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https://doi.org/10.1590/2317-4889202320220008

BJGEO Brazilian Journal of Geology

Thermal effect of igneous intrusions on organic-rich Irati Formation and the implications for petroleum systems: a case study in the Paraná Basin, Brazil

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Abstract

The organic geochemistry of organic-rich facies including shales, marls, and carbonates (Assistência Member) of the Irati Formation, Paraná Basin, Brazil, were analyzed to evaluate the thermal effects of igneous intrusions upon the kerogen present in these facies. Total organic carbon (TOC) content and hydrocarbon source potential (S_2) of the Irati source rocks range from 0.03 to 20.4% and 0.01 to 112.1 mg HC/g rock, respectively, indicating excellent potential as a source for hydrocarbon generation. Hydrogen index (HI) values reveal that the kerogen is predominantly type I (HI: up to 892.6 mg HC/g TOC) and, therefore, an oil source, except for samples having low TOC content due to severe maturation caused by the heat from diabase intrusions. The thickness of igneous intrusions in the 64 wells investigated in this study ranged from 2 to 231 m. They clearly had a major impact on TOC, HI, and S_2 values, which decrease in the vicinity of intrusions, indicating a gradual increase in maturation toward the igneous body. In wells without the influence of igneous intrusions, T_{max} values of Rock-Eval pyrolysis and %Ro indicate that the organic matter is immature for the generation of hydrocarbons.

KEYWORDS: Irati Formation; atypical petroleum system; igneous intrusion; thermal maturity; organic-rich shale.

INTRODUCTION

Numerous sedimentary basins worldwide host voluminous igneous intrusive complexes consisting of dikes, sills, and laccoliths (Galushkin 1997, Gonzaga *et al.* 2000, Othman *et al.* 2001, Araújo *et al.* 2000, Zhu *et al.* 2007, Aarnes *et al.* 2011, Cioccari 2018). Petroleum systems subjected to maturation processes for hydrocarbon generation other than burial and subsidence have been classified as atypical by Magoon and Dow (1994).

Heating of organic-rich rocks could lead to maturation and even overmaturation of organic matter and generation of hydrocarbons (Galushkin 1997, Meyers and Simoneit 1999, Araújo *et al.* 2000, Cooper *et al.* 2007, Souza *et al.* 2008, Monreal *et al.* 2009, Aarnes *et al.* 2015, Arora *et al.* 2017, Martins *et al.* 2020, Spacapan *et al.* 2018, 2020). The effects of thermal maturation of igneous bodies on source rocks have been well described and show different ranges of maturation that vary with distance and intrusive thickness (Dow 1977, Zalán *et al.* 1990, Araújo *et al.* 2000). Calculations obtained through computational modeling suggest that intrusion may affect the degree of maturity of organic matter in host rocks, showing different maturity ranges varying with the intrusive distance and thickness (Simonet *et al.* 1981, Gilbert *et al.* 1985, Galushkin 1997, Othman *et al.* 2001, Cooper *et al.* 2007, Souza *et al.* 2008, Thomaz Filho *et al.* 2008, Santos *et al.* 2009, Spacapan *et al.* 2018, 2020). As the distance between igneous intrusions and source rocks decreases, the following observations have been reported: loss of organic carbon and a gradual decrease in the total organic carbon (TOC) content and parameters derived from Rock-Eval pyrolysis, such as S_1, S_2 and hydrogen index (HI) (Araújo *et al.* 2000, Agirrezabala *et al.* 2014, Spacapan *et al.* 2018, López *et al.* 2019, Martins *et al.* 2020, Oliveira *et al.* 2022).

Local intrusion-induced maturation of sedimentary formations has been documented in the Paraná Basin in Brazil (Cerqueira and Santos Neto 1986, Araújo *et al.* 2000, Thomaz Filho *et al.* 2008, Santos *et al.* 2009, Loutfi *et al.* 2010, Euzébio *et al.* 2016, Cioccari and Mizusaki 2019, Almeida *et al.* 2020, Oliveira *et al.* 2022). In certain regions, the organic facies of the Irati Formation have reached thermal maturation due to the influence of the high heat flux caused by the igneous intrusions from Mesozoic magmatism called the Serra Geral Formation. This has led to an atypical maturation process of the organic matter, which allowed the generation, migration, and accumulation of hydrocarbons (Cerqueira and Santos Neto 1986, Araújo *et al.* 2000, Santos *et al.* 2009, Loutfi *et al.* 2010, Martins *et al.* 2020, Teixeira *et al.* 2020, Oliveira *et al.* 2022).

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The Paraná Basin contains Permian sedimentary rocks enriched in organic matter. The results of geochemical analyses indicate that the carbonates and shales (Assistência Member) of the Irati Formation are excellent source rocks (Cerqueira and Santos Neto 1986, Milani and Zalán 1999, Araújo 2001, Milani *et al*. 2007, Euzébio *et al*. 2016, Holanda *et al*. 2018, López *et al*. 2019). These shales and carbonates contain predominantly type I kerogen and have an average TOC content that varies between 8 and 13%, reaching up to 23% in the southern portion of the basin (Araújo *et al*. 2000, Araújo 2001, Santos *et al*. 2009, Loutifi et al 2010, Euzébio *et al*. 2016, Reis *et al*. 2018). These shales are interspersed by carbonate rocks, which exhibit several oil shows on the surface and mainly in the subsurface (Assistência Member). In addition, these rocks are immature in terms of hydrocarbon generation along the basin extension direction (Santos Neto 1993, Araújo 2001).

The use of Rock-Eval pyrolysis parameters, TOC determination, vitrinite reflectance measurement, and other analyses are very efficient in geochemical research to evaluate rock parameters required for hydrocarbon generation (Peters *et al*. 2015, Owusu *et al*. 2019). One of the most important components in petroleum exploration is the study of the source rock, which requires knowledge of the kerogen type. The necessary measurement parameters are obtained when the samples are subjected to pyrolysis. HI and oxygen index (OI) are parameters commonly used to classify organic matter into ranges conducive to oil, gas, or oil and gas generation (Peters and Cassa 1994).

The aim of this study is to characterize the hydrocarbon source rock potential and examine the patterns of this atypical petroleum system, emphasizing the role of igneous intrusions in the maturation and hydrocarbon generation of the Irati Formation source rocks.

GEOLOGICAL SETTING

The Paraná Basin is a wide intracratonic sedimentary-magmatic basin located in South America, covering areas in Brazil, Paraguay, Argentina, and Uruguay, totaling an area of 1.5 million square kilometers, with an extension of approximately 1.1 million square kilometers, mainly in the south-central region of Brazil (Zalán *et al*. 1990, Milani *et al*. 2007).

The basin developed during the Paleozoic and Mesozoic, and sedimentary basin infilling was controlled by tectonic-eustatic cycles linked to the evolution of Western Gondwana. The stratigraphic record ranges from the Upper Ordovician to the Upper Cretaceous, in a period between 460 and 65 million years ago. The basin has an oval shape, is 1,750 km long and 900 km wide, with the longer axis exhibiting an NNE-SSW direction, and the section with the largest thickness (7,000 m) is located in its depocenter (Zalán *et al*. 1990, Milani *et al*. 2007).

Milani *et al*. (1994, 2007) divided the basin filling history into a set of six order sequences, or supersequences, limited by regional unconformities, ranging from Ordovician to Cretaceous (Fig. 1). These unconformities represent long periods of erosion and a halt in sedimentation. The supersequences are described as follows (Fig. 1): Rio Ivaí (Upper Ordovician to Lower Silurian), Paraná (Lower Devonian to Upper Devonian), Gondwana I (Upper Carboniferous to Upper Permian), Gondwana II (Middle Triassic to Upper Triassic), Gondwana III (Upper Jurassic to Lower Cretaceous), and Bauru (Lower Cretaceous to Upper Cretaceous). The first three supersequences are represented by sedimentary successions that represent transgressive-regressive cycles linked to relative sea-level oscillations during the Paleozoic, while the others correspond to continental sedimentary packages associated with igneous rocks (Milani *et al*. 1994).

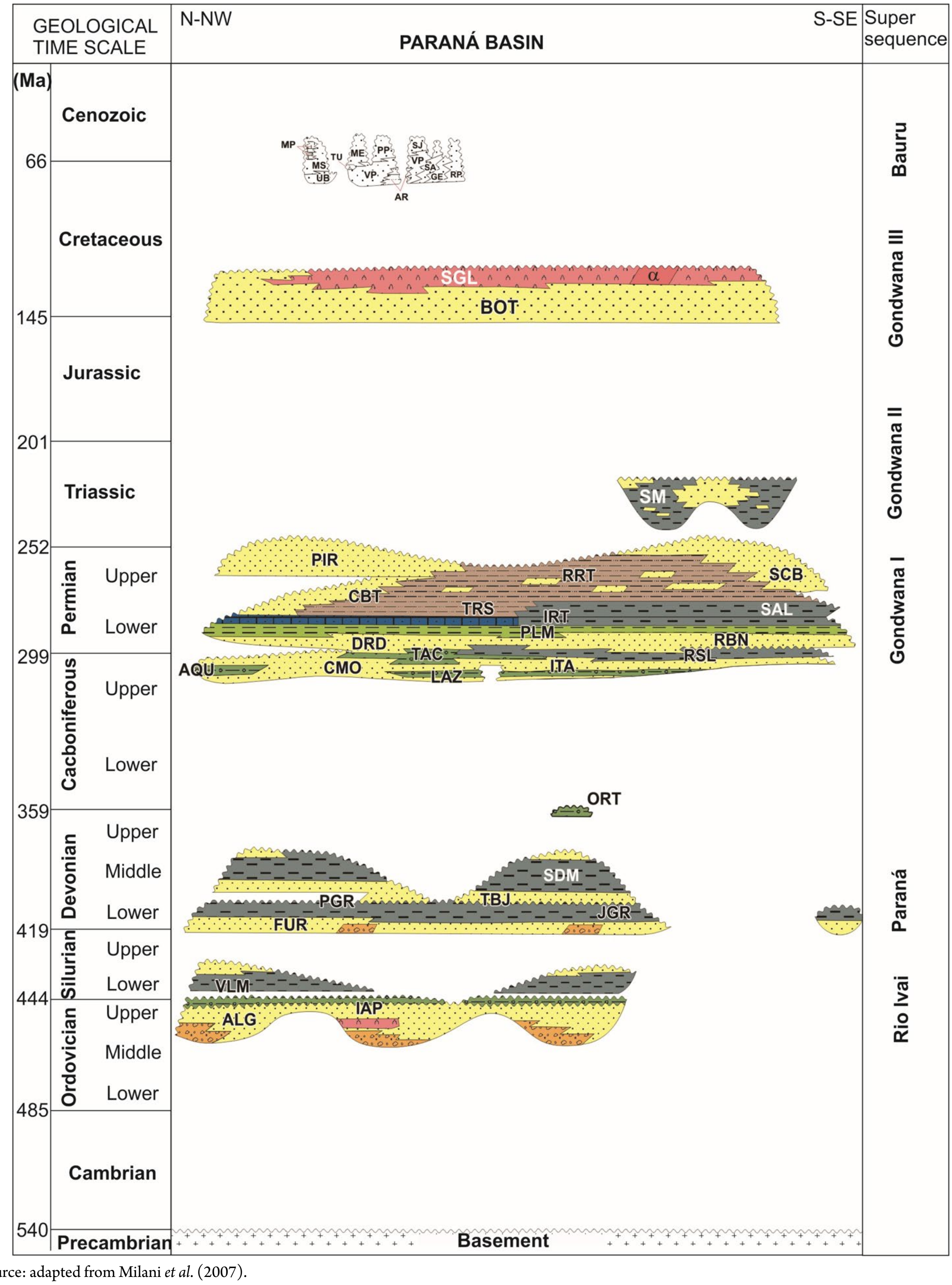
The Rio Ivaí Supersequence is composed of fluvial sandstones associated with Upper Ordovician glaciation, marine shales, and diamictites of the Alto Garças, Iapó, and Vila Maria formations, respectively, and by the Três Lagoas basalt. The Paraná Supersequence features the marine sandstones of the Furnas Formation and the shales of the Ponta Grossa Formation. The Gondwana I Supersequence includes the continental sandstones and diamictites of the Itararé Group; the deltaic sandstones of the Rio Bonito Formation; the marine shales of the Palermo Formation; the marine shales and carbonates of the Irati Formation; the marine to continental siltstones of the Serra Alta, Teresina, and Rio do Rasto Formations; and the fluvial and eolian sandstones of the Pirambóia Formation. This sequence has the largest volume of sedimentary rocks in the basin, with a thickness that reaches 2,500 m.

The Gondwana II Supersequence is represented by the fluvio-lacustrine sandstones of the Santa Maria Formation. The Gondwana III Supersequence contains the eolian sandstones of the Botucatu Formation and the igneous rocks of the Serra Geral Formation. The Bauru Supersequence includes the conglomerates and the alluvial-fluvial and eolian sandstones of the Bauru Group.

The stratigraphic interval studied here (the Irati Formation) corresponds to the Gondwana I Supersequence. The Irati Formation (Permian), with an age of 277.26 ± 0.62 Ma based on U-Pb zircon dating (Bastos *et al*. 2021), comprises organic-rich shales, dolomites, limestones, and siltstones that occupy an area of 700,000 km^2 and have a maximum thickness of 70 m (Milani *et al*. 2007). In the northern part of the Paraná Basin, the Irati Formation is subdivided into two stratigraphic units. The sequence of shales and siltstones at the base of the formation forms the Taquaral Member, which was deposited in a suboxic to oxic marine environment, with significant input of terrestrial organic matter. This is overlain by the Assistência Member characterized by a section of carbonates interspersed by organically rich bituminous shales deposited in a restricted anoxic marine environment (Santos Neto 1993, Milani *et al*. 1994, Alferes *et al*. 2011, Bastos *et al*. 2021).

SAMPLES AND METHODS

Data from 64 wells provided by the National Petroleum Agency (ANP) for the GEOQPETROL Project were selected across a portion of the Paraná Basin to improve spatial resolution (Fig. 2). The data were analyzed by many companies



Source: adapted from Milani *et al.* (2007).

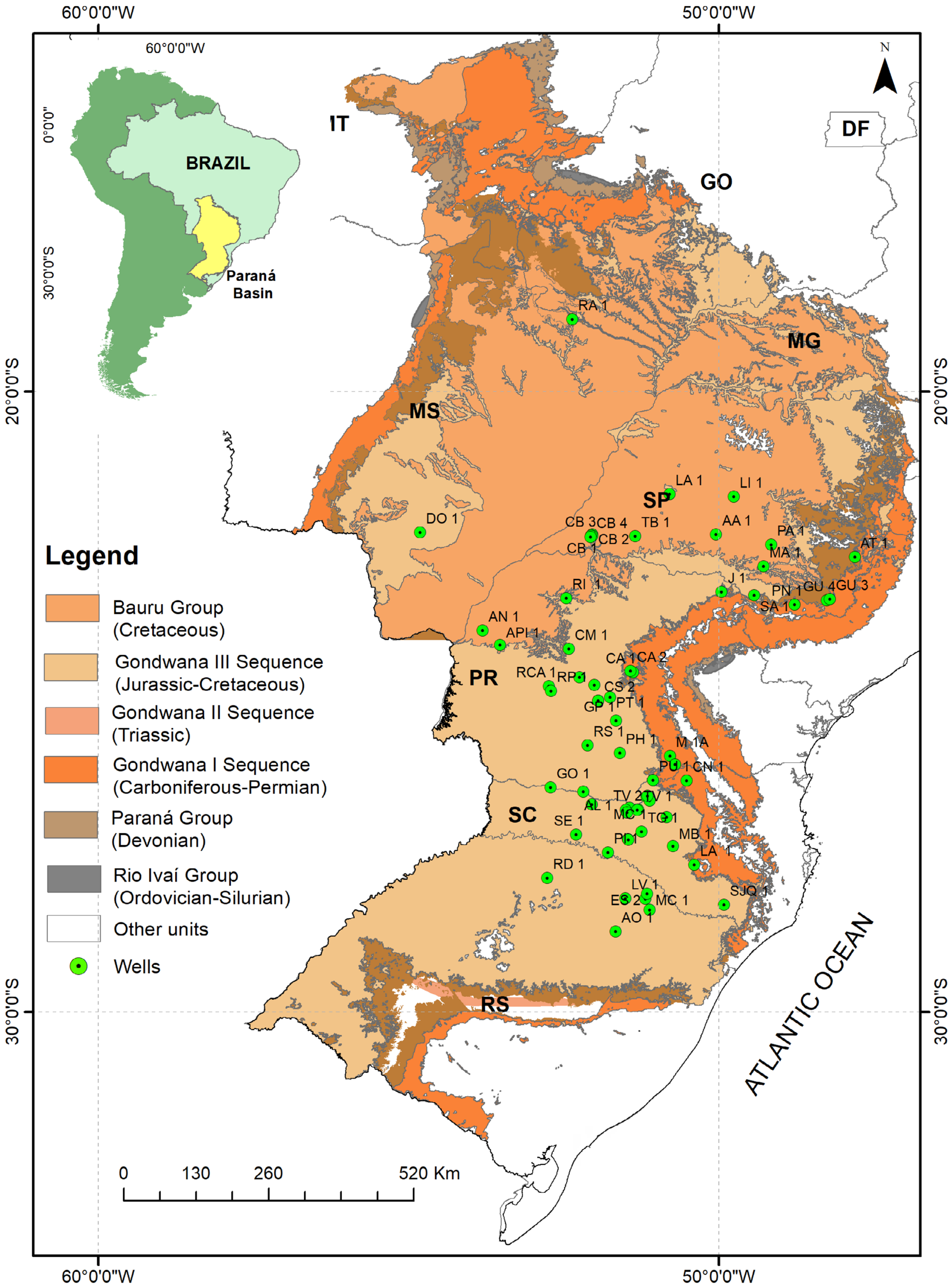
ALG: Alto Garças; IAP: Iapó; VLM: Vila Maria; FUR: Furnas; PGR: Ponta Grossa; AQU: Aquidauana; LAZ: Lagoa Azul; CMO: Campo Mourão; TAC: Taciba; RBN: Rio Bonito; PLM: Palermo; IRT: Irati; SAL: Serra Alta; TRS: Teresina; CBT: Corumbataí; RRT: Rio do Rasto; PIR: Piramboia; SCB: Sanga do Cabral; SM: Santa Maria; BOT: Botucatu; SGL: Serra Geral; JGB: Jaguariaíva; TBJ: Tibagi; SDM: São Domingos; ORT: Diamictito Ortigueira; RSL: Rio do Sul.

Figure 1. Simplified stratigraphic column of the Paraná Basin.

using different equipment models over many years. All wells contained a full set of data, including organic carbon (TOC) and insoluble residue (IR) contents, as well as Rock-Eval pyrolysis data, and some wells contained vitrinite reflectance data. A total of 547 samples, mainly from the Irati Formation, were analyzed.

Total organic carbon

The procedure used for TOC analysis consists in the removal of carbonates from the samples with 50% hydrochloric acid, which were then analyzed by LECO equipment, thus providing information on the TOC content expressed as a percentage by weight in relation to the original sample and



Source: adapted from the Companhia de Pesquisa de Recursos Minerais (CPRM 2019).

Figure 2. Geological map depicting wells with samples in the Irati Formation, Paraná Basin, Brazil.

the IR (IR = amount of sample obtained after removal of carbonates). The TOC and IR values were plotted against sample depth, providing a semiquantitative assessment of the organic matter concentration in the sedimentary layers and an evaluation using Peters and Cassa's (1994) scale.

Rock-Eval pyrolysis

Understanding the organic geochemistry of source rock is critical for the determination of the hydrocarbon generation potential. Source rock geochemistry is typically analyzed by pyrolysis and oxidation using a Rock-Eval 6 or similar instrument.

Based on TOC content, selected samples were analyzed by Rock-Eval pyrolysis to determine S_1 (mg HC/g rock), i.e., free hydrocarbons, S_2 (mg HC/g rock), i.e., potential hydrocarbons, S_3 (mg CO_2/g rock), and the temperature at which the maximum S_2 value occurs (T_{max}, °C). HI (mg HC/g TOC) and OI (mg CO_2/g TOC) were also calculated and used to determine the kerogen type. A detailed description of the programmed pyrolysis technique can be found in Espitalie *et al.* (1977), Behar *et al.* (2001), and Peters and Cassa (1994). Based on the values of S_2, HI, and T_{max}, semiquantitative assessments of the hydrocarbon generation potential and the type and stage of thermal evolution of the organic matter were performed.

Vitrinite reflectance

Vitrinite reflectance (%Ro) analysis data from the well samples were compiled from internal ANP reports and the work of Araújo (2001) to evaluate the thermal maturity of the Irati Formation. The low value of %Ro measurements is due to the lack of vitrinite particles in the Irati Formation because of the amorphous composition of its organic matter.

RESULTS AND DISCUSSION

The average results of the analyzed samples are shown in Table 1 in terms of geochemical data on TOC, IR, S_2, HI, T_{max}, production index (PI), and %Ro.

Table 1. Average values of total organic carbon content, vitrinite reflectance, and Rock-Eval pyrolysis data for the Irati Formation (Assistência Member) samples in the selected wells in the Paraná Basin, Brazil.

Wells	%TOC	%IR	Intrusion (m)	%Ro	Rock-Eval				
					S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	T_{max} (°C)	HI (mg HC/g TOC)	PI
1API 1 PR	1.14	86	169	-	0.06	0.06	419	6	0.50
1AT 1 SP	4.64	75	0	-	1.52	15.92	417	345	0.09
1BB 1 PR	8.01	96	0	-	4.38	42.03	438	519	0.10
1CA 1 PR	0.35	86	26	1.58	0.20	0.10	-	44	-
1CA 2 PR	2.05	79	0	0.50	1.54	27.36	424	512	0.05
1CS 2 PR	1.16	-	4	1.45	0.32	0.13	358	12	0.74
1ES 1 RS	3.83	77	10	0.58	1.77	4.02	417	149	0.35
1ES 2 RS	5.06	77	0	0.25*	2.32	31.27	423	525	0.11
1GO 1 SC	1.43	-	115	1.44	0.10	0.06	-	3	0.60
1GP 1 PR	1.40	85	6	0.74-0.92	0.29	2.06	435	128	0.10
1GU 4 SP	1.94	72	2	-	1.35	1.62	383	85	0.47
1HV 1 SC	4.78	-	34	-	0.26	0.03	-	-	-
1J1 PR	0.96	-	27	-	1.80	1.40	438	74	0.59
1M 1 A PR	4.14	81	0	-	2.16	6.34	423	174	0.31
1MA 1 SP	3.17	68	3	-	0.27	1.76	466	70	0.20
1MB 1 SC	3.64	87	4	-	0.56	23.01	427	417	0.20
1MC 1 RS	2.24	-	15	1.35	0.22	0.59	444	12	0.48
1MC 2 SC	2.48	77	14	-	0.52	0.20	-	8	0.72
1PA 1 SP	1.20	-	6	-	-	3.37	420	274	-
1PH 1 PR	0.63	79	15	-	0.31	0.16	351	12	0.71
1PT 1 PR	1.02	-	3	0.59-1.04	0.80	2.15	431	143	0.32
1RC 1 PR	3.91	51	0	-	0.22	13.46	426	346	0.03
1RCA 1 PR	0.23	84	58		-	-	-	-	-
1RCH 1 SC	4.20	-	138	2.39	-	-	-	-	-
1RO 1 PR	5.48	-	0	0.53-0.63	1.83	23.49	434	332	0.10
1RS 1 PR	0.21	-	155	1.80-3.00*	0.22	0.01	-	5	0.67
1SA 1 SP	2.56	76	3	0.70	2.87	12.15	409	444	0.25
1SE 1 SC	2.47	-	20	1.80*	0.19	0.34	-	6	0.76
1SJQ 1 SC	2.89	75	6		0.98	4.58	428	117	0.35
1TP 1 SC	2.94	-	6	0.79-0.94	1.14	0.53	375	17	0.65
1TP 2 SC	1.26	83	5	-	0.47	7.98	-	-	0.78
1TP 3 SC	2.80	-	16	-	0.94	2.20	-	55	0.38

Continue...

Table 1. Continuation.

Wells	%TOC	%IR	Intrusion (m)	%Ro	Rock-Eval				
					S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	T_{max} (°C)	HI (mg HC/g TOC)	PI
1TV 2 SC	2.06	75	23	-	0.06	0.08	381	4	0.43
2AA 1 SP	1.09	76	6	-	2.29	0.86	411	77	0.58
2AL 1 SC	2.07	-	31	-	0.45	0.20	420	7	0.70
2AN 1 PR	1.18	-	231	1.73	-	-	-	-	-
2AO 1 RS	2.02	85	20	-	1.56	1.51	409	107	0.54
2CA 1 SC	1.41	-	5	-	0.90	2.90	423	121	0.47
2CB 1 SP	0.56	-	105	-	0.08	0.08	-	14	0.55
2CM 1 PR	0.41	87	15	0.55	-	-	-	-	-
2CN 1 SC	7.02	86	4	0.44	2.89	15.31	420	11	0.21
2DO 1 MS	0.95	74	0	0.70	0.83	1.90	428	132	0.33
2GU 3 SP	2.12	72	2	1.30-1.60*	0.68	0.30	357	18	0.76
2LA 1 SC	3.26	69	63	-	0.08	0.02	-	1	0.93
2LA 1 SP	0.40	-	72	1.80-3.00*	-	-	-	-	-
2LI 1 SP	0.90	74	0	0.63	-	-	-	-	-
2LV 1 RS	2.11	86	102	1.35	-	-	-	-	-
2MC 1 SC	2.59	83	9	-	0.94	1.16	400	52	0.41
2PI 1 SC	0.90	87	151	-	-	-	-	-	-
2PN 1 SP	0.91	-	0	0.70-1.50*	1.25	2.95	412	276	0.25
2PU 1 SC	2.71	76	39	-	0.05	0.30	-	100	-
2RA 1 MS	0.22	52	60	2.70*	0.07	0.16	394	27	0.30
2RD 1 RS	4.00	-	120	2.70-3.00*	0.03	0.32	-	24	0.12
2RI 1 PR	1.74	-	0	0.90-1.35	0.94	2.98	439	170	0.23
2RP 1 PR	0.46	-	23	1.30-3.00*	0.07	0.08	417	13	0.56
2TB 1 SP	4.25	67	0	0.51 -0.55	3.92	27.28	428	567	0.16
2TG 1 SC	2.58	83	42	-	-	0.01	-	1	-
2TV 1 SC	0.90	72	31	-	0.16	0.34	-	21	0.32
3CB 2 SP	0.78	-	69	-	0.07	0.03	-	7	0.77
3CB 3 SP	1.79	-	141	1.80-3.00*	0.10	0.19	412	11	0.73
3CB 4 SP	4.23	-	0	-	0.53	0.59	403	15	0.56
3HV 2 SC	2.52	64	29	-	0.80	7.34	353	0	0.65
3MC 3 SC	1.87	69	12	-	0.38	0.32	-	22	0.51

-: no analysis was performed on these samples; S2"mg HC/g rock; S1"mg HC/g rock; T_{max} in °C; TOC in wt.%; IR in wt.%; HI"mg HC/g TOC; PI"S1/(S1+S2); *Ro calculated using spore color index (SCI) data; intrusion (m): sum of the thicknesses of the intrusions found in the Irati Formation.

Total organic carbon

The TOC content considering organic facies with and without heat effect of igneous intrusions ranged from 0.19 to 20.4%, with an average of 0.21–8.01% (Table 1, Fig. 3). TOC includes the measured amount of kerogen and bitumen in the rock. Value above 1% is considered good for shales, while value below 0.5% indicates less to no potential for achieving economic concentrations of hydrocarbons (Peters and Cassa 1994). Our data reveal an average TOC content of 2.5% for all data including organic facies affected by the heat from igneous intrusions. Since TOC values are generally higher than 1%, we can assume that the potential for hydrocarbon generation is higher in the Irati Formation investigated in this study. The low TOC content found in certain samples may be associated, to a large extent, with the transformation of organic matter into hydrocarbons. This is due to the effect of heating by intrusive bodies that promoted heating and cracking of organic matter, which decreased the TOC values relative to the amount of original organic carbon. Comparing the TOC map (Fig. 3) with the intrusive thickness map (Fig. 4), there is generally a decrease in content in the areas with the highest intrusive thicknesses.

Rock-Eval pyrolysis

Free hydrocarbons (S_1) have maximum values of 15.12 mg HC/g rock, with an average of 0.03–4.38 mg HC/g rock. The highest values of S_1 correlate with the highest TOC values and with low %Ro values (immature) (Table 1). These regions contain either no intrusive rocks or thin intrusive rocks within or near the Irati source rocks. Samples with relatively higher S_1 values may suggest accumulation of hydrocarbons at this

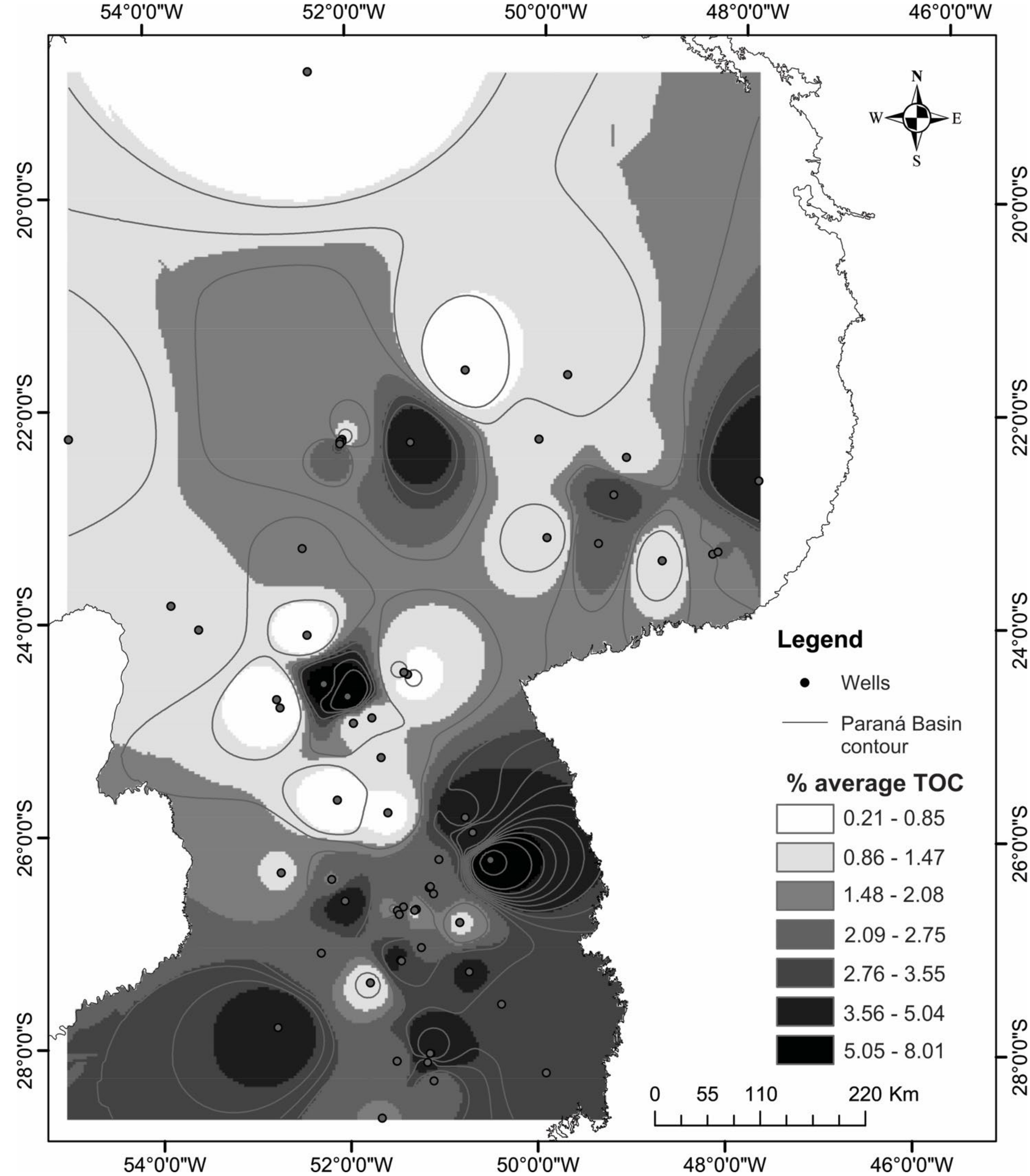


Figure 3. Residual average of the total organic carbon distribution of the Irati Formation (Assistência Member), Paraná Basin.

position (Peters and Cassa 1994). The low S_1 values (< 0.5 mg HC/g rock) demonstrated that there was migration, mainly of gas, due to the generation of hydrocarbons by thermal effect of magmatic intrusive rocks. Araújo *et al.* (2000) suggested that the efficiency of expulsion of hydrocarbons from the source rocks of the Irati Formation was almost 100%. This high efficiency can be attributed to the promotion of secondary cracking (oil to gas) by igneous intrusive.

According to Espitalié *et al.* (1985), rocks with a source potential (S_2) greater than 10 mg HC/g rock and an HI above 300 mg HC/g TOC have excellent potential for oil generation. The Irati Formation has intervals with these characteristics, and the most important are represented in wells near the basin margin (Fig. 5). In these regions, the Irati Formation is immature for hydrocarbon generation. The TOC content reaches up to 20.4%, with maximum S_2 values of 42.03 mg HC/g rock and HI values ranging from 0.16 to 892.64 mg HC/g TOC with an average of 0.41–567.37 mg HC/g TOC (Table 1, Fig. 6). OI values ranged from 0.34 to 319.99 mg CO_2/g TOC.

However, the regions containing intrusive rocks (or close to them) correlate with those with the lowest values of S_2 and HI (Figs. 4, 5, and 6). These values can be considered residual values, since the very low TOC and S_2 values found in certain samples are related to the high degree of thermal evolution (Ro values > 0.7%) caused by the heat from the basic intrusive rocks (Cerqueira and Santos Neto 1986, Araújo *et al.* 2000).

A necessary complement to this initial determination is the evaluation of the type of kerogen and its relationship with

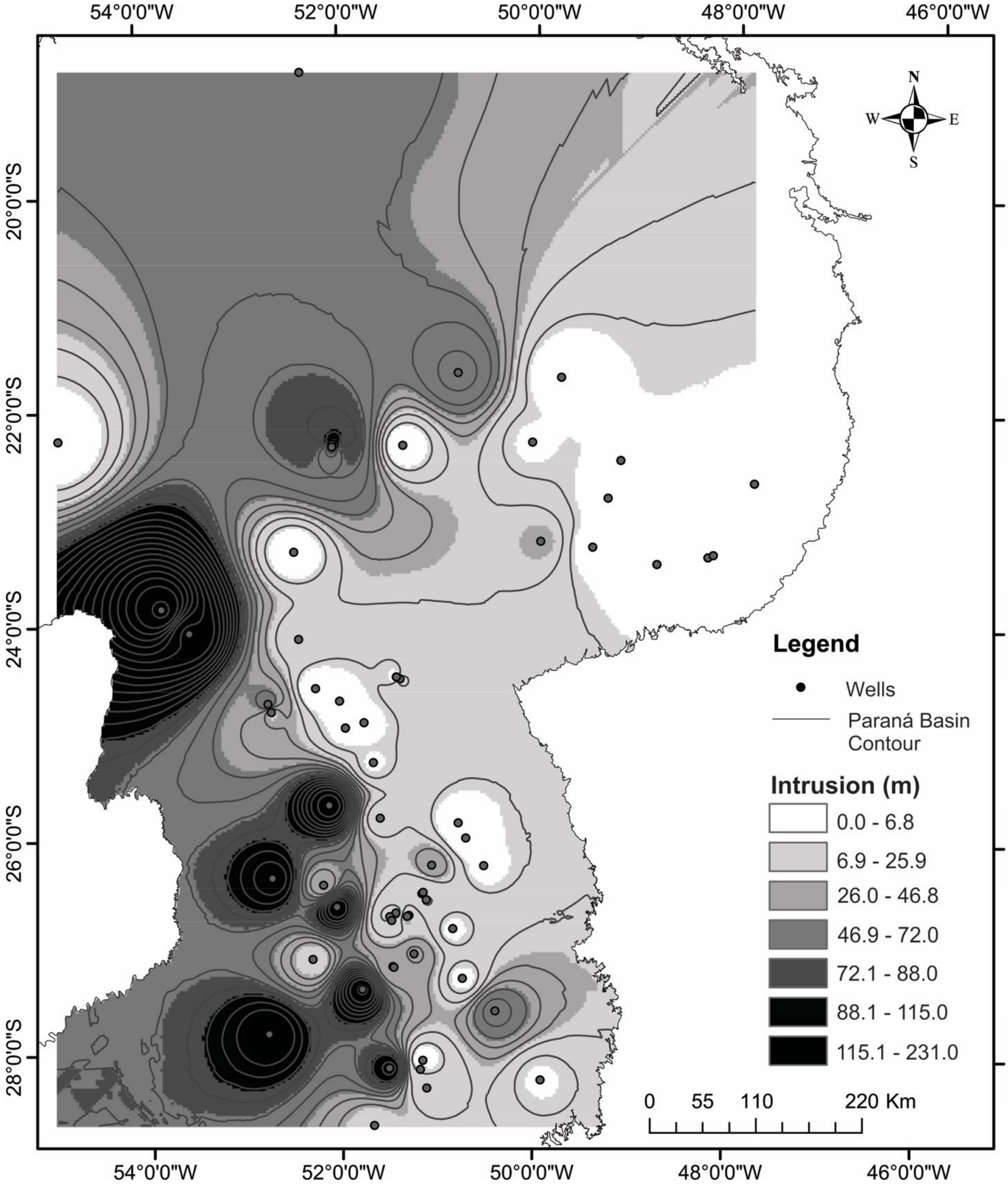


Figure 4. Map of the thickness of igneous intrusion in the Irati Formation, Paraná Basin. The higher the thickness, the higher the thermal stress range.

the potential source of hydrocarbons (S_2) in relation to the TOC content, since some of the organic carbon content may be inert or recycled. As can be seen in Fig. 7, based on this relationship, the samples from the Irati Formation show high potential for a hydrocarbon generation. In the wells affected by heating from igneous intrusions, the samples are characterized by low petroleum source potential (Fig. 8), with the exception of samples from wells with a small thickness of intrusions or with intrusions near the Irati Formation. The thermal heating halo of the intrusive body can vary from ~30 to 200% of the sill thickness, depending on host-rock temperature, sill thickness, and magma temperature (Othman *et al.* 2001, Aarnes *et al.* 2010, Arora *et al.* 2017, Cooper *et al.* 2007, Santos *et al.* 2009, Spacapan *et al.* 2018, 2020 and other). Other studies on the Irati Formation suggested that this heating is approximately 150% times the thickness of the sill (Cerqueira and Santos Neto 1986, Araújo *et al.* 2000, Santos *et al.* 2009, Cioccari 2018). This is supported by the high TOC content preserved in source rocks and high S_2 values of samples far from the area affected by heat of the intrusions.

Kerogen type

The type of organic matter can be classified according to the modified Van Krevelen plot of HI and OI (Tissot and Welte 1984, Gottardi *et al.* 2019). The HI-OI data of the samples from the Irati Formation were plotted in Fig. 9.

The samples with a low degree of thermal evolution are predominantly immature and exhibit moderate to high TOC

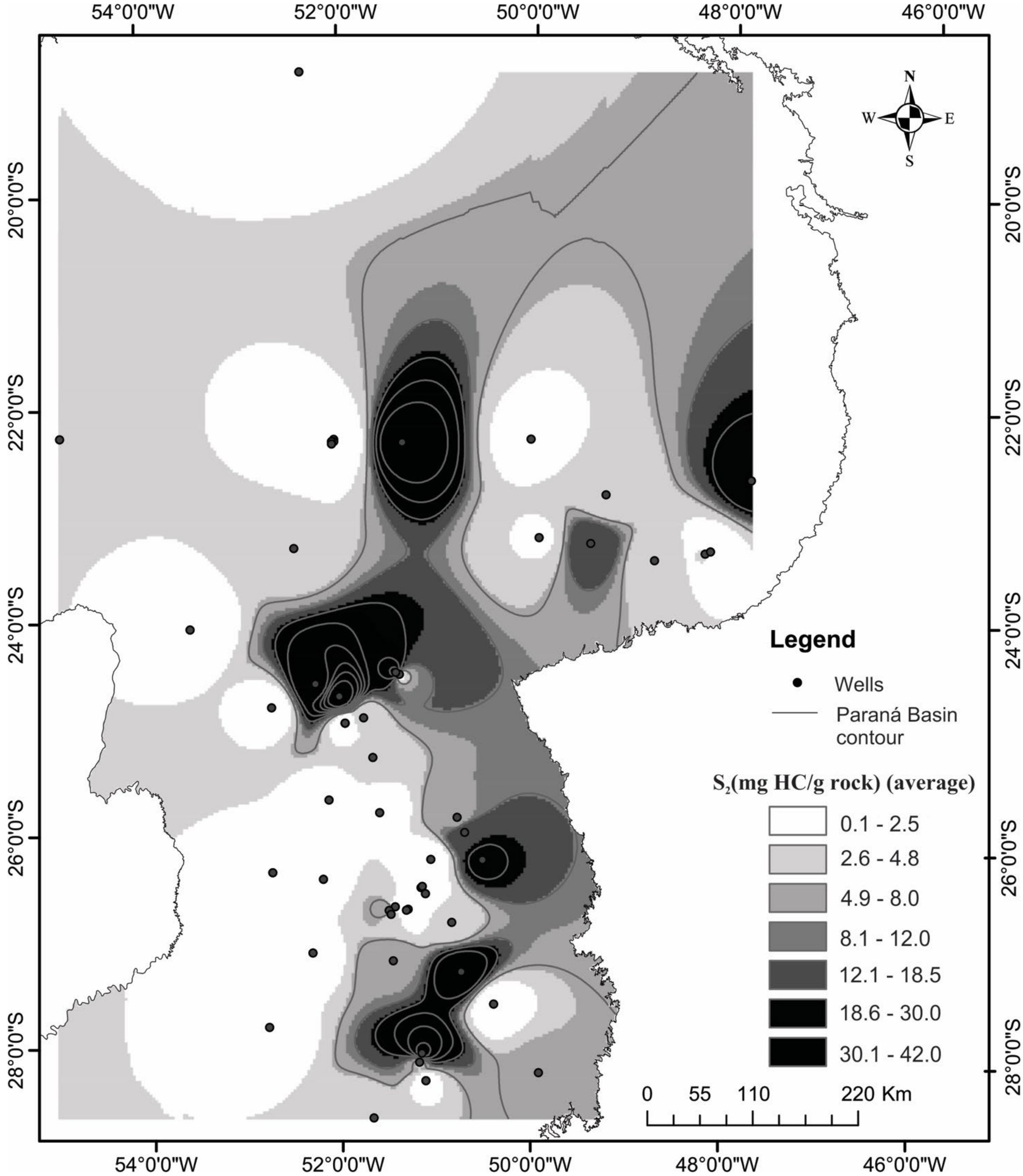


Figure 5. Residual average of source rock potential of the Irati Formation (Assistência Member) (S_2 — mg HC/g rock).

values (ranging from 1.1 to 15.6%), HI (> 500), and values of IR (ranging from 17 to 96%, with an average of 77%), suggesting an anoxic environment (Tyson 1987). According to the Van Krevelen diagram (Figs. 9 and 10), these samples exhibit types I and II kerogen characteristics (derived from amorphous organic matter). The samples showing moderate TOC values (between 0.43 and 20.4%), HI (between 150 and 495 mg HC/g TOC), and values of IR (between 8 and 96%, with an average of 57%) indicate deposition in suboxic environments or suboxic to anoxic environments (Tyson 1987). According to the Van Krevelen diagram, the samples behave as types II to II/III (Figs. 9 and 10).

Some samples corresponding, for example, to the M 1A, TB 1, and ES 1 wells, also indicate the presence of types III and IV kerogen (inertinite). As shown by de Oliveira *et al.* (2022), shales with high values of IR (between 66 and 92%, with an average of 81%), values of TOC (between 0.19 and 7.97%), and HI (< 150) and suggest the occurrence of reworked material and with bioturbation (Araújo *et al.* 2001), or even conditions that indicate a suboxic to an oxic environment (Fig. 10). This formation was deposited under intermittent anoxic conditions, with oxygen concentrations varying during deposition (Araújo 2001).

Reis *et al.* (2018) showed variations in depositional paleoenvironments of the Irati Formation, recognizing three- to fourth-order cycles and seven chemostratigraphic units. The samples with the highest TOC and HI values and the greater proportion of preserved amorphous organic matter were deposited in a more

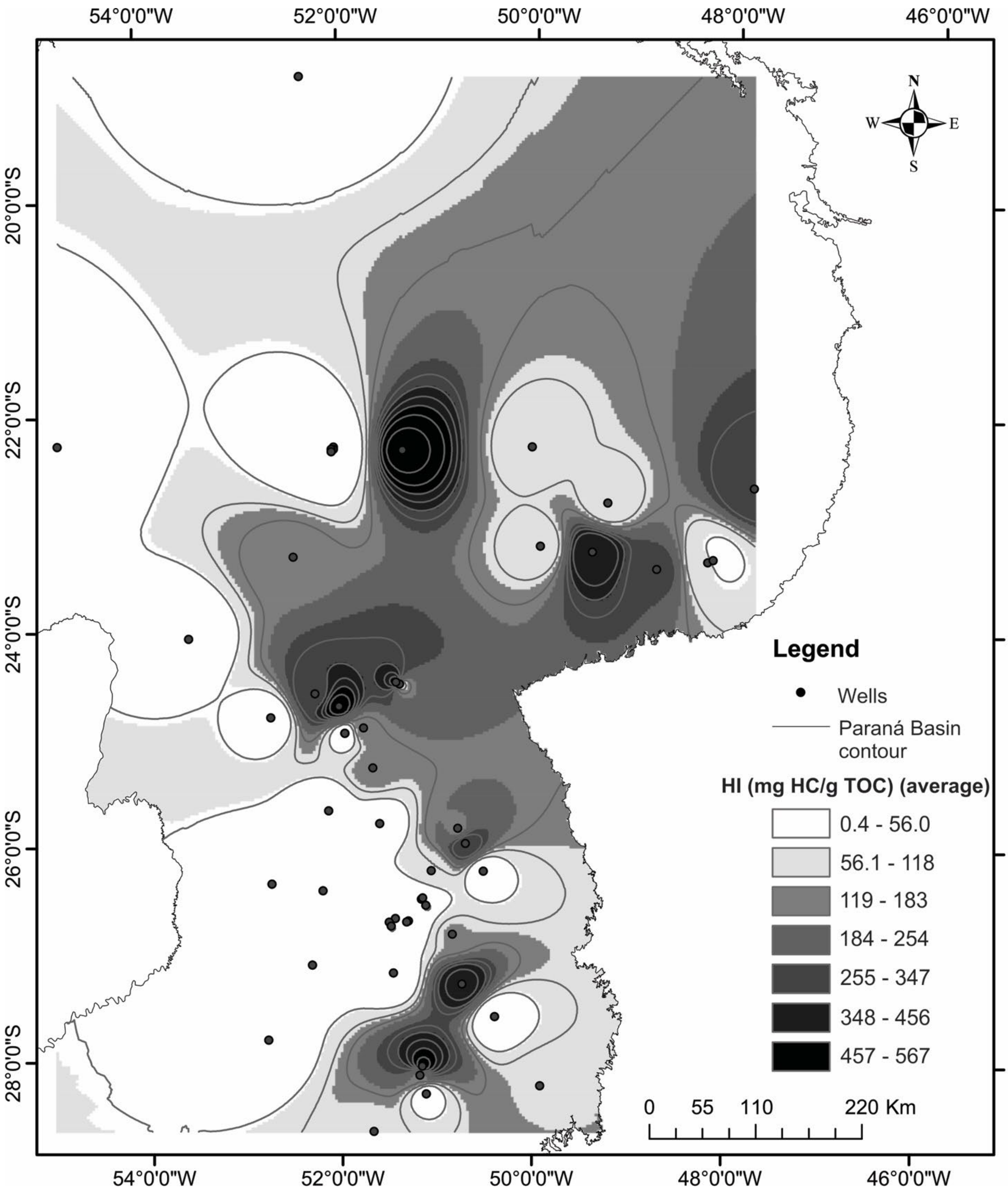


Figure 6. Residual average of the hydrogen index of the Irati Formation (Assistência Member) (HI — mg HC/g TOC).

reducing environment, predominantly an anoxic environment. Samples with a high range of IR and HI values between 50 and 300 mg HC/g TOC consist of partially oxidized amorphous organic matter or a mixture of amorphous organic matter and partially oxidized bisaccate pollen grains or even a mixture of opaque phytoclasts and partially oxidized bisaccate pollen grains, indicating variation in the depositional paleoenvironment. Silty shales, recognizable by higher values of IR, with bioturbation, TOC values below 1%, and the predominance of opaque phytoclasts, indicate an oxic environment. These sequences are similar to those defined by Araújo *et al.* (2001).

The very low HI results for the samples from wells containing intrusions indicate a predominance of types III and IV kerogen, whose HI may be residual due to the heat effect of the intrusions (Fig. 11). Samples from wells MB 1 and 2MC 1, which have fine intrusions, or samples from wells DO 1, PN 1, and RI 1, which do not have intrusions in the Irati Formation, the original features of source rock were not preserved, suggesting that they were affected by heat from nearby intrusions (Ro values > 0.70%). As discussed above for TOC and S_2, the low HI values of these samples are products of abrupt thermal cracking of kerogen with high depletion of S_2 and HI but remaining some content of residual carbon (Araújo *et al.* 2000).

Thermal maturity

The maximum value of the Rock-Eval pyrolysis temperature (T_{max}), an indicator of the thermal maturity of the kerogen,

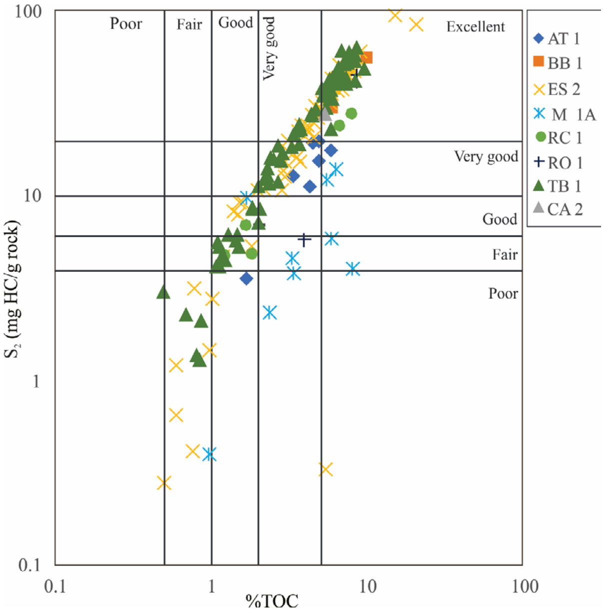
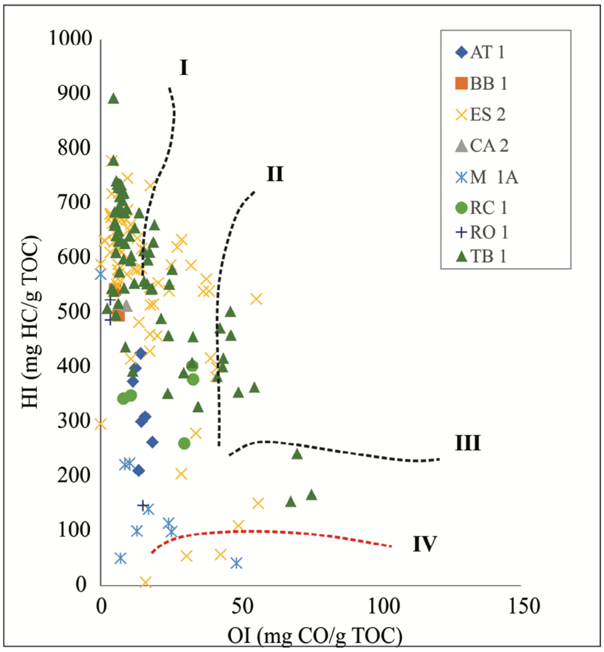


Figure 7. Hydrocarbon source potential (S_2) versus total organic carbon (TOC) of the Irati Formation (Assistência Member) in wells without igneous intrusions. Most samples are characterized by a good to excellent hydrocarbon source potential according to Peters and Cassa (1994) classification.



Source: modified from Euzébio *et al.* (2016).

Figure 9. Van Krevelen diagram showing the distribution of studied samples from the wells without diabase intrusions, showing the predominance of kerogen types I and II.

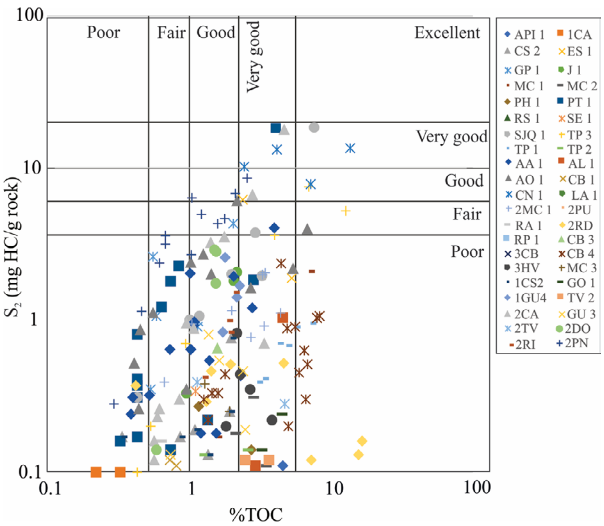


Figure 8. Hydrocarbon source potential (S_2) versus total organic carbon (TOC) of the Irati Formation (Assistência Member) in wells with igneous intrusions or with intrusions close to the Irati Formation. Most samples are characterized by a low hydrocarbon source potential due to thermal depletion caused by intrusive rocks depletion according to Peters and Cassa (1994) classification.

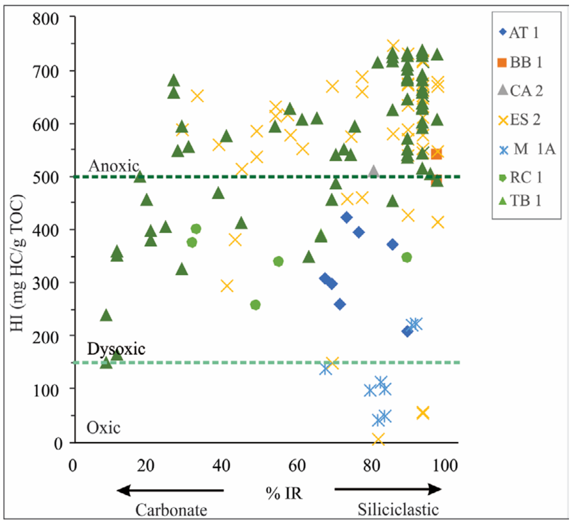


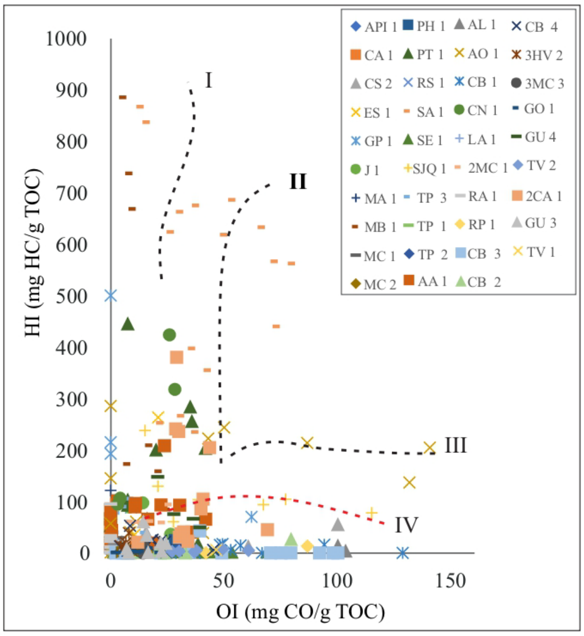
Figure 10. Relationship between the HI and IR values for the samples from the Irati Formation. Environmental conditions were proposed by Araújo (2001).

ranged from 300 to 538°C with an average of 351–465°C (Table 1). The lowest average value of T_{max} indicates immaturity in terms of hydrocarbon generation, since the initial window of oil generation normally begins at a T_{max} value of approximately 435°C (Peters and Cassa 1994). Therefore, samples with T_{max} values lower than 430°C suggest thermal immaturity for hydrocarbon generation. However, in some wells with no intrusions in the Irati Formation, the samples showed T_{max} values > 435, probably due to intrusive rocks nearby (Table 1). The deepest area of the basin is the location of the generation kitchen, in this case the depocenter of the Paraná Basin, where the thickness of the intrusive rocks is greater. Notably, most of the samples affected by the heat from intrusive rocks are in the overmature stage of thermal evolution.

Vitrinite reflectance values (Table 1) show immaturity, ranging from 0.23 to 0.63%Ro in the wells without igneous intrusions in the Irati Formation, with the exception of DO 1, PN 1, and RI 1 wells, which show an advanced degree of thermal evolution with Ro values ranging from 0.70 to 1.50%Ro. This high stage of maturation was probably caused by the presence of intrusions nearby that were not intersected by these wells, a fact also portrayed in the work of Araújo (2001). Cioccari (2018) has shown through numerical modeling that the thermal effect caused by intrusive igneous sills affects the

Irati Formation and its organic content by 1.5 times (or 150%) the thickness of the igneous body. This reinforces the idea that even without intrusions in the Irati Formation's wells, it may have been affected by the heat from the nearby intrusions. Vitrinite reflectance values of samples thermally affected by the igneous intrusions present in the Irati Formation's wells vary from 0.70 to 3.00 %Ro (Table 1), indicating differential thermal evolution from the oil window to the overmature zone.

Gas chromatography data obtained from samples from wells (CS 2, GO 1, GP 1, MC 1, AA 1, RP 1, PN 1, RD 1, RI 1) that suffered the thermal effect of intrusive rocks indicate the presence of migrated hydrocarbons. During migration, the resulting oil may have been mixed with immature bitumen. This fact is also reported in the work of Souza *et al.* (2008) and Martins *et al.* (2020). In the work of Cioccari (2018), this fact is also presented as it shows that the biomarkers used as maturation parameters did not present satisfactory results, as they were influenced by the igneous positioning, suggesting that the reasons for the biomarkers indicating thermal maturation were influenced by the primary migration of hydrocarbons.



Source: modified from Euzébio *et al.* (2016).

Figure 11. Van Krevelen diagram showing the distribution of the analyzed samples from the wells with diabase intrusions, highlighting the presence of type IV kerogen due to severe depletion of HI caused by thermal stress.

Igneous activity in the Irati Formation, Paraná Basin

The stratigraphic record of the Paraná Basin includes several igneous intrusions that reach thicknesses of up to 231 m in the Irati Formation (Fig. 4). The diabases are located between 216 and 3,345 m below the surface. Most of the present-day structures in this area are due to deformation caused by intrusion of these igneous bodies.

It is observed in the tendency maps (Fig. 4) that in several regions where diabase intrusions occur in the Irati Formation source rocks, a wide maturity range is identified through variations in the organic matter content, HI, and hydrocarbon source potential (S_2) data. Maturation trends are illustrated by the HI, TOC, and S_2 data from the Paraná Basin wells studied (Figs. 3, 5 and 6) data confirmed by %Ro (Table 1). Similar results were also observed by Clayton and Bostick (1986) and Araújo *et al.* (2000).

In those wells without intrusive rocks, for example, in well TB 1 (Fig. 12), the samples from the Irati Formation are immature (0.51–0.55 %Ro) and the original HI, TOC, and S_2 values are preserved. In wells where the Irati Formation contains 6-m-thick diabase intrusions that are on average, such as in well SA 1, the HI, TOC, and S_2 values of the source rocks decrease toward the intrusive bodies (Fig. 12). These results indicate a trend that thermal maturation of the kerogen increases toward

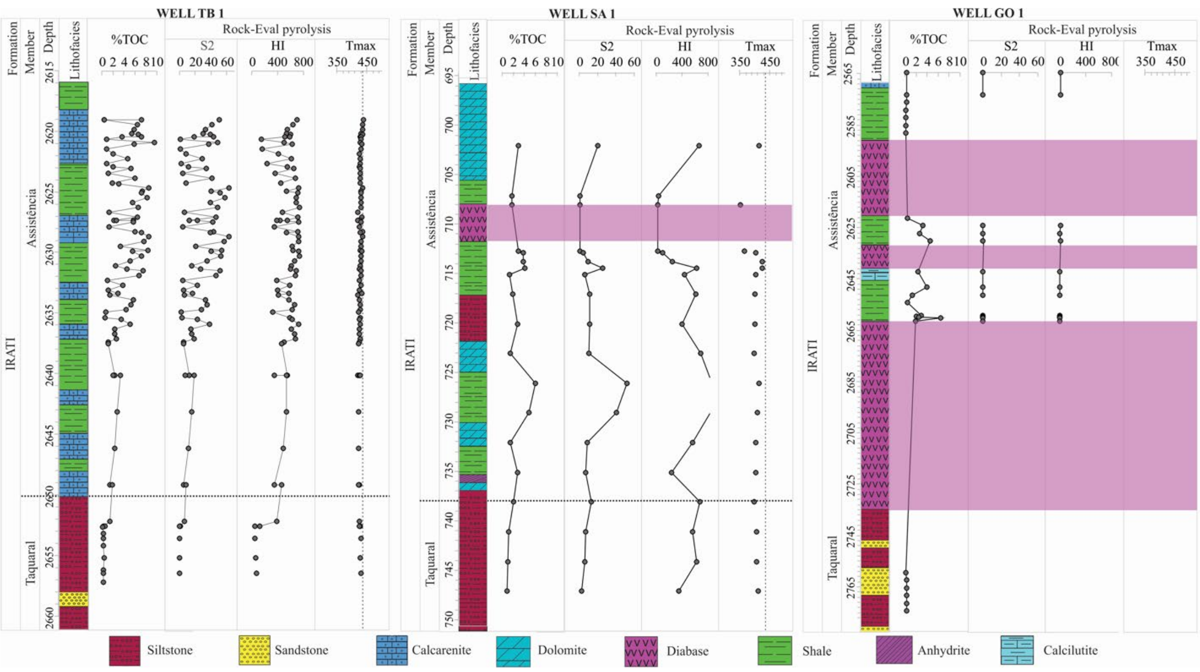


Figure 12. In-depth TOC, S_2, HI, and T_{max} logs of source rock samples and correlations in the wells studied. The Irati Formation comprises the Taquaral and Assistência Members, with the igneous intrusions highlighted.

the diabase intrusion. In the wells with diabase intrusions, which averaged 25–231 m thick, the organic facies (shale, marge, and carbonate) are overmature (up to 1.35 %Ro) and have very low HI, TOC, and S_2 values, for example, in well GO 1 (Fig. 12). These differences in maturation could be related to the thickness distribution of the intrusion. The average diabase thickness in the studied section ranges from 1 to 231 m. Therefore, certain differences can be found in the degree of organic matter maturation between the wells.

CONCLUSIONS

The results of geochemical analyses associated with igneous bodies have shown that the Irati Formation has the potential for hydrocarbon generation. Samples from the Irati Formation contain types I and II kerogen, which have relatively high HI values, typically > 200 mg HC/g TOC, and are prone to oil generation. Average TOC values ranged from 0.21 to 8.01%, indicating a concentration of organic matter suitable for hydrocarbon generation. The conspicuous depletion in HI, S_2, and TOC values indicates content changes induced by intense and abrupt thermal heating (> 1,000°C) of igneous intrusive rocks.

Samples exhibited T_{max} values ranging from 351 to 465°C during Rock-Eval Pyrolysis, indicating varying degrees of thermal maturity. Most samples had T_{max} values below 435°C; therefore, the Irati Formation (Permian) is largely immature, indicating a low degree of thermal evolution for hydrocarbon generation and the original HI, TOC, and S_2 values have been preserved. Higher T_{max} values are derived from dubious data acquisition during pyrolysis. Ro values confirm a better assessment of organic matter maturation. Samples from wells without igneous intrusions had Ro values < 0.63%, samples from wells with low thickness intrusions or without intrusions but with thermal effects of intrusions in nearby regions showed Ro values between 0.59 and 1.45%. Samples from wells with thick intrusions showed Ro values ranging from 1.3 to 3%, an overmature stage of thermal evolution.

In some areas, large sections of source rocks have been locally matured due to thermal anomalies associated with igneous intrusions of the Serra Geral Formation (Cretaceous). In these regions, the samples exhibit residual TOC contents due to thermal cracking of the organic matter as a result of the proximity of intrusive bodies.

Maturity is influenced by three observed trends: where the source rocks are affected by thick igneous intrusions, TOC, HI, and S_2 values are residual; where the source rocks are affected by thin igneous intrusions, only geochemical data near the contact are affected, while further away TOC, HI, and S_2 values are well preserved; and based on samples from wells without intrusions, indicating a low degree of thermal evolution for hydrocarbon generation (immature zone).

ACKNOWLEDGMENTS

This research was carried out in association with the ongoing P&D project registered as ANP no. 20075-8, "Petroleum Systems Research Project in Brazilian Sedimentary Basins" (UFBA/Shell Brasil/ANP) — title of the ANP project (Research in Petroleum Systems of Brazilian Sedimentary Basins), sponsored by Shell Brasil under the ANP and P&D fee as "Investment Commitment to Research and Development". The authors are also grateful for the support of Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB, Brazil) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for providing grants, scholarships, and other financial support. This study also was also partially funded by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior — Brasil (CAPES) — finance code 001.

ARTICLE INFORMATION

Manuscript ID: 20220008. Received on: 13 JAN 2022. Approved on: 04 NOV 2022.

How to cite this article: Martins C.M.S., Celino J.J., Cerqueira J.R., Garcia K.S., Queiroz A.F.S. (2022). Thermal effect of igneous intrusions on organic-rich Irati Formation and the implications for the petroleum systems: a case study in the Paraná Basin, Brazil. *Brazilian Journal of Geology*, **53**(1):20220008. https://doi.org/10.1590/2317-4889202220220008

C.M.S.M.: Writing — review & editing, Writing — original draft, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Validation, Supervision, Software. J.R.C.: Writing — review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization. J.J.C.: Writing — review & editing, Supervision, Software, Project administration, Funding acquisition, Conceptualization. K.S.G.: Writing — review & editing, Visualization, Supervision, Project administration, Funding acquisition, Data curation. A.F.S.Q.: Writing — review & editing, Writing — original draft, Visualization, Validation, Supervision, Software, Project administration, Funding acquisition, Conceptualization.

Competing interest: the authors declare no competing interests.

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