calcareous siltstone	0.69	0.71	0.03	0.56	0.54	429	81	85	78	4.3	0.05	5	–	0.562

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-9710	9710	Tumaco Fm	Calcareous sandstone	0.58	0.6	0.05	0.43	0.54	427	74	82	93	8.6	0.10	10	0.4033	0.526
T-9790	9790	Tumaco Fm	Calcareous sandstone	1.15	1.18	0.09	0.81	0.63	425	70	77	55	7.8	0.10	10	–	0.490
T-9810	9810	Tumaco Fm	Sandstone	0.57	0.59	0.08	0.64	0.59	426	112	124	104	14.0	0.11	11	–	0.508
T-9870	9870	Tumaco Fm	Calcareous siltstone	0.65	0.67	0.07	0.66	0.68	422	102	112	105	10.8	0.10	10	–	0.436
T-9950	9950	Tumaco Fm	Calcareous siltstone	0.75	0.77	0.06	0.66	0.62	423	88	95	83	8.0	0.08	8	–	0.454
T-9990	9990	Tumaco Fm	Calcareous siltstone	0.63	0.65	0.06	0.61	0.64	419	97	106	102	9.5	0.09	9	0.3577	0.382
T-10015	10015	Tumaco Fm	Siltstone	0.48	0.49	0.03	0.27	0.36	434	56	62	75	6.3	0.10	10	–	0.652
T-10026	10,026	Tumaco Fm	Siltstone	0.55	0.57	0.04	0.46	0.44	415	84	91	80	7.3	0.08	8	–	0.31
T-10030	10030	Tumaco Fm	Siltstone	0.89	0.92	0.07	1	0.65	429	112	120	73	7.9	0.07	7	–	0.562
T-10033	10,033	Tumaco Fm	Calcareous siltstone	0.80	0.82	0.05	0.73	0.6	428	91	96	75	6.3	0.06	6	–	0.544
T-10046	10,046	Tumaco Fm	Siltstone	0.66	0.68	0.05	0.49	0.6	432	74	81	91	7.6	0.09	9	–	0.616
T-10051	10,051	Tumaco Fm	Siltstone	0.64	0.66	0.05	0.4	0.62	431	63	70	97	7.8	0.11	11	0.5131	0.598
T-10059	10,059	Tumaco Fm	Siltstone	0.81	0.83	0.04	0.44	0.57	429	54	58	70	4.9	0.08	8	–	0.562

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. SI/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-10069	10,069	Tumaco Fm	Mudstone	0.84	0.86	0.04	0.79	0.49	431	94	99	58	4.8	0.05	5	–	0.598
T-10079	10,079	Tumaco Fm	Mudstone	1.00	1.03	0.05	1.01	0.63	433	101	106	63	5.0	0.05	5	–	0.634
T-10087	10,087	Tumaco Fm	Mudstone	0.57	0.59	0.02	0.25	0.5	429	44	47	88	3.5	0.07	7	–	0.562
T-10098	10,098	Tumaco Fm	Mudstone	0.80	0.82	0.03	0.47	0.65	432	59	63	81	3.8	0.06	6	0.3691	0.616
T-10105	10,105	Tumaco Fm	Mudstone	0.46	0.47	0.03	0.36	0.48	432	78	84	104	6.5	0.08	8	–	0.616
T-10125	10,125	Tumaco Fm	Mudstone	0.41	0.42	0.03	0.29	0.53	432	71	78	129	7.3	0.09	9	–	0.616
T-10135.5	10,135.5	Tumaco Fm	Mudstone	0.61	0.63	0.03	0.38	0.4	433	62	66	66	4.9	0.07	7	–	0.634
T-10142	10,142	Tumaco Fm	Siltstone	0.85	0.87	0.04	0.56	0.66	433	66	71	78	4.7	0.07	7	–	0.634
T-10162	10,162	Tumaco Fm	Siltstone	0.60	0.62	0.03	0.34	0.56	430	57	62	93	5.0	0.08	8	0.384	0.58
T-10175	10,175	Tumaco Fm	Calcareous siltstone	0.52	0.53	0.03	0.36	0.45	432	69	75	87	5.8	0.08	8	–	0.616
T-10184	10,184	Tumaco Fm	Siltstone	0.72	0.74	0.03	0.52	0.47	433	72	76	65	4.2	0.05	5	–	0.634
T-10196.5	10,196.5	Tumaco Fm	Siltstone	0.82	0.84	0.04	0.57	0.52	431	70	75	63	4.9	0.07	7	–	0.598
T-10209	10,209	Tumaco Fm	Siltstone	0.64	0.66	0.03	0.39	0.66	431	61	65	103	4.7	0.07	7	–	0.598
T-10226	10,226	Tumaco Fm	Siltstone	0.77	0.79	0.04	0.52	0.58	430	68	73	75	5.2	0.07	7	0.3616	0.58
T-10241.5	10,241.5	Tumaco Fm	Siltstone	0.70	0.72	0.04	0.54	0.51	433	77	82	73	5.7	0.07	7	–	0.634
T-10251	10,251	Tumaco Fm	Siltstone	0.69	0.71	0.04	0.52	0.46	432	75	80	67	5.8	0.07	7	–	0.616
T-10259	10,259	Tumaco Fm	Siltstone	0.67	0.69	0.05	0.54	0.66	431	81	88	99	7.5	0.08	8	–	0.598
T-10269	10,269	Tumaco Fm	Siltstone	0.54	0.55	0.03	0.37	0.53	431	69	75	98	5.6	0.08	8	–	0.598

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-10276	10,276	Tumaco Fm	Siltstone	0.61	0.63	0.04	0.38	0.5	431	62	69	82	6.6	0.10	10	0.371	0.598
T-10349	10,349	Tumaco Fm	Siltstone	0.77	0.79	0.03	0.47	0.63	431	61	65	82	3.9	0.06	6	0.4157	0.598
T-10390	10,390	Tumaco Fm	Calcareous sandstone	0.81	0.83	0.08	0.71	1.06	424	88	97	131	9.9	0.10	10	–	0.472
T-10410	10,410	Tumaco Fm	Calcareous siltstone	0.42	0.43	0.07	0.67	1.16	336	160	174	276	1.7	0.09	9	–	–
T-10450	10,450	Tumaco Fm	Calcareous sandstone	0.72	0.74	0.06	0.56	0.88	429	78	86	122	8.3	0.10	10	–	0.562
T-10470	10,470	Tumaco Fm	Calcareous siltstone	0.45	0.46	0.07	0.62	0.76	429	138	152	169	15.6	0.10	10	0.4523	0.562
T-10610	10,610	Tumaco Fm	Calcareous siltstone	0.58	0.6	0.08	0.46	0.96	368	79	92	166	13.8	0.15	15	–	–
T-10630	10,630	Tumaco Fm	Calcareous siltstone	0.36	0.37	0.09	0.54	0.44	424	150	171	122	25.0	0.14	14	–	0.472
T-10670	10,670	Tumaco Fm	Calcareous sandstone	0.31	0.32	0.09	0.52	0.39	430	168	193	126	29.0	0.15	15	–	0.580
T-10690	10,690	Tumaco Fm	Calcareous sandstone	0.52	0.53	0.15	0.69	0.73	418	133	158	140	28.8	0.18	18	–	0.364
T-10770	10,770	Tumaco Fm	Calcareous sandstone	0.66	0.68	0.09	0.64	0.87	423	97	109	132	13.6	0.12	12	0.3929	0.454

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-10850	10,850	Tumaco Fm	Calcareous siltstone	0.73	0.75	0.05	0.67	0.74	426	92	98	101	6.8	0.07	7	–	0.508
T-10870	10,870	Tumaco Fm	Calcareous siltstone	0.70	0.72	0.08	0.71	0.93	415	101	111	133	11.4	0.10	10	–	0.310
T-10930	10,930	Tumaco Fm	Calcareous sandstone	0.76	0.78	0.14	1	1.03	366	132	148	136	18.4	0.12	12	–	–
T-11010	11,010	Tumaco Fm	Calcareous sandstone	0.66	0.68	0.11	0.79	0.91	367	120	135	138	16.7	0.12	12	–	–
T-11030	11,030	Tumaco Fm	Calcareous sandstone	0.55	0.57	0.06	0.61	0.69	417	111	121	125	10.9	0.09	9	0.4268	0.346
T-11050	11,050	Tumaco Fm	Calcareous sandstone	0.68	0.7	0.08	0.65	0.83	374	96	107	122	11.8	0.11	11	–	–
T-11090	11,090	Tumaco Fm	Calcareous sandstone	0.45	0.46	0.09	0.74	0.77	353	164	181	171	20.0	0.11	11	–	–
T-11170	11,170	Tumaco Fm	Calcareous siltstone	0.64	0.66	0.08	0.58	0.73	381	91	102	114	12.5	0.12	12	–	–
T-11230	11,230	Tumaco Fm	Siltstone	0.54	0.55	0.06	0.43	0.64	421	80	90	119	11.1	0.12	12	–	0.418
T-11250	11,250	Tumaco Fm	Calcareous siltstone	0.43	0.44	0.06	0.39	0.66	364	91	103	153	14.0	0.13	13	–	–

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	H.Io (mg/gTOC)	O.I. (S3×100/TOC)	SI/TOC (%)	P.I. S1/S2	T.R. (%)	Ro (%)	Rc (%)
T-111330	11,330	Tumaco Fm	Calcareous siltstone	0.61	0.63	0.09	0.82	0.96	358	134	147	157	14.8	0.10	10	–	–
T-111410	11,410	Tumaco Fm	Calcareous siltstone	0.69	0.71	0.11	0.9	0.83	365	130	144	120	15.9	0.11	11	–	–
T-111430	11,430	Tumaco Fm	Sandstone	0.63	0.65	0.1	0.88	0.71	366	140	154	113	15.9	0.10	10	–	–
T-111490	11,490	Tumaco Fm	Sandstone	0.73	0.75	0.09	0.75	0.63	420	103	115	86	12.3	0.11	11	–	0.400
T-111570	11,570	Tumaco Fm	Calcareous siltstone	1.66	1.71	0.2	1.88	0.84	432	113	124	51	12.0	0.10	10	0.4404	0.616
T-111610	11,610	Tumaco Fm	Calcareous siltstone	2.30	2.36	0.43	4.96	1.16	432	216	231	50	18.7	0.08	8	–	0.616
T-111650	11,650	Tumaco Fm	Calcareous siltstone	1.76	1.81	0.42	5.83	1.14	432	331	349	65	23.9	0.07	7	–	0.616
T-111670	11,670	Tumaco Fm	Calcareous sandstone	1.54	1.59	0.25	3.53	1.09	433	229	243	71	16.2	0.07	7	–	0.634
T-111690	11,690	Tumaco Fm	Calcareous siltstone	2.05	2.11	0.33	4.19	1.17	433	204	217	57	16.1	0.07	7	–	0.634
T-111710	11,710	Tumaco Fm	Calcareous siltstone	2.13	2.18	0.8	9.49	1.6	431	446	470	75	37.6	0.08	8	0.4700	0.598
T-111730	11,730	Tumaco Fm	Calcareous siltstone	1.27	1.31	0.29	4.56	1.21	431	359	375	95	22.8	0.06	6	–	0.598

Table 1 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	TOC (%)	TOC _o (wt%)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	T _{max} (°C)	H.I. S2×100/TOC	Hlo (mg/gTOC)	O.I. (S3×100/TOC)	S1/TOC (%)	P.I. S1/S1+S2	T.R. (%)	Ro (%)	Rc (%)
T-11790	11,790	Tumaco Fm	Calcareous siltstone	1.10	1.13	0.16	2.25	0.97	432	205	218	88	14.5	0.07	7	–	0.616
T-11810	11,810	Tumaco Fm	Calcareous siltstone	1.07	1.1	0.2	2.55	0.72	431	238	252	67	18.7	0.07	7	–	0.598
T-11870	11,870	Tumaco Fm	Calcareous siltstone	0.99	1.02	0.13	1.66	0.68	435	168	179	69	13.1	0.07	7	0.3938	0.670
T-11930	11,930	Tumaco Fm	Calcareous siltstone	0.81	0.83	0.1	1.03	0.72	431	127	138	89	12.3	0.09	9	–	0.598

Original TOC and hydrogen index (TOC_o and Hlo) were calculated using ZetaWare Software, Inc

S1, mgHC/g rock; S2, mgHC/g rock; S3, mgCO₂/g rock; rock H.I. = (S2/TOC) × 100; O.I. = (S3/TOC) × 100; P.I., Potential Index; SAT/ARO, saturate/aromatic ratio; –, data not available

Fig. 3 Modified van Krevelen diagram based on IH versus IO for Tumaco-ST-P well, Tumaco basin, Colombia. $HI = (S2/TOC) \times 100$, $OI = (S3/TOC) \times 100$

Fig. 4 Kerogen type and thermal maturity using HI (mg HC/g TOC) versus T_{max} (°C)

Fig. 5 Kerogen type (pseudo van Krevelen diagram) using S2 peak (mg HC/g rock) versus present-day TOC, %

oil and reported in this paper as R_o (Pawlewicz and Finn 2013). Additionally, the R_c was calculated from T_{max} (Jarvie et al. 2001). Although this approach works better when T_{max} is between 420 and 500 °C, it has been used in this study due to this conversion works marginally well for type III kerogen which includes the most of the analyzed samples. Fifty samples were selected through the stratigraphic column for R_o analysis in order to better understand its thermal maturity and hydrocarbons potential. The average R_o value was $0.4046 \pm 0.065\%$ indicating an immature O.M.

Macerals are the individual components of the kerogen that have petrographically and geochemically distinct properties and an independent assessment of the quality, quantity, and thermal maturity of organic matter (Hall et al. 2016). Vitrinite, liptinites, and inertinites were the most common maceral groups found in the dispersed organic matter in Tumaco-1-ST-P samples, which in turn allow to identify the following maceral types: esporinite, cutinite, resinite, alginite, colotelinite, colodetrinite, funginite, exsudinite, exsudatinite, inertodetrinite, among others as is shown in the photomicrographs of Fig. 7. The origin of macerals identified has a resin of higher plants, spores/pollen, cuticular plants, algae, and mixtures of the above. These macerals come from type II kerogen, while the vitrinite identified in relatively high concentration comes from type III kerogen and probably originated from tissues of wood and other vegetables. The inertinite that groups types of macerals as nertodecrinite, fusinite, etc., could originate from wood carbonized fragments. The petrographic analysis indicates that

the rocks studied are in immature state. Figure 8 shows the plot of depth (ft) versus R_o (%) for modeling of the evolution of the thermal maturity. However, rocks with O.M. in the hydrocarbon generation window can exist at 1700 ft in stratigraphic column between 950 and 11,900 ft

The variation of R_o with depth and the petrographic analysis indicates that almost all samples in the Tumaco-1-ST-P well are in the immature state where samples from Cascajal and Tangareal del Mira Fms show the lowest maturity, while the highest maturities were found in the Tumaco Fm. suggesting a consistent light increment of maturity with depth. This linear regression with confidence bounds of 95%, suggests a depth range up to approximately 17,000 feet (see ellipse) where it is expecting that the potential source rock will enter into the generation window for Tumaco Basin, Colombia.

To estimate the extension of the petroleum-generation process and the total generative capacity in an already mature source rock, information on the TOC and HI of organic matter prior to the onset of hydrocarbon generation is required (Jarvie 2012, Hall et al. 2016). Although TOC_{pd} and HI_{pd} classified the organic matter deposited in Tumaco 1-ST-P as immature for what one could assume that HI_{pd} should be equal HI_o (Jarvie 2012), we have used KinEx source rock modeling software (www.zetaware.com) to calculate the original TOC and HI based on present-day analyses (Table 1). The minimum differences in the original and present-day TOC and HI confirm that the O.M. in Tumaco-1-ST-P is very immature and that the data could be

Fig. 6 Lithology, paleoenvironment and stratigraphic correlation for Tumaco-1-ST-S and Tumaco-1-ST-P wells (ANH-Antek S.A. 2013)

Fig. 7 Photomicrograph in reflected light and fluorescent ($\times 50$) of sample T-11570. **a** Grains of vitrinite with different thermal maturities. **b** Inertinite and exudatinitite, and **c** inertinite with exudatinitite

used to calibrate the maturity in the basin (Jarvie 2012). On average, the H_{lo} (117.57 mg HC/g TOC) differs from H_{pd} (109.85 mg HC/g TOC) and is about 7.72 mg HC/g TOC confirming an immature stage of the O.M. in the sample rocks.

Figure 9 presents an idealized geochemical logging based on screening values (TOC and RE-Py) and the experimental vitrinite reflectance (Ro) associated with lithofacies, stratigraphic units and the age for Tumaco-1-ST-P well applying the molecular stratigraphy concepts, which allows observing the changes of organic facies that occur laterally or vertically

into the column (Demaision in Peters 1986; Espitalié et al. 1987; Burwood et al. 1990; Peter et al. 2005). T_{max} and Ro increase consistently with increasing depth and maturity; H_{pd} shows a few variation with depth in Tumaco Fm, except in the deepest interval where it is consistent with TOC_{pd} contents, indicating a few kerogen conversion to petroleum or gas (low transformation ratios values).

Fig. 8 Linear regression of depth versus Ro (%) with confidence bounds of 95%, showing the depth up to approximately 17,000 feet (ellipse) where is expecting that the potential source rock will enter into the generation window for Tumaco Basin, Colombia

Bitumen extracts and SARA fractionation

Table 1 also displays organic geochemical characteristics based on EOM %, SARA, and GC/FID analysis of the bitumen extracted. The EOM is very low, ranging between 0.0018 and 0.75%, being the deepest units of the Tumaco-1-ST-P well (11,650 ft) which contains the largest concentrations. Thus, the EOM values characterize the Cascajal and Tangareal del Mira formations as poor, while Tumaco Fm varies between fair and good quality (Bacon et al. 2000). The quantity and composition of the bitumen extracted depend on the original organic matter, organic facies, depositional environment, thermal maturity, and the extension of the expulsion and could also reflect contamination by drilling mud/fluids or migration of hydrocarbons. These last two

events are discarded in Tumaco-1-ST-P well due to the low amount of O.M. extracted.

SARA fractionation shows the highest values for the resin fractions (NSO compounds), in most of the organic extracts, varying between 17.47 and 62.33%. Asphaltene fractions vary between 4.65 and 59.02%, and the aromatic fractions range between 0.1 and 21.28%. Finally, the fraction of saturated hydrocarbons varies between 4.99 and 43.81%. Tissot and Welte (1984) proposed a ternary diagram to identify the organic matter type based on the SARA fractionation. Thus, Tumaco-1-ST-P well samples classify as naphthenic bitumen due to its high resin and asphaltene concentrations. The SARA analysis shows a relatively low dispersion on its fraction, indicating that this bitumen has the same source and origin. The saturate/aromatic ratios are in all samples very high, except in the sample T2928 (0.29%). Thus, the

Fig. 9 Idealized geochemical logging based on RE-pyrolysis indexes, TOC and Ro for Tumaco-ST-P, Tumaco basin, Colombia (modified from J.G. Demaison in Peters 1986). Ro is experimental vitrinite reflectance

SAT/ARO ratio indicates a very low content of aromatic hydrocarbons in the entire column and limits the use of the aromatic fraction as maturity indicator as it will be discussed later in Sect. 4.4.2.1.

Source and depositional environment

n-alkanes and isoprenoids

Gas chromatographic profiles of selected crude oils are shown in Fig. 10. The geochemical ratios based on *n*-alkanes distribution are displayed in Table 2. In general, the *n*-alkanes are the most abundant components in the saturate fraction for all samples (range 4.39–43.81%) although as stated above saturated hydrocarbons are the major fraction of the bitumen extract. Bitumen extracts have a *n*-alkanes distribution between *n*-C₁₀ and *n*-C₃₃, with bimodal distribution and maximum between *n*-C₁₅ and *n*-C₁₇, indicating an algal/microbial input and *n*-C₂₅ to *n*-C₂₇, showing a significant input of terrigenous organic matter, suggesting that this O.M. was originated from a type II/III or III kerogen. A dominance of *n*-alkanes around of *n*-C₁₇ is thus interpreted as an indication of a marine source (Jones 1986). The GC profiles for samples T5509 and T-8243 show a special

characteristic associated with the presence of high concentration of unknown organic compounds around *n*-C₂₉ to *n*-C₃₁ and related to recent O.M. (immature) in a process of decomposition and consistent with the concept that many of these samples are in an early diagenetic stage.

A marine-deltaic transitional environment has been strongly supported by the geological model proposed in the original ANH-Antek technical report (ANH-Antek S.A. 2013). The terrestrial origin of a large part of the organic extracts studied comes from the epicuticular wax high plants, which presents a wide distribution of *n*-alkanes with a marked predominance of hydrocarbons with odd number of carbon atoms (*n*-C₂₅, *n*-C₂₇, *n*-C₂₉, *n*-C₃₁); while samples of marine origin located more toward the bottom and in the deepest part of the column have a significant bacterial, algal, and phytoplanktonic contribution, characterized by a predominance of heptadecane (*n*-C₁₇). Some of the chromatographic profiles allow observing a hump or the so-called unresolved complex mixture (UCM), which confirms that different levels of diagenetic biodegradation are in progress in the basin.

The Pr/Ph ratio in Tumaco-1-ST-P displays values below 3.0, although most of the samples fall between 1.0 and 1.5, which indicates that these samples were deposited

Fig. 10 GC/FID C15⁺ chromatograms of saturate fractions of selected rock extracts in the Tumaco-1-ST-P, Tumaco basin, Colombia

in a suboxic to oxic environment and were derived from marine shales. There are some samples with values of Pr/Ph ratio < 1.0 , suggesting a more carbonatic bitumen. Bitumen and crude oils derived from marine shale have a CPI values ranging from low to moderate (1.0–3.0), while those derived from source rocks containing mainly terrestrial O.M. present Pr/Ph ratios between 3.0 and 10. Carbonate rocks show Pr/Ph < 1.0 (Didyk et al. 1978). When the Pr/Ph is used as an indicator of redox conditions, a value < 3.0 for the organic extracts of the Tumaco-1-ST-P well, indicates that this O.M. was generated under suboxic–oxic conditions. According to Didyk et al. 1978, Pr/Ph < 1 in bitumen and crude indicates an environment at anoxic depositional environment, while Pr/Ph > 1 indicates an oxic deposition. In Tumaco-1-ST-P rocks, the Pr/Ph ratios display values below 3.0, with a high population of data ranging between 1.0 and 1.5, suggesting that these samples were deposited in a suboxic to an oxic environment.

The *n*-alkanes/isoprenoids ratios (Pr/*n*-C₁₇ and Ph/*n*-C₁₈) decrease with the maturity since more *n*-alkanes are released from kerogen by cracking (Tissot et al. 1971) and are more thermally stable than isoprenoids. Figure 11 shows that most of the samples in Tumaco-1-ST-P well have been originated from type II–III kerogen (transitional marine–terrestrial) and

type III kerogen (terrestrial), although a few samples from Tangareal del Mira and Tumaco formations seem to have been originated from a type II kerogen (marine). Thus, Pr/*n*-C₁₇ varies between 0.53 and 5.74 and Ph/*n*-C₁₈ ranging between 0.22 and 4.88, suggesting a broad range of maturities and biodegradation processes and a depositional environment from suboxic to oxic characteristics.

The carbon preference index (CPI) relates the odd/even hydrocarbon predominance (Bray and Evans 1961). Immature rocks with a significant contribution of superior plants are dominated by odd *n*-alkanes, especially *n*-C₂₇, *n*-C₂₉ and *n*-C₃₁. These *n*-alkanes are originated from the epicuticular waxy (plant leaves) and are synthesized directly by plants or by defunctionalization from alcohols, acids or esters, in whose case, the CPI values will be > 1.0 . *n*-alkanes derived from marine O.M. tend to have a small or not marked CPI. Regarding to hypersaline carbonates or evaporitic rocks, CPI presents a slight pair preference of numbers of carbon. In all cases, the CPI decreases with the maturity of the O.M. This is due to a geochemical process that combines the *n*-alkanes generation from the kerogen and derived from different biological precursors and thermal cracking of hydrocarbons in the early diagenesis. The CPI values found in Tumaco-1-ST-P well present a wide dispersion ranging between 0.47 and

Table 2 Geochemical ratios based on SARA fractionation and GC/FID analyses of the organic extracts from rocks and cuttings in Tumaco-1-ST-P, Tumaco basin, Colombia

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	EOM (%)	SAT (%)	ARO (%)	RES (%)	ASP (%)	CPI	Pr/Ph	Pr/n-C17	Ph/n-C18	TAR
T-1130	1130	Cascajal Fm	Siltstone	0.0571	33.45	4.78	37.03	24.74	1.59	1.48	1.03	0.49	0.76
T-1190	1190	Cascajal Fm	Sandstone	0.0500	33.32	5.31	22.69	38.68	1.20	1.98	0.65	0.22	0.65
T-1290	1290	Cascajal Fm	Siltstone	0.0048	12.60	6.87	59.54	20.99	1.71	1.28	0.89	0.53	2.16
T-2490	2490	Tangareal de Mira Fm	Sandstone	0.0261	14.71	0.34	17.66	67.29	2.15	1.23	0.72	0.45	1.36
T-2550	2550	Tangareal de Mira Fm	Calcareous siltstone	0.0381	20.92	10.89	39.21	28.98	1.36	1.53	0.76	0.41	0.28
T-2570	2570	Tangareal de Mira Fm	Sandstone	0.0368	34.28	2.68	35.34	27.70	1.69	1.26	0.77	0.50	0.67
T-2590	2590	Tangareal de Mira Fm	Sandstone	0.0234	18.24	3.20	51.51	27.05	1.23	1.21	0.78	0.46	0.12
T-2610	2610	Tangareal de Mira Fm	Calcareous sandstone	0.1790	5.67	1.89	47.26	45.18	3.41	0.44	0.64	1.38	1.15
T-4130	4130	Tangareal de Mira Fm	Sandstone	0.0431	15.78	2.52	41.86	39.84	1.51	1.20	0.75	0.63	0.40
T-4330	4330	Tangareal de Mira Fm	Calcareous siltstone	0.0451	20.26	2.67	40.73	36.34	3.41	0.44	0.64	1.38	1.15
T-4410	4410	Tangareal de Mira Fm	Calcareous sandstone	0.0636	22.09	2.97	36.18	38.76	2.64	0.50	0.80	1.58	0.97
T-4470	4470	Tangareal de Mira Fm	Calcareous sandstone	0.0692	15.14	3.29	32.26	49.31	2.80	0.52	0.80	1.37	1.16
T-5030	5030	Tangareal de Mira Fm	Calcareous sandstone	0.0277	17.92	4.02	38.92	39.14	1.47	1.31	1.64	1.16	0.51
T-5394	5394	Tangareal de Mira Fm	Calcareous mudstone	0.0054	42.99	6.79	27.14	23.08	3.21	0.37	1.21	1.25	Biod.
T-5475	5475	Tumaco Fm	Mudstone	0.0290	15.76	3.07	48.80	32.37	1.24	0.75	2.06	2.44	1.33
T-5509	5509	Tumaco Fm	Calcareous mudstone	0.0900	16.86	2.35	38.26	42.53	1.80	0.34	3.07	10.93	3.53
T-5560	5560	Tumaco Fm	Calcareous siltstone	0.0112	15.17	6.25	48.18	30.40	0.47	0.47	1.92	2.67	1.00
T-5570	5570	Tumaco Fm	Calcareous sandstone	0.0744	25.87	3.59	37.72	32.82	1.46	1.07	0.78	0.64	0.30
T-5650	5650	Tumaco Fm	Calcareous siltstone	0.0080	18.68	2.67	60.05	18.60	1.48	1.15	0.69	0.45	0.09
T-5750	5750	Tumaco Fm	Calcareous siltstone	0.0267	16.74	3.54	53.05	26.67	1.43	1.01	0.53	0.45	0.25
T-5810	5810	Tumaco Fm	Siltstone	0.0159	19.35	3.63	59.85	17.17	1.17	1.20	0.72	0.58	0.11
T-5890	5890	Tumaco Fm	Calcareous siltstone	0.0433	16.33	3.16	51.60	28.91	1.45	1.30	0.75	0.55	0.15
T-5910	5910	Tumaco Fm	Siltstone	0.0106	24.31	4.05	42.55	29.09	1.47	1.34	0.77	0.52	0.22
T-5950	5950	Tumaco Fm	Calcareous siltstone	0.0181	16.47	4.11	52.11	27.31	1.41	1.42	0.87	0.58	0.66
T-5990	5990	Tumaco Fm	Calcareous siltstone	0.0120	11.21	3.06	47.37	38.37	1.47	1.22	0.88	2.08	0.47
T-6010	6010	Tumaco Fm	Siltstone	0.0084	21.34	4.93	47.61	26.12	1.54	1.19	0.84	1.56	1.04
T-6070	6070	Tumaco Fm	Calcareous sandstone	0.0214	17.45	2.68	57.69	22.18	1.76	1.16	1.02	0.86	2.36
T-6090	6090	Tumaco Fm	Calcareous siltstone	0.0060	31.91	7.09	44.33	16.67	2.23	0.65	1.16	2.28	3.88
T-6110	6110	Tumaco Fm	Calcareous sandstone	0.0065	20.81	6.94	53.50	18.75	1.32	1.23	0.72	0.95	0.77
T-6130	6130	Tumaco Fm	Calcareous sandstone	0.1500	7.98	2.13	33.54	56.35	1.16	1.56	0.87	1.13	1.35
T-6150	6150	Tumaco Fm	Siltstone	0.1350	6.99	1.75	26.23	65.03	1.41	0.90	0.95	2.54	0.37
T-6170	6170	Tumaco Fm	Calcareous sandstone	0.0145	18.24	3.77	54.08	23.91	2.80	0.99	1.00	2.33	2.09
T-6190	6190	Tumaco Fm	Siltstone	0.1020	8.80	1.04	22.79	67.37	1.79	0.84	1.03	2.51	0.68
T-6210	6210	Tumaco Fm	Calcareous siltstone	0.0264	11.50	2.60	46.76	39.14	2.98	1.19	0.82	0.59	1.60
T-6250	6250	Tumaco Fm	Calcareous siltstone	0.0301	13.05	2.70	62.10	22.15	1.30	1.19	0.74	0.50	0.51
T-6310	6310	Tumaco Fm	Calcareous sandstone	0.0185	10.91	2.60	55.06	31.43	1.11	1.39	0.72	0.40	1.16

Table 2 (continued)

Sample I.D.	Depth (Ft)	Estrat. unit	Lithology	EOM (%)	SAT (%)	ARO (%)	RES (%)	ASP (%)	CPI	Pr/Ph	Pr/n-C17	Ph/n-C18	TAR
T-6390	6390	Tumaco Fm	Calcareous sandstone	0.2750	12.10	1.34	27.54	59.02	1.65	1.15	0.63	0.38	0.08
T-6430	6430	Tumaco Fm	Sandstone	0.0123	19.46	4.32	48.11	28.11	1.34	1.23	0.68	0.45	0.22
T-6550	6550	Tumaco Fm	Sandstone	0.0106	16.24	3.75	51.20	28.81	1.41	1.23	0.69	0.41	0.23
T-6570	6570	Tumaco Fm	Sandstone	0.1580	8.68	0.12	29.05	62.15	1.25	1.11	0.69	0.42	0.28
T-6590	6590	Tumaco Fm	Siltstone	0.0919	8.64	1.73	29.82	59.81	1.31	1.27	0.72	0.41	0.34
T-6630	6630	Tumaco Fm	Siltstone	0.0427	4.34	0.96	18.33	76.37	1.06	1.06	0.74	0.49	0.39
T-6710	6710	Tumaco Fm	Calcareous siltstone	0.0177	18.60	3.95	56.35	21.10	1.62	1.23	0.92	0.67	0.72
T-6750	6750	Tumaco Fm	Sandstone	0.0168	20.96	3.97	49.85	25.22	1.38	1.22	0.85	0.55	0.82
T-6770	6770	Tumaco Fm	Calcareous siltstone	0.0165	23.19	4.00	58.36	14.45	1.50	1.40	0.82	0.57	1.02
T-6790	6790	Tumaco Fm	Calcareous sandstone	0.2440	10.55	0.13	27.31	62.01	1.90	1.12	1.03	0.77	0.26
T-6810	6810	Tumaco Fm	Calcareous sandstone	0.0169	14.75	2.11	61.10	22.04	1.66	1.31	1.06	0.80	0.67
T-6830	6830	Tumaco Fm	Calcareous sandstone	0.0142	18.83	5.94	58.45	16.78	1.75	1.34	0.95	0.69	0.82
T-6850	6850	Tumaco Fm	Calcareous sandstone	0.0199	36.17	4.91	39.75	19.17	2.09	1.27	0.94	0.71	0.91
T-6890	6890	Tumaco Fm	Siltstone	0.0134	21.69	5.21	59.00	14.10	1.91	1.33	0.94	0.72	0.94
T-7011	7050	Tumaco Fm	Calcareous mudstone	0.0165	10.35	2.07	70.39	17.19	1.32	1.19	1.04	0.62	0.52
T-7043	7110	Tumaco Fm	Siltstone	0.0988	16.70	0.25	20.02	63.03	1.66	1.18	0.80	0.48	0.53
T-7130	7130	Tumaco Fm	Calcareous sandstone	0.0036	27.10	2.46	41.87	28.57	1.68	1.34	1.08	0.72	0.19
T-7210	7210	Tumaco Fm	Calcareous sandstone	0.0091	19.77	4.24	53.65	22.34	1.29	1.09	1.02	0.51	0.26
T-7230	7230	Tumaco Fm	Calcareous siltstone	0.0018	22.67	0.00	62.33	15.00	0.92	0.85	1.00	0.53	0.18
T-7290	7290	Tumaco Fm	Calcareous siltstone	0.0039	36.62	6.86	43.48	13.04	1.12	1.27	0.77	0.58	0.13
T-7310	7310	Tumaco Fm	Calcareous siltstone	0.0203	18.36	3.82	42.84	34.98	1.31	1.32	0.72	0.59	0.50
T-7330	7330	Tumaco Fm	Calcareous siltstone	0.0068	28.72	4.31	38.76	28.21	1.09	1.47	0.66	0.50	1.13
T-7450	7450	Tumaco Fm	Calcareous siltstone	0.0064	26.92	6.33	45.92	20.83	1.76	0.79	0.93	0.67	2.27
T-7470	7470	Tumaco Fm	Siltstone	0.0182	30.98	1.72	29.26	38.04	1.16	0.90	0.87	0.59	1.28
T-7591	7591	Tumaco Fm	Siltstone	0.0129	30.24	13.23	25.82	30.71	0.69	1.27	2.07	1.54	0.28
T-7693	7693	Tumaco Fm	Calcareous mudstone	0.0156	18.33	5.87	46.19	29.61	5.32	1.69	1.78	1.41	3.28
T-7712	7712	Tumaco Fm	Calcareous mudstone	0.1620	10.64	0.47	32.28	56.61	2.60	1.36	1.56	1.43	4.67
T-7777	7777	Tumaco Fm	Calcareous mudstone	0.0080	23.87	7.02	46.33	22.78	4.80	0.67	2.28	2.29	13.40
T-7861	7861	Tumaco Fm	Calcareous siltstone	0.0190	43.81	6.92	36.13	13.14	3.33	1.13	3.05	2.97	4.89
T-7895	7895	Tumaco Fm	Calcareous siltstone	0.0192	18.19	7.28	48.51	26.02	4.46	2.32	3.63	1.96	10.53
T-7911	7911	Tumaco Fm	Calcareous siltstone	0.0113	20.17	6.37	52.03	21.43	1.07	3.00	2.62	1.10	0.37
T-7928	7928	Tumaco Fm	Sandstone	0.1870	6.12	21.28	17.31	55.29	4.25	1.35	5.74	4.88	16.17
T-8084	8084	Tumaco Fm	Siltstone	0.1580	10.11	0.22	31.94	57.73	1.45	1.20	1.60	0.86	0.83
T-8145	8145	Tumaco Fm	Siltstone	0.0140	17.02	3.65	21.88	57.45	1.17	1.02	1.27	0.68	Biod.
T-8211	8211	Tumaco Fm	Mudstone	0.0089	23.29	6.47	50.47	19.77	2.02	1.54	4.31	2.95	3.16
T-8233	8233	Tumaco Fm	Calcareous mudstone	0.0047	26.39	7.20	45.58	20.83	0.84	1.74	2.11	1.05	0.32

Table 2 (continued)

Sample I.D.	Depth (ft)	Estrat. unit	Lithology	EOM (%)	SAT (%)	ARO (%)	RES (%)	ASP (%)	CPI	Pr/Ph	Pr/n-C17	Ph/n-C18	TAR
T-8243	8243	Tumaco Fm	Calcareous mudstone	0.0326	22.55	8.46	37.84	31.15	6.73	1.64	5.17	2.88	15.85
T-8255.5	8255.5	Tumaco Fm	Calcareous mudstone	0.0604	31.74	5.29	25.92	37.05	5.46	1.80	2.77	1.91	11.60
T-8275	8275	Tumaco Fm	Calcareous siltstone	0.0229	28.25	6.52	46.73	18.50	4.74	1.98	3.95	2.72	9.02
T-8302.5	8302.5	Tumaco Fm	Siltstone	0.0141	15.90	11.48	43.27	29.35	2.98	2.29	3.90	2.25	6.14
T-8312.5	8312.5	Tumaco Fm	Siltstone	0.0130	11.94	9.18	57.83	21.05	2.45	1.88	3.68	3.01	5.65
T-8317	8317	Tumaco Fm	Calcareous siltstone	0.0040	4.99	4.98	59.80	30.23	0.88	1.78	1.38	0.60	0.50
T-8332.5	8332.5	Tumaco Fm	Siltstone	0.0088	15.11	10.07	56.64	18.18	4.21	1.73	2.91	1.36	6.02
T-8338	8338	Tumaco Fm	Mudstone	0.0244	28.35	5.00	38.35	28.30	4.00	1.50	4.27	2.74	12.09
T-8354.5	8354.5	Tumaco Fm	Calcareous siltstone	0.0184	12.77	6.96	59.77	20.50	3.07	1.79	4.27	2.93	7.43
T-8370.5	8370.5	Tumaco Fm	Siltstone	0.0142	25.17	10.90	42.78	21.15	3.05	2.34	2.49	1.16	5.50
T-8380	8380	Tumaco Fm	Siltstone	0.0205	15.70	9.56	52.57	22.17	3.62	2.44	4.82	2.49	11.28
T-8431	8431	Tumaco Fm	Siltstone	0.0316	5.89	4.81	37.45	51.85	1.04	2.72	2.75	1.33	1.44
T-8448	8448	Tumaco Fm	Siltstone	0.0122	27.78	7.71	47.06	17.45	2.56	2.48	3.14	1.56	5.83
T-8850	8850	Tumaco Fm	Siltstone	0.0079	13.94	11.15	52.96	21.95	1.40	1.62	1.03	0.52	1.47
T-8870	8870	Tumaco Fm	Calcareous sandstone	0.0100	26.57	5.31	46.76	21.36	1.99	1.98	0.97	0.48	0.62
T-8890	8890	Tumaco Fm	Calcareous sandstone	0.2480	11.90	3.04	29.15	55.91	0.82	1.39	0.81	0.48	0.15
T-9150	9150	Tumaco Fm	Calcareous siltstone	0.0090	27.08	7.39	50.48	15.05	1.44	1.31	1.44	1.05	0.80
T-9790	9790	Tumaco Fm	Calcareous sandstone	0.0165	31.73	5.40	42.53	20.34	1.68	1.49	1.30	1.03	0.91
T-10079	10,079	Tumaco Fm	Mudstone	0.0401	25.01	3.70	30.41	40.88	1.78	1.02	4.01	3.43	2.00
T-11610	11,610	Tumaco Fm	Calcareous siltstone	0.2120	20.91	5.07	32.31	41.71	1.17	1.66	0.87	0.47	0.18
T-11650	11,650	Tumaco Fm	Calcareous siltstone	0.7900	19.87	2.28	42.33	35.52	0.97	1.48	0.79	0.48	0.05
T-11670	11,670	Tumaco Fm	Calcareous sandstone	0.0793	18.17	3.05	45.59	33.19	1.22	1.47	0.91	0.54	0.26
T-11690	11,690	Tumaco Fm	Calcareous siltstone	0.0399	13.15	2.19	32.88	51.78	1.16	1.39	1.02	0.44	0.20
T-11710	11,710	Tumaco Fm	Calcareous siltstone	0.7200	23.40	2.27	24.53	49.80	0.68	1.38	0.83	0.50	0.06
T-11730	11,730	Tumaco Fm	Calcareous siltstone	0.2470	26.40	4.20	33.18	36.22	0.93	1.41	0.80	0.50	0.16
T-11790	11,790	Tumaco Fm	Calcareous siltstone	0.1340	21.43	2.65	33.48	42.44	1.02	1.29	0.85	0.51	0.20
T-11810	11,810	Tumaco Fm	Calcareous siltstone	0.0743	29.87	2.99	33.42	33.72	1.02	1.36	0.90	0.53	0.13
T-11870	11,870	Tumaco Fm	Calcareous siltstone	0.1280	35.89	4.20	55.26	4.65	0.84	1.40	0.78	0.48	0.06

EOM, extractable organic matter; CPI, carbon preference index = $[(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33})/n-C_{24} + n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32}) + (n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33})/n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32}]/2$; Pr/Ph, pristane/phytane; Ph/n-C₁₇, pristane/n-C₁₇; phytane/n-C₁₈; TAR, terrestrial/aquatic O.M. ratio = $n-C_{27} + n-C_{29} + n-C_{31}/n-C_{15} + n-C_{17} + n-C_{19}$; Biod., biodegraded

Fig. 11 Geochemical correlation between Isoprenoids/*n*-alkanes showing the sources and depositional environment of the organic matter in the Tumaco-1-ST-P, Tumaco basin, Colombia

6.73, with a high amount of CPI values ranging between 1 and 3 and a few number of samples (<6%) with CPI < 1.0. High values of CPI indicate low maturity and terrestrial origin, bitumen with CPI around 1 originating from marine contributions. Samples from Cascajal Fm present CPI values ranging between 1.20 and 1.71 indicating a marine-deltaic transitional O.M. source located in a paleoenvironment of deltaic plain highly immature. The Tangareal del Mira bitumen presents CPI in the range between 1.23 and 3.41 confirming a transitional marine-deltaic depositional environment, while the Tumaco Fm maintains the same marine-deltaic influence of the previous formation up to a depth of approximately 8000 ft, from which up to 12,000 ft, becomes a paleoenvironment with a tendency to the marine platform (shelf marine).

The vertical distribution of terrestrial/aquatic O.M. ratio (TAR) values is relevant to determine the relative changes in the contribution of the terrestrial versus aquatic O.M. over the time, particularly considering recent sediments (Meyers 1997). TAR displays values varying between 0.05 and 16.17 (average 2.18), which confirms the constant variations of organic facies from algal/bacterial and/or land origin through the stratigraphic column. High TAR values in recent sediment extracts, as in the case of Tumaco-1-ST-P, indicate a great contribution by land plants that aquatic to the depositional environment (Bourbonniere and Meyers 1996, cited by Peter et al. 2005). This ratio should be used with care since it is susceptible to drastic changes by effects of maturation and biodegradation.

Terpanes and steranes

The biological markers were identified based on full-scan GC/MS analysis, comparing the mass fragmentograms of the specific biomarkers with data previously reported (Philp 1985; Wang 1993; Peter et al. 2005) and with bitumen and crude oils of known composition (e.g., NGS NSO-1 oil sample, NPD-Nigoga; Boscan crude oil, Venezuela; Cauca/Patia and Buenaventura rock extracts, Colombia) (NPD-Nigoga 2000; Antek S.A. 2011).

Figure 12 (on the left) shows the tri-, tetra-, and penta-cyclic terpane mass fragmentograms (m/z 191) and steranes (m/z 217) (on the right) for Tumaco-1-ST-P selected samples, while Table 3 displays the main geochemical correlation from terpane and sterane results. The terpane chromatographic profiles exhibit a particular features such as that the $C_{30}\alpha\beta(H)$ -hopane is the biggest terpane; the tricyclic terpane fraction extends from $C_{19}/3$ until $C_{30}/3-R/S$, $T_s < T_m$; the oleanane and gammacerane are present in medium to high concentrations; homohopanes are present in relatively low concentration and in some samples do not exist. When they are present, are distributed between C_{31} and C_{35} , decreasing in the order $C_{31} > C_{32} > C_{33} > C_{34} > C_{35}-R/S$.

Geochemical correlations based on the tricyclic terpanes such as TT19/TT23, TT23/TT30, TT24/TT30 and TT25/TT26 are excellent indicators of source and depositional environment. Thus, Table 3 shows that TT19/TT23 ratios vary between 0.06 and 0.58, except for the sample T-1190 that presents a value of 1.10. These low ratios suggest an important bacterial/algal over terrestrial origin. TT21/TT23

Fig. 12 Mass fragmentograms showing the terpene (m/z 191) and sterane (m/z 217) distribution in Tumaco-1-ST-P well, Tumaco basin, Colombia

ratios present values > 1.0 for most of the samples corroborating a marine origin associated with prokaryotic organisms (algal/bacterial). However, in the shallower intervals of the Cascajal and Tangareal del Mira Fm, the TT21/TT23 ratios display values slightly higher than 1, indicating a combined contribution of bacterial/algal O.M. with a significant terrestrial input.

TT23/30H ratios and Σ tricyclic terpanes/ Σ hopanes do not show a trend that clearly shows the origin of the O.M. along the stratigraphic column. Values vary alternately around 1.0, indicating a significant higher plant (continental) contribution to the O.M. toward the shallower formation of Cascajal and Tangareal del Mira, while in the deepest part of the well, the Tumaco Fm, the O.M. is mainly marine contributions from bacterial/algal inputs. C24TeT/C30-hopane ratios are quite used in the characterization of the paleodepositional environment (Peter et al. 2005). The highest abundances of tetracyclic terpene C24TeT have been found in marine-deltaic and lacustrine saline environments (Rocha-Mello et al. 1988). In Tumaco-1-ST-P, C24Te/H30 ratios present values < 0.44 , which dismisses a carbonate or evaporitic environment but it supports a marine shale or marine-deltaic

depositional environment. Burwood et al. (1990) found that marine bitumen and crude oils from West Africa showed TT25/TT26 ratios > 1.0 , while terrestrial bitumen showed TT25/TT26 values < 1.0 . Thus, in the Tumaco-1-ST-P well, this ratio confirms the marine origin of the studied samples as is shown in Fig. 13. Since TT24/TT23 is greater than 0.5 for most of the samples in Tumaco-1-ST-P suggest organic facies associated with marine shales.

Steranes in selected samples from Tumaco-1-ST-P (Fig. 12) allow observing that pregnanes, excellent indicators of salinity, are present in medium concentration, although in some samples these are biodegraded or have not been formed. The C₂₇ diasteranes (rearranged steranes) are present in significant concentrations, which suggest a siliclastic environment ($27D/29\alpha\alpha R > 1.0$). C₂₇-, C₂₈-, and C₂₉-steranes are present in varying concentrations and without any predominance between them, which suggest alternating contributions of algal/microbial and land plants (transitional environment) origin. The configuration of $\alpha\alpha R$ -sterane in most of the samples is greater than $\beta\beta R$ -S or $\beta\beta S$, which indicates an immature O.M.

Table 3 Geochemical ratios based on terpanes (m/z 191 and 177) and steranes (m/z 217 and 218) in organic extracts from rocks and cuttings in Tumaco-1-ST-P, Tumaco basin, Colombia

Sample I.D.	HOAPNES, m/z 191 and m/z 177													
	TT19/TT23	TT21/TT23	TT23/H30	TTe24/H30	TT25/TT26	Ts/(Ts+Tm)	M30/H30	O.I.	G.I.	HH32 I.I.	HH32. H.I.	TT/TP	BNH Index	
T-1130	0.80	0.60	2.40	0.28	1.18	0.18	0.47	8.99	36.86	0.51	19.12	2.20	11.40	
T-1190	1.10	0.87	0.54	0.15	1.16	0.52	0.18	7.16	5.62	0.55	22.40	1.03	11.08	
T-1290	0.16	0.49	0.25	0.10	1.10	0.54	0.27	6.45	16.30	0.56	22.51	0.54	6.34	
T-2490	0.23	0.58	2.06	0.32	1.76	0.37	0.96	15.59	Biod.	0.51	Biod.	1.50	8.54	
T-2550	0.22	0.56	1.78	0.23	1.67	0.43	0.65	12.03	53.56	0.55	18.84	1.63	3.93	
T-2570	0.06	0.57	2.23	0.24	1.67	0.48	0.57	10.47	50.91	0.55	19.69	1.85	3.82	
T-2590	0.09	0.48	1.90	0.25	1.77	0.52	0.66	12.58	70.97	0.56	18.99	1.60	2.92	
T-2610	0.37	0.76	0.82	0.26	1.40	0.52	1.25	18.54	Biod.	0.43	Biod.	0.60	6.72	
T-4130	0.58	0.95	0.84	0.20	1.48	0.41	1.47	11.20	Biod.	0.52	Biod.	1.26	1.86	
T-4330	0.26	0.84	1.06	0.18	1.53	0.53	1.96	23.65	Biod.	0.57	Biod.	1.26	9.17	
T-4410	0.38	1.01	0.71	0.21	1.73	0.48	1.83	26.84	Biod.	0.54	Biod.	0.99	7.13	
T-4470	0.31	0.82	0.68	0.19	1.81	0.42	1.73	21.90	Biod.	0.49	Biod.	0.92	5.05	
T-5030	0.22	0.51	0.30	0.10	1.27	0.51	0.11	8.17	3.75	0.59	24.56	0.57	1.53	
T-5394	0.11	0.72	0.89	0.20	1.33	0.35	1.40	36.30	Biod.	0.59	Biod.	1.03	71.57	
T-5475	0.24	0.59	0.13	0.06	1.85	0.51	0.81	9.04	Biod.	0.64	Biod.	0.68	7.97	
T-5509	0.36	0.74	0.12	0.07	2.27	0.33	2.23	19.34	Biod.	0.60	Biod.	0.41	17.87	
T-5560	0.12	1.55	0.28	0.10	2.08	0.74	1.87	24.53	Biod.	0.28	Biod.	0.68	11.85	
T-5570	0.16	0.69	0.93	0.12	2.50	0.53	0.42	11.11	50.61	0.56	19.00	1.05	57.53	
T-5650	0.32	0.87	2.23	0.34	2.01	0.63	0.45	11.05	52.97	0.55	23.02	2.56	21.07	
T-5750	0.20	0.77	2.19	0.23	2.43	0.63	0.68	14.92	96.14	0.58	Biod.	1.90	3.35	
T-5810	0.29	0.84	2.04	0.21	2.10	0.64	0.82	15.85	Biod.	0.56	Biod.	1.18	86.78	
T-5890	0.33	0.87	2.18	0.25	2.34	0.64	0.83	15.39	Biod.	0.61	Biod.	1.56	Biod.	
T-5910	0.38	0.92	1.93	0.27	1.91	0.58	0.68	9.80	99.37	0.56	Biod.	1.59	Biod.	
T-5950	0.30	0.80	1.12	0.34	1.67	0.64	0.97	13.55	Biod.	0.55	Biod.	0.99	94.95	
T-5990	0.51	0.77	0.73	0.32	1.51	0.58	0.90	16.27	Biod.	0.57	Biod.	0.72	65.18	
T-6010	0.40	0.75	0.49	0.23	1.38	0.47	0.44	8.32	46.13	0.54	Biod.	0.86	20.54	
T-6070	0.33	0.71	0.79	0.34	1.56	0.60	1.13	17.14	Biod.	0.51	Biod.	0.67	41.15	
T-6090	0.36	0.80	0.68	0.38	1.79	0.59	1.08	14.96	Biod.	0.45	Biod.	0.65	Biod.	
T-6110	0.54	0.66	0.66	0.36	1.08	0.20	0.34	13.40	36.37	0.54	Biod.	1.12	84.49	
T-6130	0.56	0.75	0.55	0.28	1.37	0.40	0.43	8.38	46.85	0.55	Biod.	1.05	19.90	
T-6150	0.41	0.75	0.85	0.36	1.72	0.61	1.08	15.63	Biod.	0.57	Biod.	0.68	Biod.	
T-6170	0.44	0.74	0.74	0.35	1.42	0.52	0.92	17.65	Biod.	0.67	Biod.	0.59	70.44	
T-6190	0.39	0.72	0.77	0.38	2.27	0.58	1.09	15.00	Biod.	0.39	Biod.	0.60	91.64	
T-6210	0.21	0.64	1.70	0.28	2.01	0.52	1.06	15.99	Biod.	0.54	Biod.	1.29	41.06	

Table 3 (continued)
Sample I.D. HOAPNES, m/z 191 and m/z 177

Sample I.D.	TT19/TT23	TT21/TT23	TT23/H30	TTe24/H30	TT25/TT26	Ts/(Ts + Tm)	M30/H30	O. I.	G. I.	HH32 I. I.	HH32. H.I.	TT/TP	BNH Index
T-6250	0.39	0.82	1.52	0.32	2.10	0.57	0.67	14.57	94.69	0.55	Biod.	1.39	75.42
T-6310	0.31	0.78	0.94	0.38	1.48	0.52	0.33	14.64	29.54	0.56	24.30	1.35	30.53
T-6390	0.22	0.77	1.35	0.30	1.73	0.52	0.32	8.34	28.30	0.55	Biod.	1.93	13.48
T-6430	0.25	0.86	2.08	0.37	2.04	0.55	0.45	14.48	55.75	0.56	Biod.	2.04	41.79
T-6550	0.38	0.78	1.21	0.37	1.68	0.55	0.53	12.67	76.32	0.57	Biod.	1.36	35.98
T-6570	0.25	0.74	1.23	0.35	1.87	0.58	0.55	13.09	77.43	0.56	Biod.	1.50	35.19
T-6590	0.22	0.72	1.08	0.38	1.63	0.56	0.36	12.22	39.81	0.53	Biod.	1.34	26.09
T-6630	0.32	0.77	1.04	0.33	1.53	0.54	0.37	9.62	44.23	0.58	Biod.	1.44	30.20
T-6710	0.46	0.81	0.61	0.20	1.49	0.61	0.88	12.82	Biod.	0.42	Biod.	0.96	21.63
T-6750	0.27	0.70	0.97	0.23	1.89	0.54	0.54	10.41	74.72	0.58	Biod.	1.10	36.77
T-6770	0.32	0.73	0.85	0.19	1.87	0.58	0.76	12.86	Biod.	0.75	Biod.	1.15	32.82
T-6790	0.30	0.76	6.76	2.07	1.58	0.64	9.63	Biod.	Biod.	0.51	Biod.	1.10	Biod.
T-6810	0.39	0.81	0.58	0.14	1.82	0.55	0.86	12.06	Biod.	0.41	Biod.	0.69	23.14
T-6830	0.34	0.87	0.49	0.16	1.76	0.54	0.77	9.64	Biod.	0.46	Biod.	0.73	18.10
T-6850	0.22	0.61	0.34	0.12	1.62	0.58	0.43	7.53	59.25	0.59	Biod.	0.65	28.52
T-6890	0.30	0.78	0.53	0.15	1.47	0.56	0.67	9.17	Biod.	0.74	Biod.	0.90	28.49
T-7050	0.26	0.75	0.76	0.25	1.44	0.51	0.68	13.36	99.60	0.69	Biod.	1.07	43.30
T-7110	0.28	0.72	0.42	0.17	1.35	0.49	0.36	6.52	37.92	0.83	Biod.	0.95	6.81
T-7130	0.34	0.76	0.58	0.26	1.27	0.53	0.57	10.62	86.35	0.71	Biod.	1.20	12.20
T-7210	0.39	0.75	0.44	0.24	1.37	0.50	0.68	9.94	Biod.	0.71	Biod.	0.96	10.58
T-7230	0.25	0.71	0.38	0.20	1.58	0.49	0.51	8.38	75.05	0.65	Biod.	0.87	7.71
T-7290	0.32	0.84	0.43	0.25	1.37	0.49	0.51	9.16	71.17	0.72	Biod.	0.95	16.85
T-7310	0.31	0.70	0.48	0.29	1.30	0.49	0.45	10.61	55.14	0.77	Biod.	0.96	19.04
T-7330	0.32	0.71	0.55	0.36	1.34	0.48	0.37	10.61	34.65	0.85	Biod.	1.04	11.82
T-7450	0.23	0.80	0.33	0.12	1.77	0.42	0.44	1.69	43.85	0.80	Biod.	0.77	11.80
T-7470	0.22	0.74	0.63	0.19	1.48	0.52	0.59	11.25	84.61	0.80	Biod.	1.04	12.71
T-7591	0.21	0.64	0.44	0.14	1.70	0.54	0.99	15.85	Biod.	0.55	Biod.	0.91	63.28
T-7693	0.16	0.59	0.65	0.16	2.11	0.16	0.66	21.80	87.48	0.66	Biod.	0.86	13.09
T-7712	0.16	1.49	0.63	0.22	1.80	0.49	1.00	16.50	Biod.	0.47	Biod.	1.20	60.72
T-7777	0.29	0.59	0.33	0.10	1.88	0.56	0.80	18.78	Biod.	0.44	Biod.	1.04	28.97
T-7861	0.25	0.54	0.33	0.15	1.53	0.30	1.08	29.49	Biod.	0.43	Biod.	0.91	13.89
T-7895	0.22	0.94	0.44	0.13	2.81	0.17	0.83	50.48	94.37	0.45	Biod.	0.71	Biod.
T-7911	0.18	0.63	1.75	0.44	2.29	0.26	1.05	68.86	80.20	0.40	Biod.	0.71	Biod.
T-7928	0.19	0.56	0.20	0.11	2.17	0.34	0.61	24.55	Biod.	0.44	Biod.	0.57	Biod.

Table 3 (continued)

Sample I.D.	HOAPNES, m/z 191 and m/z 177												
	TT19/TT23	TT21/TT23	TT23/H30	TTe24/H30	TT25/TT26	Ts/(Ts+ Tm)	M30/H30	O. I.	G. I.	HH32 I. I.	HH32. H.I.	TT/TP	BNH Index
T-8084	0.11	0.71	0.47	0.16	1.94	0.24	0.38	19.02	29.20	0.66	Biod.	0.93	Biod.
T-8145	0.09	0.61	0.78	0.18	1.82	0.28	0.37	44.00	20.92	0.83	Biod.	0.64	Biod.
T-8211	0.20	0.37	0.37	0.14	1.82	0.26	0.91	34.35	Biod	0.39	Biod.	0.69	Biod.
T-8233	0.20	0.95	0.79	0.23	2.42	0.21	0.80	96.51	Biod.	0.44	Biod.	1.38	Biod.
T-8243	0.22	0.45	0.21	0.09	2.45	0.16	0.59	68.70	99.03	0.31	Biod.	0.60	13.90
T-8255.5	0.17	0.53	0.51	0.14	1.82	0.11	0.81	79.98	Biod.	0.26	Biod.	0.71	14.23
T-8275	0.24	0.61	0.47	0.14	2.76	0.17	0.69	70.51	Biod.	0.33	Biod.	0.54	15.06
T-8302.5	0.16	0.31	0.50	0.41	Biod.	0.13	0.59	48.22	77.47	0.50	Biod.	1.97	Biod.
T-8312.5	0.20	0.49	0.29	0.12	Biod.	0.11	0.48	Biod.	92.02	0.47	Biod.	0.60	Biod.
T-8317	0.14	0.57	0.96	0.28	1.84	0.14	0.58	76.62	31.48	0.38	Biod.	0.76	Biod.
T-8332.5	0.22	0.57	0.37	0.12	2.14	0.07	0.42	69.84	68.53	0.36	Biod.	0.57	Biod.
T-8338	0.27	0.31	0.15	0.11	2.88	0.05	0.33	52.82	68.76	0.38	Biod.	0.55	Biod.
T-8354.5	0.19	0.31	0.19	0.11	2.58	0.07	0.52	40.39	64.61	0.40	Biod.	0.58	Biod.
T-8370.5	0.17	0.90	0.29	0.13	2.25	0.33	0.62	48.84	56.59	0.54	Biod.	0.70	Biod.
T-8380	0.20	0.44	0.32	0.14	1.93	0.31	0.90	71.52	Biod.	0.39	Biod.	0.63	22.82
T-8431	0.17	0.68	0.81	0.33	3.75	0.20	0.46	99.64	74.51	0.32	Biod.	0.51	Biod.
T-8448	0.17	0.78	0.21	0.10	4.76	0.26	0.29	56.13	39.74	0.19	Biod.	0.46	Biod.
T-8850	0.30	0.74	0.56	0.32	1.39	0.56	0.49	31.31	59.15	0.83	Biod.	0.59	89.83
T-8870	0.23	0.60	0.58	0.32	1.70	0.51	0.44	33.44	41.25	0.73	Biod.	0.55	Biod.
T-8890	0.23	1.62	0.11	0.06	1.10	0.02	0.27	1.36	30.78	0.56	Biod.	0.32	2.26
T-9150	0.29	0.74	0.35	0.21	1.20	0.52	0.68	16.86	88.36	0.60	Biod.	0.80	10.89
T-9790	0.34	0.70	0.27	0.13	1.52	0.46	0.47	39.76	49.47	0.71	Biod.	0.57	39.34
T-10079	0.29	0.72	0.12	0.06	1.01	0.12	0.55	47.98	43.74	0.71	Biod.	0.38	14.90
T-11610	0.36	1.52	0.12	0.07	1.29	0.03	0.28	1.61	28.93	0.56	Biod.	0.33	2.99
T-11650	0.28	1.62	0.10	0.06	1.04	0.03	0.28	1.14	31.62	0.55	Biod.	0.28	2.42
T-11670	0.24	1.59	0.09	0.06	1.13	0.05	0.28	1.95	34.20	0.55	Biod.	0.26	2.73
T-11690	0.31	0.86	0.29	0.18	1.42	0.48	0.42	19.22	32.19	0.68	Biod.	0.47	54.31
T-11710	0.21	1.53	0.12	0.07	1.06	0.03	0.26	1.16	28.65	0.56	Biod.	0.34	2.30
T-11730	0.30	1.54	0.12	0.06	1.10	0.06	0.27	1.51	28.96	0.55	Biod.	0.33	2.40
T-11790	0.26	1.38	0.12	0.06	1.24	0.05	0.26	2.12	29.67	0.54	Biod.	0.31	2.87
T-11810	0.30	1.47	0.14	0.06	1.21	0.06	0.26	2.41	28.03	0.54	Biod.	0.36	2.79
T-11870	0.33	0.12	0.16	0.07	1.25	0.06	0.26	1.82	28.30	0.55	Biod.	0.33	2.68

Table 3 (continued)

Sample I.D.	Steranes, m/z 217 and m/z 218										
	PREGIndex	$C_{27}\beta\beta S$ %	$C_{28}\beta\beta S$ %	$C_{29}\beta\beta S$ %	$C_{27}\alpha\alpha R$ %	$C_{28}\alpha\alpha R$ %	$C_{29}\alpha\alpha R$ %	$C_{29}\alpha\alpha (S/R)$	$C_{29}\alpha\alpha S/S+R$	$C_{29}\beta\beta/\alpha\alpha + \beta\beta$	$C_{27}Dial/C_{29}\alpha\alpha-R$
T-1130	40.36	27.97	31.41	40.62	27.54	25.23	47.23	0.37	0.27	0.40	1.69
T-1190	19.99	27.48	29.16	43.36	32.66	25.25	42.09	0.84	0.46	0.48	2.56
T-1290	18.41	28.34	41.53	30.13	31.08	26.43	42.49	0.73	0.42	0.39	1.65
T-2490	38.55	31.86	29.73	38.41	31.29	17.00	51.71	0.24	0.20	Biod.	1.24
T-2550	33.28	27.66	26.91	45.43	26.83	23.89	49.28	0.37	0.27	0.13	1.34
T-2570	34.97	25.45	27.81	46.74	22.33	23.61	54.06	0.35	0.26	0.14	1.46
T-2590	29.41	32.46	26.44	41.10	33.95	15.95	50.10	0.26	0.21	0.13	1.13
T-2610	15.97	24.16	44.19	31.65	33.23	19.91	46.85	0.05	0.05	0.02	Biod.
T-4130	34.15	26.12	31.64	42.24	46.03	18.77	35.21	0.14	0.12	0.33	0.42
T-4330	36.68	30.83	37.42	31.75	2.19	37.67	60.14	0.16	0.14	0.25	Biod.
T-4410	31.44	29.42	30.93	39.65	45.92	20.85	33.23	0.11	0.10	0.26	Biod.
T-4470	30.11	28.98	32.43	38.58	46.32	20.20	33.49	0.11	0.10	0.26	Biod.
T-5030	17.37	33.50	30.34	36.16	25.62	26.39	47.98	0.57	0.36	0.45	1.31
T-5394	Biod.	Biod.	Biod.	Biod.	40.87	18.30	40.83	0.03	0.03	0.25	Biod.
T-5475	20.37	43.92	34.40	21.68	50.95	16.26	32.79	0.15	0.13	0.18	Biod.
T-5509	14.00	41.27	36.13	22.60	49.27	21.63	29.10	0.09	0.08	0.21	Biod.
T-5560	16.34	39.75	36.76	23.49	42.60	25.49	31.91	0.07	0.06	0.25	Biod.
T-5570	25.72	40.15	40.89	18.96	37.94	26.31	35.75	0.41	0.29	0.32	0.85
T-5650	41.07	35.03	39.23	25.74	40.58	21.43	37.99	0.29	0.23	0.35	1.69
T-5750	36.78	33.94	37.58	28.48	37.46	21.72	40.82	0.14	0.12	0.30	0.71
T-5810	38.19	36.00	43.66	20.34	38.08	23.58	38.33	0.07	0.07	0.29	0.50
T-5890	42.91	41.06	43.23	15.71	38.26	22.81	38.93	0.09	0.08	0.32	0.47
T-5910	41.74	31.60	44.26	24.15	36.35	22.86	40.79	0.09	0.08	0.34	0.71
T-5950	36.44	28.08	47.26	24.66	38.71	22.70	38.59	0.07	0.07	0.30	0.61
T-5990	26.80	31.43	48.67	19.90	40.19	21.14	38.67	0.08	0.08	0.27	0.61
T-6010	27.30	33.66	45.83	20.51	34.53	24.54	40.93	0.25	0.20	0.32	1.19
T-6070	22.22	30.46	49.97	19.57	37.42	18.51	44.07	0.08	0.07	0.26	0.45
T-6090	26.17	22.21	50.45	27.34	40.66	19.35	39.98	0.06	0.06	0.29	0.51
T-6110	28.92	25.66	49.67	24.67	37.35	23.62	39.03	0.30	0.23	0.39	2.03
T-6130	30.87	25.67	43.83	30.50	37.37	23.84	38.79	0.27	0.22	0.34	1.52
T-6150	25.68	28.78	50.41	20.81	37.24	20.60	42.16	0.06	0.06	0.26	0.42
T-6170	23.29	35.52	52.66	11.82	33.21	20.04	46.75	0.06	0.06	0.26	0.48
T-6190	26.73	31.92	51.96	16.12	37.47	19.76	42.77	0.05	0.04	0.25	0.43
T-6210	29.76	37.56	38.30	24.15	32.19	18.65	49.15	0.11	0.10	0.26	0.50

Table 3 (continued)

Sample I.D.	Steranes, m/z 217 and m/z 218													
	PREGIndex	$C_{27}\beta\beta S$ %	$C_{28}\beta\beta S$ %	$C_{29}\beta\beta S$ %	$C_{27}\alpha\alpha R$ %	$C_{28}\alpha\alpha R$ %	$C_{29}\alpha\alpha R$ %	$C_{29}\alpha\alpha (S/R)$	$C_{29}\alpha\alpha S/S+R$	$C_{29}\beta\beta/\alpha\alpha + \beta\beta$	$C_{27}Dial/C_{29}\alpha\alpha R$			
T-6250	37.15	37.21	48.06	14.73	33.66	23.06	43.29	0.11	0.10	0.28	0.65			
T-6310	34.39	35.03	41.24	23.73	29.24	25.64	45.12	0.33	0.25	Biod.	2.03			
T-6390	40.47	34.05	45.59	20.36	39.57	21.87	38.56	0.32	0.24	0.34	1.41			
T-6430	42.09	39.22	50.15	10.63	36.06	22.24	41.70	0.19	0.16	0.32	1.16			
T-6550	35.39	38.93	51.18	9.88	34.61	25.94	39.45	0.14	0.12	0.29	0.95			
T-6570	35.08	34.42	51.98	13.60	37.11	25.74	37.15	0.12	0.11	0.27	0.87			
T-6590	35.69	32.64	45.76	21.60	38.03	23.25	38.72	0.27	0.21	0.35	2.07			
T-6630	36.70	37.13	46.38	16.49	42.40	22.31	35.29	0.20	0.17	0.28	1.29			
T-6710	23.66	39.38	46.15	14.47	37.02	22.80	40.18	0.05	0.04	0.26	0.35			
T-6750	29.27	32.93	50.90	16.17	37.43	24.55	38.01	0.17	0.15	0.30	0.77			
T-6770	25.71	26.59	53.76	19.65	36.73	23.47	39.80	0.08	0.07	0.28	0.46			
T-6790	23.48	21.08	53.92	25.00	38.18	22.40	39.43	0.06	0.05	0.24	0.32			
T-6810	19.73	24.94	57.53	17.53	36.22	23.45	40.33	0.06	0.06	0.24	0.24			
T-6830	22.26	39.38	49.27	11.35	37.05	23.48	39.47	0.08	0.07	0.26	0.36			
T-6850	13.51	35.74	46.15	18.12	33.61	24.49	41.90	0.24	0.19	0.37	1.18			
T-6890	22.77	45.38	50.65	3.97	36.60	23.83	39.57	0.10	0.09	0.28	0.53			
T-7050	31.10	42.01	47.34	10.65	38.33	23.13	38.55	0.21	0.18	0.29	0.81			
T-7110	28.46	33.32	45.71	20.97	35.30	26.39	38.32	0.29	0.22	0.32	0.89			
T-7130	30.67	33.24	50.17	16.59	42.63	22.75	34.62	0.17	0.15	0.30	0.84			
T-7210	31.93	28.85	57.15	14.00	37.08	24.89	38.03	0.19	0.16	0.28	0.78			
T-7230	28.08	26.02	51.37	22.61	40.60	23.80	35.60	0.17	0.14	0.27	0.81			
T-7290	30.51	34.20	56.35	9.45	37.84	23.67	38.49	0.19	0.16	0.30	0.96			
T-7310	30.44	37.99	46.26	15.75	36.08	24.58	39.33	0.29	0.22	0.30	1.61			
T-7330	33.79	35.03	44.14	20.83	38.14	25.43	36.42	0.42	0.30	0.32	2.74			
T-7450	26.28	31.19	52.47	16.34	32.76	27.15	40.10	0.23	0.19	0.31	0.67			
T-7470	28.62	28.87	51.99	19.14	36.22	24.05	39.73	0.19	0.16	0.30	0.68			
T-7591	Biod.	Biod.	Biod.	Biod.	23.97	14.89	61.14	0.03	0.03	0.24	Biod.			
T-7693	Biod.	Biod.	Biod.	Biod.	20.87	19.54	59.58	0.01	0.01	0.29	Biod.			
T-7712	Biod.	Biod.	Biod.	Biod.	25.86	19.19	54.95	0.01	0.01	0.25	Biod.			
T-7777	Biod.	Biod.	Biod.	Biod.	32.64	23.93	43.43	0.02	0.02	0.25	Biod.			
T-7861	6.01	21.57	47.76	30.67	24.29	25.45	50.27	0.01	0.01	0.23	Biod.			
T-7895	Biod.	21.17	33.43	45.40	23.14	28.75	48.11	Biod.	Biod.	Biod.	Biod.			
T-7911	Biod.	Biod.	Biod.	Biod.	17.97	17.04	64.99	Biod.	Biod.	Biod.	Biod.			
T-7928	Biod.	14.34	36.37	49.29	21.39	35.88	42.72	0.00	0.00	0.27	Biod.			
T-8084	10.08	10.02	41.03	48.95	22.84	31.42	45.74	0.06	0.06	0.37	Biod.			

Table 3 (continued)

Sample I.D.	Steranes, <i>m/z</i> 217 and <i>m/z</i> 218										
	PREGIndex	C ₂₇ ββS %	C ₂₈ ββS %	C ₂₉ ββS %	C ₂₇ ααR %	C ₂₈ ααR %	C ₂₉ ααR %	C ₂₉ αα (S/R)	C ₂₉ αα S/S + R	C ₂₉ ββ/αα + ββ	C ₂₇ Dia/C ₂₉ αα-R
T-8145	21.61	29.71	60.68	9.61	39.37	21.73	38.91	0.08	0.07	0.48	Biod.
T-8211	Biod.	12.68	37.20	50.12	22.79	29.37	47.84	0.00	0.00	0.26	Biod.
T-8233	Biod.	Biod.	Biod.	Biod.	20.85	27.28	51.87	0.00	0.00	0.26	Biod.
T-8243	Biod.	9.54	42.73	47.73	16.51	25.38	58.12	0.00	0.00	0.23	Biod.
T-8255.5	Biod.	Biod.	Biod.	Biod.	18.77	22.34	58.88	0.00	0.00	0.29	Biod.
T-8275	Biod.	10.99	48.05	40.96	22.25	28.13	49.62	Biod.	Biod.	Biod.	Biod.
T-8302.5	Biod.	12.19	35.98	51.83	19.43	26.75	53.82	0.01	0.01	0.30	Biod.
T-8312.5	Biod.	15.31	48.60	36.09	21.29	32.77	45.94	0.01	0.01	0.32	Biod.
T-8317	8.38	16.28	31.44	52.28	25.28	15.67	59.05	0.04	0.04	0.41	Biod.
T-8332.5	Biod.	Biod.	Biod.	Biod.	20.21	28.35	51.44	0.01	0.01	0.30	Biod.
T-8338	Biod.	Biod.	Biod.	Biod.	23.53	32.02	44.45	0.01	0.01	0.27	Biod.
T-8354.5	Biod.	Biod.	Biod.	Biod.	19.96	28.73	51.31	0.01	0.01	0.27	Biod.
T-8370.5	Biod.	Biod.	Biod.	Biod.	20.64	27.13	52.24	0.01	0.01	0.28	Biod.
T-8380	Biod.	12.19	35.16	52.65	18.84	27.41	53.75	0.00	0.00	0.26	Biod.
T-8431	Biod.	Biod.	Biod.	Biod.	12.47	17.54	70.00	0.01	0.01	0.30	Biod.
T-8448	Biod.	Biod.	Biod.	Biod.	19.87	24.55	55.58	0.01	0.01	0.33	Biod.
T-8850	15.25	23.00	50.80	26.20	19.47	22.46	58.07	0.02	0.02	0.21	0.17
T-8870	12.05	20.60	46.16	33.24	21.50	24.58	53.92	0.05	0.05	0.29	0.28
T-8890	13.21	25.90	43.51	30.59	13.13	51.35	35.52	0.50	0.33	0.23	0.07
T-9150	18.34	29.75	44.92	25.33	32.12	28.03	39.84	0.06	0.06	0.28	0.54
T-9790	17.55	47.46	34.61	17.93	32.75	29.28	37.97	0.08	0.08	0.28	0.39
T-10079	Biod.	Biod.	Biod.	Biod.	32.69	38.10	29.21	0.05	0.04	0.26	Biod.
T-11610	15.57	45.83	31.19	22.98	13.81	50.48	35.72	0.49	0.33	0.25	0.09
T-11650	11.80	41.88	27.98	30.14	12.77	51.59	35.64	0.52	0.34	0.24	0.05
T-11670	11.33	44.43	28.36	27.21	12.48	50.82	36.69	0.48	0.32	0.24	0.08
T-11690	11.53	44.18	31.22	24.60	21.15	28.86	49.99	0.06	0.05	0.27	0.25
T-11710	14.70	45.19	32.13	22.68	12.73	52.35	34.92	0.53	0.35	0.24	0.07
T-11730	14.18	47.33	32.58	20.09	14.02	50.67	35.31	0.49	0.33	0.24	0.08
T-11790	14.94	45.90	28.74	25.36	16.88	48.17	34.95	0.47	0.32	0.25	0.11
T-11810	17.04	48.93	34.42	16.65	18.37	47.11	34.52	0.43	0.30	0.25	0.10
T-11870	18.89	50.04	31.28	18.68	17.14	48.41	34.44	0.45	0.31	0.24	0.12

TT19/TT23: C₁₉ tricyclic terpane/C₂₃ tricyclic terpane; TT21/TT23: C₂₁ tricyclic terpane/C₂₃ tricyclic terpane; TT23/H30: C₂₃ tricyclic terpane/C₃₀αβ-Hopane; TT24/H30: C₂₄ tricyclic terpane/C₃₀αβ-Hopane; TT24/H30: C₂₄ tricyclic terpane/C₃₀αβ-Hopane; TT25/TT26: C₂₅ tricyclic terpane/C₂₆ tricyclic terpane; Ts/(Ts + Tm): 18α(H)-22,29,30-trisnorhopane/18α(H)-22,29,30-trisnorhopane + 17α(H)-22,29,30-trisnorhopane; 29Ts/H30: C₂₉ trisnorhopane/C₃₀αβ-Hopane; M30/H30: C₃₀ moretane/C₃₀αβ-Hopane; O.I.: Oleanane Index (Oleanane/C₃₀αβ-Hopane) × 100; G.I.: Gamacerane Index (Gamacerane/C₃₀αβ-Hopane) × 100; HH32 I.I.: C₃₂ Isomerization Index; HH35/HH34: C₃₅ Homohopane Index; HH35/HH34: C₃₅ Homohopane/C₃₄ Homohopane; TT/PT: Σ Tricyclic Terpane/Σ Pentacyclic Terpane; BNH I.: Bisnorhopane Index (25-Norhopane/C₃₀αβ-Hopane) × 100

Fig. 13 Geochemical correlation between 26/25 tricyclic terpanes versus 24/23 tricyclic terpanes in the organic extracts from rock in Tumaco-1-ST-P, Tumaco basin, Colombia

The diasteranes/steranes ratio is routinely used in geochemical studies to distinguish between carbonate and siliciclastic source rocks. Low values of this ratio in bituminous extracts indicate anoxic carbonate source rocks poor in clays. On the contrary, high diasteranes/steranes ratios are typical of bitumen derived from source rocks containing abundant clays (Cortes et al. 2018). The diasterane/sterane (27-dia/29 α R) ratios for Tumaco-1-ST-P well show values > 2.0 , which clearly indicates a higher diasteranes content over the regular steranes, suggesting that this organic matter was deposited on siliciclastic rocks in a transitional marine-continental environment.

The 20S/(20S + 20R) ratio is one of the maturity parameters more frequently used in petroleum geochemistry. The isomerization of carbon C20 on the C29-5 α (H), 14 α (H), 17 α (H)-sterane causes an increase in the 20S/(20S + 20R) ratio between 0.0 to ≈ 0.5 with an increment of the maturity (equilibrium between 0.52 and 0.55, Seifert and Moldowan 1986) (Cortes et al. 2018). Bitumen in Tumaco-1-ST-P well has values in the range between 0.0 and 0.4 (average 0.13), which indicates a very low maturity. The C29 $\beta\beta/(\beta\beta + \alpha\alpha)$ ratio typically presents its thermal equilibrium between 0.68 and 0.72. Bitumen extracts from Tumaco-1-ST-P rocks show a value around 0.1, confirming that these samples are immature or in the diagenetic stage.

Maturity evolution

Aromatic hydrocarbons

Thermal maturity is the most important process in evaluation of oil and gas potential. Geochemical correlations based on aromatic hydrocarbons can be potentially better than those obtained in the saturated biomarkers fraction due to they are sensitive to differences in thermal maturity from the middle stage to the final part of the window of hydrocarbons generation (Radke 1988). A great variety of geochemical ratios based on the composition of the aromatic fraction has been proposed associated with the relationship between the concentration of the more thermally stable isomers and their counterparts less stable (Radke and Welte 1983; van Aarssen and de Leeuw 1999).

Maturity parameters derived from methylnaphthalenes (MN) are based on the idea that naphthalenes with compound methyl β -substituted are more stable than those with methyl α -substituted. The maturity parameters based on the phenanthrene (P) and methylphenanthrenes (MP) are based on the high stability of the 3-MP and 2-MP compared with 9-MP and 1-MP (Radke and Welte 1983). The isomers of the alkyldibenzothiophenes (MDBT) with a methyl substituent in position 4 are more thermodynamically stable, whereas

isomers with a methyl substituent in position 1, have low stability (Chakhmakhchev et al. 1997).

In Tumaco-1-ST-P bitumen extracts, the aromatic hydrocarbons were identified based on full-scan GC/MS analysis and quantified by GC/MS-SIM mode using the selected ions for alkylnaphthalenes, alkylphenanthrenes, alkyldibenzothiophenes, mono- and triaromatic steroids (Sect. 3.6) comparing the mass fragmentograms with data previously reported (Hughes 1984; Budzinski et al. 1995; van Aarssen and de Leeuw 1999) and with bitumen and crude oils of known composition (e.g., NGS NSO-1 oil sample, NPD-Nigoga) (NPD-Nigoga 2000).

Figure 14 shows the alkylnaphthalenes, alkylphenanthrenes, and alkyldibenzothiophenes fragmentograms for sample T-11610 of Tumaco-1-ST-P well, while Table 4 displays the main geochemical correlation with aromatic results. There is evidence that in the hydrocarbon generation window, the aromatic hydrocarbons show systematic changes with an increment in the thermal maturity (Hughes 1984; Radke and Welte 1983; Alexander et al. 1985). However, in an early stage (diagenesis), the geochemical parameters based on the alkylaromatics, as in Tumaco-1-ST-P, show an irregular behavior due to quick variations in the organic facies, control from source effects, thermal stress, and biodegradation of the O.M.

Methylnaphthalenes are found and widely distributed in the sedimentary organic matter (Tissot and Welte 1984). Their distribution is highly variable among samples (even in the same producer field or in a stratigraphic column) (van Aarssen and de Leeuw 1999). The sesquiterpanes and triterpenoids derived from microorganisms and superior plants appear to be the origin of the MN (Püttman and Villar 1987), where they are produced through isomerization and transmethylation reaction in an environmental rich in acid clays. In Tumaco-1-ST-P, MN ratios vary between 0.25 and 5.19 (mean 1.68 ± 0.73) indicating a high variability in the maturity and suggesting a common origin but different states of thermal maturity consistent with an intense diagenetic biodegradation process. As the thermal maturity increases, the predominance of 2-MN over 1-MN increases. This increment toward the depth must be interpreted as an increase in the maturity toward deeper intervals (Tumaco Fm, late Oligocene). The dimethylnaphthalenes ratios (DNR) vary between 0.03 and 21.5 indicating a wide maturity distribution. Among TMNs, the most abundant isomer for a mixture in equilibrium (highly mature) is the 2,3,6-TMN, and one of the less abundant is the 1,2,5-TMN, which is often the most abundant in immature samples (Budzinski et al. 1995). van Aarssen and de Leeuw (1999) found that the presence of 2,3,6-TMN is very low in the diagenetic stage and increases dramatically in samples highly mature in which this isomer is dominant over the 1,3,7-TMN and 1,3,6-TMN.

The distribution of alkylphenanthrenes can be used as an indicator of source, in addition to its well known use as a parameter of maturity (Armstroff et al. 2006). Differences due to variations in the thermal maturity are in many cases gradual, while changes in the source of the O.M. are characterized by drastic differences. The alkylphenanthrenes distribution is dominated by 2-MP and 9-MP isomers at any stage of maturity. In Tumaco-1-ST-P well, 2-MP and 9-MP are predominant over 1-MP and 3-MP indicating a marine origin (Budzinski et al. 1995).

Methylphenanthrene-1 and -2 indices (MP-1 and MP-2) proposed by Radke and Welte (1983) are perhaps the most widely used indices to determine the maturity based on aromatic hydrocarbons. The utility of this geochemical parameter rests on the relative stability of the various methylphenanthrene isomers. Due to its linear relationship with the vitrinitic reflectance within the generation window, MPI-1 is often used to infer the value of the equivalent vitrinitic reflectance (R_c , %) in crude oils (Radke 1988) and could be used in source rocks and bituminous extracts of outcrops where the vitrinitic reflectance cannot be measured. The MPI-1 values in Tumaco-1-ST-P show an average value of 0.60 and a mean value of R_c of 0.76%.

Since 4-methyldibenzothiophene isomer is more stable than 1-methyldibenzothiophene, the 4-/1-methyldibenzothiophene (MDBTR) was proposed as an indicator of maturity (Radke et al. 1986). This ratio is quite sensitive to the maturity, correlating well with the vitrinitic reflectance and with T_{max} parameter from pyrolysis Rock-Eval in rock samples (Radke 1988). Dzou and Hughes (1993) noted that MDBTR is particularly robust to assess maturity in samples with high thermal maturity (condensates, lighter crudes). The organic extracts of the Tumaco-1-ST-P well presented an average value of 5.40, indicating that the 4-methyldibenzothiophene is in the highest concentration that 1-methyldibenzothiophene. The maturity based on MDBT ratios increases from surface to bottom in the column reaching the highest values in the Tumaco Fm between the early and middle Miocene.

The dibenzothiophene/phenanthrene ratio (DBT/P) is thought to be an indicator of source rock lithology (Radke et al. 1986; Hughes et al. 1995) with carbonates having ratios > 1 and shales < 1 . When this ratio is plotted against Pr/Ph, the depositional paleoenvironment may be inferred regarding microbiological and chemical processes (Hughes et al. 1995). Figure 15 shows a plot of DBT/P versus Pr/Ph associated with rock lithology for a bituminous extract of Tumaco-1-ST-P, indicating that samples fall in the area of a lacustrine and marine shale environment (zones 2 and 3, respectively). The zone 2 suggests a variable lithology of the rock with values of DBT/P < 1 and values of Pr/Ph < 1 and characterizing an lacustrine environment, while the zone 3

Alkyl naphthalenes

◀**Fig. 14** Alkyl naphthalenes, alkylphenanthrenes, dibenzothiophene and alkyl dibenzothiophenes de la muestra T-11610, Tumaco-1-ST-P, Tumaco basin, Colombia (see foot Table 4 for compound identification)

presents a lithology of shale, in an marine environment and $DBT/P < 1$ and Pr/Ph in the range between 1 and 3.

Molecular stratigraphy in Tumaco-1-ST-P

The molecular stratigraphic interpretation allows to conclude that organic facies and lithology in Tumaco-1-ST-P are characterized in Cascajal and Tangareal del Mira Fms. (1000–5000 ft) by a marine-deltaic paleoenvironment with an important terrestrial contribution and varying between deltaic plain and prodelta during the late Miocene as is supported by C_{15}^+ *n*-alkanes profiles, CPI, Pr/Ph , TAR, oleanane index, and tricyclic/pentacyclic terpanes (Internal communication stratigraphy Antek S.A.-Paleoexplorer in ANH-Antek S.A. 2013). At the top of Tumaco Fm (5000–9000 ft) in the late to medium Miocene, the depositional environment was like to the marine delta of the Tangareal del Mira Fm, changing to a marine platform environment at 8000 to 10,000 ft depth in the middle to early Miocene, which is confirmed by high Σ tricyclic terpanes/ Σ pentacyclic terpanes, low oleanane index, high C_{35}/C_{34} homohopanes ratios. Toward the bottom of the column (10,000–12,000 ft), Tumaco Fm was deposited in the late Oligocene under a marine shelf environment, which is supported by $Pr/Ph < 1.0$, $DBT/P < 1.0$, low C_{26}/C_{25} tricyclic terpanes ratios, high C_{24}/C_{23} tricyclic terpanes ratios.

Conclusions

Total organic carbon in samples from Tumaco-1-ST-P presented an average value of 0.95% on a population of 250 samples analyzed, with a variation between 0.09 and 2.30%. This variability suggests a temporal and spatial variations of organofacies in the sedimentary record. Results of Rock–Eval pyrolysis showed that S1 peak varies between 0.02 and 0.80 mg HC/g rock, which classifies the O.M. with a “poor to acceptable” generation potential. S2 peak varied between 0.07 and 10.45 mg HC/g rock (average 1098 ± 1.36 mg HC/g rock). Peak S3 showed values between 0.20 and 7.60 mg CO_2 /g rock, while T_{max} values varied in the range between 328 and 445 °C, which indicates a relative immaturity of the O.M. (diagenetic maturity).

Geochemical correlations based on screening data allowed to conclude that S2/S3 varied in the range between 0 and 10, whereas HI_{pd} presented three major peaks that classified the O.M. quality with a type III and/or type II/III kerogen. This classification would expect that the main

product generated will be crude oil and/or crude oil/gas, special in the deepest intervals of the well. Production index varied between 0.02 and 0.36 classifying these rocks in a immature generation stage. However, the combination of the I.P with other maturity parameters allowing to look, in a more discreet way, that the column covers a wide range of maturity from a kerogen oil–gas-prone type II/III to a kerogen non-generator type IV, indicating that the O.M. in the study does not come from a single and unique kerogen due to the large variation in paleodepositional environments. On the basis of the modified van Krevelen diagram, the type III kerogen, which is responsible for the majority of immature samples from Tumaco-1-ST-P well was characterized to have low H.I (50–200 mg HC/g TOC), low H/C atomic ratios (0.7–1.0), and high O/C values (> 0.3).

Vitrinite reflectance (R_o) varied between 0.1978 and 0.5418% (mean $0.4046 \pm 0.056\%$), suggesting an immature O.M. The maceral groups found were vitrinite, liptinite, and inertinite, which allowed us to identify the following types of macerals: esporinite, cutinite, resinite, alginite, colotelinite, colodetrinite, funginite, exsudinite, exsudatinite, inerto-detrinite, among others. The EOM, % oscillation between 0.0018% and 0.75%, being the highest contents toward the late Oligocene in the Tumaco Fm.

SARA fractionation presented high values for the resin fraction in most of the organic extracts, varying between 17.47 and 62.33%. The asphaltenes varied in a range between 4.65 and 59.02%, the aromatic fraction ranging between 0 and 21.28% is the fraction of which were obtained lower recoveries. Finally, saturated fraction ranged between 4.99 and 43.81%. The Tissot and Welte’s ternary diagram indicates that the organic matter extracted was of naphthenic characteristics.

C_{15}^+ GC/FID analysis of the saturated fraction showed a bimodal distribution in hydrocarbons resolved between *n*- C_{15} and *n*- C_{32} , although some chromatograms extend their distribution to *n*- C_{36} , with a maximum around *n*- C_{19} to *n*- C_{20} suggesting an algal/bacterial input, while the second peak occurs around *n*- C_{29} to *n*- C_{31} , indicating a continental contribution (terrestrial), allowing to conclude that this is a mixed O.M. originated from type II/III kerogen. The geochemical correlations based on C_{15}^+ saturated fraction show a CPI characteristic of a low maturity and marine/continental origin. Pr/Ph ratio suggests a bitumen derived from marine shale, additionally $Pr/Ph < 3.0$, indicating that O.M. was deposited in suboxic to oxic conditions. $Pr/n-C_{17}$ varied between 0.53 and 5.74, while $Ph/n-C_{18}$ ranges between 0.22 and 4.88, indicating low maturity. TAR values suggested that O.M. has an important aquatic algal/bacterial input over terrestrial contributions.

Geochemical correlations based on saturated fraction biomarkers analyzed by GCMS showed that TT21/TT23 present values > 1.0 for most of the samples corroborating the

Table 4 Geochemical ratios based on Aromatic Hydrocarbons in organic extracts from rocks and cuttings in Tumaco-1-ST-P, Tumaco basin, Colombia

Sample	Alkyl naphthalenes			Alkylphenanthrenes		Alkylbenzothiophenes			Monoaromatic and triaromatic steroids		
	MNR	DNR	TMNR	MPR	MPI-1	DBR	MDBTR	DBT/P	TAS/ (MAS + TAS)	26S/28S (TAS)	27R/28R (TAS)
T-1130	1.75	2.15	0.97	0.92	0.61	3.20	2.29	0.23	0.90	0.61	0.99
T-1190	2.33	2.40	0.20	2.30	1.14	3.70	3.29	0.14	0.17	0.35	0.59
T-1290	2.45	2.72	0.12	2.43	1.32	3.09	4.46	0.24	0.53	0.46	0.70
T-2490	2.26	3.57	0.34	1.99	0.67	3.70	2.99	0.14	0.46	0.45	0.81
T-2550	1.09	3.17	0.28	2.16	0.84	4.38	4.34	0.16	0.36	0.34	0.49
T-2570	1.61	5.67	0.41	1.96	0.85	5.05	3.76	0.14	0.34	0.39	0.46
T-2590	1.50	3.23	0.30	2.35	0.92	3.95	3.81	0.11	0.43	0.38	0.42
T-2610	1.52	2.06	0.24	1.81	0.68	2.79	3.29	0.12	0.10	0.96	1.15
T-4130	1.37	2.21	0.41	1.95	0.49	3.13	2.14	0.28	0.30	1.21	0.57
T-4330	0.70	1.92	0.36	1.64	0.63	3.65	1.83	0.23	0.34	1.27	0.32
T-4410	0.96	3.44	0.45	1.79	0.60	3.97	2.06	0.30	0.39	1.18	0.36
T-4470	0.66	1.11	0.40	1.53	0.64	1.96	1.45	0.28	0.40	1.47	0.49
T-5030	1.47	1.49	0.37	1.86	0.71	2.47	3.49	0.11	0.64	0.49	0.83
T-5394	2.18	9.91	0.33	1.79	0.91	5.02	2.28	0.10	0.09	0.79	0.18
T-5475	1.85	2.96	0.36	1.60	0.47	2.67	2.64	0.15	0.15	1.30	1.18
T-5509	1.07	5.48	0.47	1.43	0.44	3.36	4.75	0.18	0.34	3.41	0.09
T-5560	1.94	4.94	0.32	0.94	0.50	3.56	5.40	0.14	0.18	3.01	0.08
T-5570	1.13	4.63	0.52	1.84	0.87	4.19	3.60	0.13	0.14	0.76	0.65
T-5650	1.41	1.87	0.22	2.15	1.00	2.54	3.25	0.17	0.22	0.92	1.16
T-5750	5.19	21.47	0.21	1.93	1.21	4.06	4.80	0.17	0.10	1.00	1.54
T-5810	1.72	1.66	0.41	2.05	0.86	2.81	3.46	0.13	0.11	1.12	1.44
T-5890	2.01	1.18	0.37	1.94	0.67	2.41	3.36	0.12	0.12	0.99	1.64
T-5910	2.25	0.99	0.26	1.92	0.77	1.82	3.31	0.18	0.16	0.91	1.83
T-5950	2.01	1.27	0.38	2.00	0.41	2.53	3.47	0.10	0.13	1.20	1.97
T-5990	2.69	1.85	0.24	1.70	0.50	2.97	3.06	0.10	0.16	1.30	1.80
T-6010	2.40	0.86	0.20	1.84	0.50	1.59	3.11	0.10	0.18	1.02	2.01
T-6070	1.58	1.96	0.42	1.71	0.38	3.29	3.37	0.08	0.12	1.19	1.90
T-6090	2.06	2.02	0.25	1.63	0.60	3.12	2.01	0.10	0.11	1.54	6.10
T-6110	1.89	1.31	0.23	1.67	0.58	2.39	3.78	0.15	0.15	0.94	1.89
T-6130	1.27	1.36	0.22	2.36	0.49	2.21	3.68	0.11	0.14	1.02	1.85
T-6150	1.44	0.74	0.20	1.72	0.64	1.50	3.36	0.12	0.12	1.16	1.96
T-6170	1.78	1.90	0.38	1.73	0.58	3.63	3.00	0.13	0.13	0.97	2.01
T-6190	2.97	1.38	0.22	1.90	0.69	2.77	3.03	0.11	0.13	1.19	1.93
T-6210	1.01	2.59	0.38	2.16	0.69	3.76	3.56	0.13	0.24	0.60	0.63
T-6250	1.92	1.36	0.34	1.97	0.65	2.22	3.80	0.14	0.17	0.98	1.82
T-6310	2.19	1.25	0.31	2.13	0.47	2.40	4.39	0.10	0.28	0.75	1.64
T-6390	1.76	0.79	0.23	2.29	0.72	1.52	4.17	0.08	0.15	0.82	1.74
T-6430	2.22	2.20	0.21	1.95	0.90	2.91	3.75	0.11	0.19	0.99	1.77
T-6550	2.18	1.24	0.29	2.02	0.74	2.26	3.35	0.10	0.16	1.00	1.97
T-6570	2.37	1.42	0.21	2.13	0.78	2.40	3.60	0.10	0.16	1.11	2.02
T-6590	1.82	0.94	0.22	1.96	0.72	1.82	3.65	0.11	0.18	0.88	1.82
T-6630	1.17	0.72	0.20	2.00	0.67	1.58	3.70	0.10	0.14	0.89	1.83
T-6710	0.82	2.82	0.46	2.02	0.64	4.23	3.26	0.14	0.07	1.16	2.41
T-6750	1.50	1.84	0.41	1.93	0.71	3.12	3.47	0.12	0.09	0.94	1.97
T-6770	2.00	1.21	0.36	1.88	0.67	2.42	3.15	0.12	0.08	0.92	2.98
T-6790	0.96	1.79	0.41	1.93	0.66	3.19	3.14	0.11	0.11	1.17	2.49

Table 4 (continued)

Sample	Alkyl naphthalenes			Alkylphenanthrenes		Alkylbenzothiophenes			Monoaromatic and triaromatic steroids		
	MNR	DNR	TMNR	MPR	MPI-1	DBR	MDBTR	DBT/P	TAS/ (MAS + TAS)	26S/28S (TAS)	27R/28R (TAS)
T-6810	0.88	2.03	0.42	1.88	0.65	3.41	3.14	0.11	0.07	1.20	2.66
T-6830	1.77	1.17	0.25	1.84	0.65	2.14	2.95	0.10	0.07	1.36	2.46
T-6850	1.39	2.13	0.44	1.92	0.69	3.16	3.34	0.11	0.06	0.81	1.32
T-6890	1.95	1.11	0.31	1.90	0.70	2.04	3.08	0.11	0.09	0.92	1.89
T-7050	0.84	1.06	0.31	2.17	0.75	2.68	3.30	0.10	0.12	1.02	1.98
T-7110	2.37	1.00	0.18	1.95	0.72	2.32	3.31	0.11	0.09	0.88	1.80
T-7130	2.47	1.53	0.19	1.70	0.67	3.07	3.15	0.18	0.08	0.88	1.97
T-7210	2.74	2.82	0.10	1.55	0.56	4.68	2.90	0.13	0.08	0.96	2.20
T-7230	0.89	2.75	0.10	1.57	0.64	5.23	2.84	0.15	0.16	1.02	2.19
T-7290	1.99	1.07	0.25	1.71	0.51	2.40	2.71	0.15	0.07	1.06	2.31
T-7310	1.74	1.06	0.43	2.30	0.68	2.03	2.99	0.12	0.11	0.93	2.29
T-7330	1.91	1.16	0.30	2.06	0.45	2.29	3.29	0.16	0.16	0.91	2.10
T-7450	1.94	4.35	0.17	1.88	1.05	4.87	2.58	0.09	0.12	0.84	1.39
T-7470	1.47	1.14	0.20	1.83	0.74	2.56	3.14	0.11	0.13	0.93	1.86
T-7591	1.33	3.98	0.14	1.31	0.71	7.24	1.56	0.22	0.06	0.45	2.37
T-7693	2.17	1.35	0.52	1.42	0.61	2.05	1.83	0.24	0.20	0.47	0.61
T-7712	2.04	3.69	0.41	1.15	0.49	3.02	2.45	0.18	0.10	0.71	1.50
T-7777	2.51	10.20	0.26	1.30	0.58	5.70	1.64	0.14	0.08	0.94	3.36
T-7861	1.30	3.51	0.51	0.99	0.52	3.67	1.98	0.25	0.10	0.36	3.13
T-7895	0.41	0.82	0.63	1.65	0.16	1.47	6.75	0.01	0.26	0.48	0.83
T-7911	1.87	0.49	0.59	1.62	0.19	1.18	9.05	0.01	0.30	0.21	0.59
T-7928	1.48	0.73	0.60	1.50	0.21	1.40	9.92	0.01	0.24	0.52	1.49
T-8084	1.82	2.11	0.40	1.29	0.32	2.00	5.29	0.02	0.18	0.34	0.52
T-8145	2.08	5.63	0.25	1.36	0.43	4.30	4.09	0.03	0.10	0.45	0.47
T-8211	1.79	0.34	0.56	2.45	0.14	0.87	4.06	0.01	0.14	1.76	0.67
T-8233	3.04	1.02	0.34	2.32	0.15	1.61	8.62	0.01	0.30	0.76	0.52
T-8243	1.09	0.24	0.64	2.11	0.19	0.97	11.18	0.01	0.34	0.41	0.98
T-8255.5	2.18	1.03	0.44	1.87	0.36	1.67	4.75	0.12	0.15	0.61	2.22
T-8275	0.47	0.22	0.75	1.55	0.29	1.05	5.97	0.12	0.27	0.28	1.07
T-8302.5	0.25	0.30	0.68	2.10	0.16	0.94	15.26	0.01	0.34	1.60	0.43
T-8312.5	1.63	0.13	0.59	1.96	0.17	0.78	17.92	0.01	0.38	0.75	1.84
T-8317	2.05	0.13	0.41	2.16	0.18	0.90	16.53	0.01	0.38	0.34	0.50
T-8332.5	1.96	0.72	0.37	1.80	0.15	1.44	10.82	0.01	0.53	0.55	1.63
T-8338	2.01	0.37	0.51	3.57	0.29	0.96	14.70	0.02	0.39	0.45	1.19
T-8354.5	0.28	0.19	0.66	2.17	0.16	1.02	15.36	0.01	0.35	0.37	1.15
T-8370.5	0.29	0.32	0.67	1.72	0.16	1.18	11.54	0.01	0.47	0.38	0.56
T-8380	1.93	0.90	0.15	2.11	0.70	1.74	2.95	0.17	0.22	0.50	0.68
T-8431	0.38	0.43	0.68	1.55	0.16	1.24	10.02	0.01	0.59	0.28	0.63
T-8448	0.49	0.28	0.65	1.68	0.15	1.05	9.57	0.01	0.49	0.33	0.56
T-8850	2.24	0.78	0.23	1.92	0.25	1.69	8.16	0.03	0.35	0.56	0.77
T-8870	2.06	0.15	0.41	1.72	0.23	0.74	10.98	0.02	0.47	0.57	0.63
T-8890	1.25	3.20	0.45	3.12	1.04	3.71	11.01	0.09	0.31	0.22	1.47
T-9150	3.54	1.67	0.15	2.05	0.66	2.81	3.66	0.16	0.11	0.68	1.87
T-9790	1.90	0.86	0.27	1.84	0.66	1.85	3.75	0.08	0.15	0.61	1.39
T-10079	0.99	0.29	0.63	1.38	0.16	0.98	14.10	0.01	0.07	0.20	0.30
T-11610	1.80	6.22	0.44	2.79	1.00	4.66	8.76	0.15	0.17	0.27	1.35
T-11650	1.13	4.67	0.49	1.96	0.84	4.05	11.25	0.11	0.25	0.18	1.35

Table 4 (continued)

Sample	Alkyl naphthalenes			Alkylphenanthrenes		Alkylbenzothiophenes			Monoaromatic and triaromatic steroids		
	MNR	DNR	TMNR	MPR	MPI-1	DBR	MDBTR	DBT/P	TAS/ (MAS + TAS)	26S/28S (TAS)	27R/28R (TAS)
T-11670	1.53	3.36	0.44	2.91	1.08	3.72	14.06	0.09	0.23	0.25	1.36
T-11690	1.90	0.62	0.22	1.96	0.28	1.55	9.90	0.02	0.32	0.46	1.12
T-11710	1.13	3.85	0.51	3.04	1.09	3.71	8.24	0.10	0.36	0.19	1.31
T-11730	1.46	4.92	0.51	2.88	1.02	4.66	11.13	0.09	0.26	0.22	1.47
T-11790	1.45	2.24	0.38	2.70	1.03	3.18	8.16	0.10	0.19	0.29	1.62
T-11810	1.21	2.59	0.43	2.49	0.13	3.53	7.47	0.01	0.13	0.34	1.60
T-11870	1.10	3.05	0.44	3.05	1.07	3.64	8.42	0.10	0.22	0.28	1.61

MNR = [2MN]/[1MN], Methyl naphthalene ratio; DNR = [2,6-DMN] + [2,7-DMN]/[1,5-DMN], Dimethyl naphthalene ratio; MPR = [2-MP]/[1-MP], Methylphenanthrene ratio; MPI-1 = 1.5[2-MP] + [3-MP]/[P] + [1-MP] + [9-MP], Methylphenanthrene Index-1; MPI-2 = 3[2-MP]/[P] + [1-MP] + [9-MP], Methylphenanthrene Index-2; DBTR-1 = [2- + 3-MDBT]/[1-MDBT], Dibenzothiophene ratio-1; DBTR-2 = [4-MDBT]/[DBT], Dibenzothiophene Ratio-2; DBTR-4 = [1-MDBT]/[DBT], Dibenzothiophene ratio-4; MDBTR = [4-MDBT]/[1-MDBT], Methyl dibenzothiophene ratio; MDBTR-1 = [2,4-DMDBT]/[1,4-DMDBT], Dimethyldibenzothiophene ratio-1; MDBTR-2 = [4,6-DMDBT]/[1,4-DMDBT], Dimethyldibenzothiophene ratio-2; Ro = Vitritine Reflectance; – = data not available

Fig. 15 Geochemical correlation between DBT/P versus Pr/Ph in the organic extracts from rock in Tumaco-1-ST-P, Tumaco basin, Colombia

marine origin associated with prokaryotic organisms (algal/bacterial). However, in the deepest intervals (late Oligocene of Tumaco Fm), TT21/TT23 present values slightly higher than 1.0, indicating a combined and alternated contribution of bacterial/algal with less terrestrial contribution. $C_{24}Te/H_{30}$ ratios showed values < 0.44 , which dismisses a carbonate or evaporitic environment but supports a marine shale or marine-deltaic depositional environment. TT25/TT26 ratios

in all samples, without exceptions, showed values > 1 , which confirms a marine origin.

$T_m \leq T_s$ suggests a diagenetic maturity. $T_s/(T_s + T_m)$ ratios presented values < 0.7 , with a high amount of results ranging between 0.02 and 0.5 suggesting a low maturity. When this parameter is used as an depositional environment indicator, the average value of 0.40 found in the Tumaco-1-ST-P well indicates a marine-deltaic environment. The oleanane index $> 20\%$ corroborates a terrestrial O.M. input

with marine contribution and the Miocene–Pliocene as the age of this organic matter. Many samples in the Tumaco-1-ST-P well showed a high concentration of gammacerane and low Pr/Ph ratios indicating a high salinity and saline stratification of the water column during deposition.

The $\beta\beta$ -steranes values decreased as $\%C27\alpha\beta\beta > \%C28\alpha\beta\beta > \%C29\alpha\beta\beta$, corroborating a marine environment with minor terrestrial contributions. $C27\ \alpha\alpha$ -R, $C28\ \alpha\alpha$ -R and $C29\ \alpha\alpha$ -R (biosteranes) are present in high concentrations confirming a thermal immaturity of these samples. $C29\ \alpha\alpha\alpha$ - (S/R) ratios present values < 1.0 , which indicates that the $\alpha\alpha$ -R-sterane configurations are in higher concentrations over the $\alpha\alpha$ -S configuration (geosteranes, more stable thermodynamically) and consequently highly immature. Dias-teranes/steranes ($27\text{-DIA}/29\ \alpha\alpha$ -R) ratios in Tumaco-1-ST-P well presented values > 2.0 , indicating that this organic matter was deposited on siliclastic rocks in a transitional marine-terrestrial environment. $20S/(20S + 20R)$ ratios are in the range between 0.0 and 0.4 (average 0.13), which indicates a very low maturity, while the $C29\beta\beta/(\beta\beta + \alpha\alpha)$ ratios with a value around 0.1 indicate that the O.M. studied is below the equilibrium range (below hydrocarbons generation window).

The geochemical correlations based on aromatic hydrocarbons showed that methylnaphthalene ratios (MNR) and trimethylnaphthalene ratios (TMNR) presented a high variability in the samples maturity suggesting a common origin but different stages of thermal maturity consistent with an intense diagenetic biodegradation in progress. The mono-aromatic steroids (MAS) decreased in concentration with depth (Pliocene to Oligocene) suggesting a light increment in the thermal maturity. On the other hand, the concentration of triaromatic steroids (TAS) increased proportionally with depth as a result of the MAS transformation into its respective TAS counterpart. This maturity model, although in the diagenetic stage, is consistent with a maturation process in progress in the Tumaco basin, where the Oligocene (Tumaco Fm) showed the greater maturity.

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