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Effects of Igneous Intrusion on the Organic Content of Irati Formation, Paraná Basin, in Sapopema (PR)

Efeito das Intrusões Ígneas no Conteúdo Orgânico da Formação Irati, Bacia do Paraná, na Região de Sapopema (PR)

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Resumo

O efeito térmico de intrusões ígneas em rochas sedimentares ricas em matéria orgânica pode fornecer informações importantes sobre a maturação térmica. A Formação Irati, de idade permiana, na Bacia do Paraná é uma sequência carbonática-pelítica, onde folhelhos ricos em matéria orgânica por vezes encontram-se intrudidos por rochas básicas Jurássicas/Cretáceas. O atual estudo apresenta justamente os efeitos de uma intrusão ígnea no conteúdo orgânico da Formação Irati, no município de Sapopema, Paraná. Dados de carbono orgânico total (COT), teor de enxofre (S) e resíduo insolúvel (R.I) foram combinados com microscopia eletrônica de varredura (MEV) e espectroscopia por dispersão de energia (EDS) e revelaram que os teores relativamente baixos de COT registrados no poço SP-58-PR, onde a Formação Irati encontra-se em contato com um sill de diabásio de 60 m de espessura, são residuais e estão associados com a depleção do carbono orgânico. A transferência de calor da rocha intrusiva foi responsável por promover o craqueamento da matéria orgânica, reduzindo assim os valores de COT, os quais são bem menores em relação aos observados no poço SP-32-PR, na mesma região, onde não há o contato entre a Formação Irati e a rocha ígnea. Nesse contexto, ao comparar os principais picos de COT do Membro Assistência em ambos os poços, observou-se que houve um decréscimo que variou entre 80,7 e 84% no poço que estava em contato com a rocha intrusiva. Imagens de MEV revelaram que a matéria orgânica presente no Membro Taquaral tem formato regular e subarredondado, enquanto que no Membro Assistência a matéria orgânica apresenta características de material termicamente evoluído.

Palavras-chave: *Formação Irati; Carbono orgânico; Intrusão ígnea*

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Abstract

The thermal effects of an igneous intrusion on organic-rich sedimentary rocks can be considering an important source of maturation of organic matter. The Permian Irati Formation of Paraná Basin (Brazil) is a carbonatic and organic-rich shale sequence intruded by Jurassic-Cretaceous basic rocks. This study reports possible effects of igneous intrusion on the organic matter content of Irati Formation, in Sapopema region (Paraná State). Total organic carbon (TOC), total sulfur (S) and insoluble residue (IR) data were combined with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The relatively low TOC values recorded in well where Irati Formation is in contact with 60 m of diabase sill (SP-58-PR) are residuals, associated with the depletion of organic carbon, caused by the thermal effect from the overlying intrusive rock. It was responsible to promote the cracking of the organic matter and reduced those values in relation to the original ones, observed in SP-32-PR (without thermal influence). When comparing the TOC peaks of the Assisting Member in both wells, it was observed that there was a decrease between 80.7 and 84% in the SP-58-PR. SEM images reveal that organic matter in Taquaral Member is sub-rounded and regular shape, while the organic matter in Assistência Member presents a characteristic pattern of thermally evolved organic matter.

Keywords: *Irati Formation; Organic carbon; Igneous intrusion*

1 Introduction

The thermal effect of an igneous intrusion in sedimentary rocks depends on different factors, such as intrusion and host rock temperatures, nature of the magma and of the host rocks, geometry and depth of the intrusion, mechanism of heat transfer, and other parameters (Galushikin, 1997). These factors can affect the degree of organic matter maturation and mineralogical composition of host rocks prior to the igneous intrusion. Furthermore, pore water content will also strongly affect the type and rate at which the chemical reactions take place.

In its stratigraphic record, the Paraná Basin exhibits igneous rocks related to the rupture of the Gondwana Supercontinent, which gave rise to the opening of the Atlantic Ocean ca. 120 Ma. The Serra Geral Formation is constituted by a thick pile of lava flows, which can reach thicknesses of 2.000 m in some regions. It is characterized by a network of dikes, cutting the entire Paleozoic-Mesozoic sedimentary succession, and multiple diabase sills that intrude into the stratification planes of Paleozoic sediments, preferentially along Irati Formation horizons (Mizusaki & Thomaz-Filho, 2004).

Irati Formation (Permian) is one of the most studied geological formations among Brazilian sedimentary ones, due to its unique fossiliferous occurrences, and because it contains oil shale with a high organic content, among the highest recorded in sedimentary deposits in the world, reaching approximately 23% (Milani *et al.,* 2007). Basin-wide, various studies stressed out the importance of igneous intrusions to the process of organic matter maturation (Milani, 1997; Milani & Zalán, 1999; Araújo *et al.,* 2000; Correa & Pereira, 2005; Costa *et al.,* 2016, among others).

In the present study we have analyzed Irati Formation samples from core SP-58-PR (Paraná state), whose top were in contact with a diabase sill approximately 60 m thick. As excepted, the intrusion of the diabase sill was responsible for modifications of the original organic geochemistry content of the pelitic-carbonatic sequence.

2 Geological Context

The study area is part of the tectonic-stratigraphic context of the Paraná Basin, a vast region composed of sedimentary and magmatic rocks, which extends from the southern part of Brazil to Eastern Paraguay and the northeast of Argentina and northwest of Uruguay, covering a total area of approximately 1.4 million square kilometers (Milani, 1997).

Irati Formation lies within the tectonic sequence of Gondwana I, corresponding to the basal unit of Passa Dois Group. Previously studies suggested that the deposition of Irati rocks occurred in a restrict marine environment with saline and anoxia fluctuations (Araujo, 2001; Rodrigues *et al.,* 2010; Alferes *et al.,* 2011). Further, the Formation is subdivided in two members, Taquaral and Assistencia (Milani & Zalán, 1999). The lowermost Taquaral Member is composed, in general, of dark-gray siltstones and shales where the occurrences of marine acritarchs suggest a marine epicontinental to restricted environment with normal salinity (Santos Neto, 1993; Rodrigues *et al.,* 2019). The boundary between Taquaral and Assistência Members can be easily identified by the occurrence of the carbonates that, in some cases, can present dolomitic composition. Also, carbonates are interbedded with shales and organic-rich shales deposited restrict marine environment (Hachiro, 1996; Araújo, 2001; Holz *et al.,* 2010; Rodrigues *et al.,* 2019).

Costa *et al*. (2016) demonstrated, through 2D seismic interpretation, that the Irati Formation contains post-Triassic, basic igneous bodies, composed of dykes and sill with thicknesses that vary in different parts of the basin. In the study area, the isopach map of Serra Geral Formation shows the occurrence of thick intervals of igneous rocks in contact with Irati Formation (Figure 1).

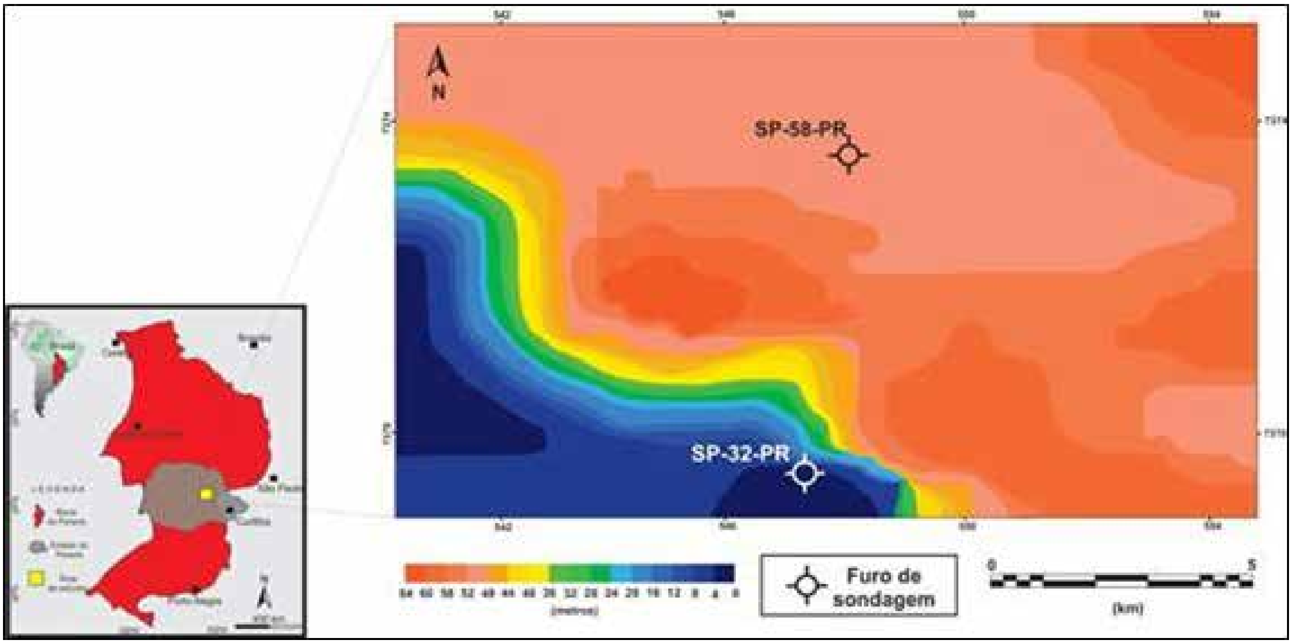

Figure 1 Isopach map of Serra Geral Formation in study area.

3 Methodology

In the present work, the Irati Formation was studied based on core samples of well SP-58-PR (Coordinates Córrego Alegre, Zone 22S: 7383382N/549372E), located in the municipality of Sapopema, northeast Paraná state, drilled by Serviço Geológico do Brasil (CPRM) in the 1970s. The analyses were carried out utilizing total organic carbon (TOC), total sulfur (S), insoluble residue (IR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS).

3.1 Total Organic Carbon (TOC), Total Sulfur (S) and Insoluble Residue (IR)

TOC, S and IR analyses were carried out for the entire interval of the Irati Formation. The samples analyzed were taken starting at a depth of 475.7 m, down to 510.0 m, totalizing 60 samples.

The TOC, S and IR values were obtained after the removal of the carbonatic constituents of the rocks, through a hydrochloric acid (50%) treatment. Then, they were read with Leco SC-632 equipment. These values were registered according to the depth of each sample, allowing a semiquantitative assessment of those parameters at the different intervals analyzed.

3.2 Scanning Electron Microscopy (SEM)

Sample preparation for analysis in the SEM followed the norm established by the Laboratório de Análise Mineralógica of CENPES/PETROBRAS. The samples were first ground, in order to offer a fresh and irregular surface, then glued to a brass conductive support, and finally covered by a thin layer of gold-palladium with the EMITECH K750X metallizer, to make it electrically conductive. Then, it was glued to an aluminum conducting support and analyzed in the ZEISS EVO LS-15 scanning electron microscope, with images produced by backscattered electrons, operating at high vacuum, at 20 kV, and using a working distance of 12.50 mm.

The image produced by backscattered electrons represents, in its shades of grey, the variation of the average atomic composition of the feature that was imaged, meaning that materials of heavier atomic weight will produce images in lighter shades of grey, while lower atomic weight materials will produce darker images.

3.3 Energy Dispersive Spectroscopy (EDS)

The EDS microanalyses were obtained with the OXFORD Inca-AZtec Microanalysis System, coupled to the SEM, which provide the compositional (semiquantitative) tables of the chemical elements identified as oxides (calculated stoichiometrically). The EDS detector does not detect the elements H, He, Li and Be.

4 Results

Figure 2 summarizes the TOC, S and IR data for the Taquaral and Assistência members. TOC ranges between 0.32 and 1.12 for the Taquaral Member, with an average value of 0.51%.Only a single sample exhibited a value above 1% (493.9 m). The S values were on average 0.36%, with minimum and maximum values of 0.13 and 0.81%, respectively. The IR values were on average 89%, exhibiting the lowest (70%) and highest (95%) values in samples from depths of 507.2 m and 506.3 m, respectively.

TOC ranges between 0.25 and 2.11 for the Assistência Member, with an average value of 0.68%. The lowest value (0.25 %) is recorded by samples closer to the contact with the intrusive rock, whereas the highest TOC value (2.11%) was recorded 3 meters away from the contact, at a depth of 479.6m. The S values exhibited the highest values in samples close to the contact with the intrusive rock, with a peak of 15.2%. It can be associated with pyrite nodules observed in Figure 3C. The lowest values of IR were recorded at the base of Assistência Member, where the most representative carbonatic interval of Irati Formation is located.

In Assistência Member, some macroscopic changes within the pelitic section can be observed: (i) gradation of the pelitic section characterized by strong millimetric/centimetric lamination with dark grey levels intercalated with light grey in an interval of massive texture and beige color; (ii) occurrence of millimetric levels rich in pyrite crystals with cubic habit and metallic luster, oriented parallel to the rock lamination; (iii) next to the contact with the rocks from the Serra Geral Formation (approximately 40 cm), bioturbation marks and fossiliferous content, such as centimetric Mesosaurus articulated vertebra can be observed (Figure 3).

Detailed scanning electron microscopic images reveal that organic matter in Taquaral Member is sub-rounded and regular shape usually (Figure 4A). However the organic matter in Assistência Member presents a patchy pattern and fills most of the intergranular and over grain contact regions - bituminous residue (Figure 4B). EDS spectrum and chemical analysis for organic matter shows high levels of carbon in both Taquaral and Assistência Member. Nevertheless, the sulfur concentration is higher in the upper member (Figures 4A' and 4B'), confirming the pattern observed in Figure 2.

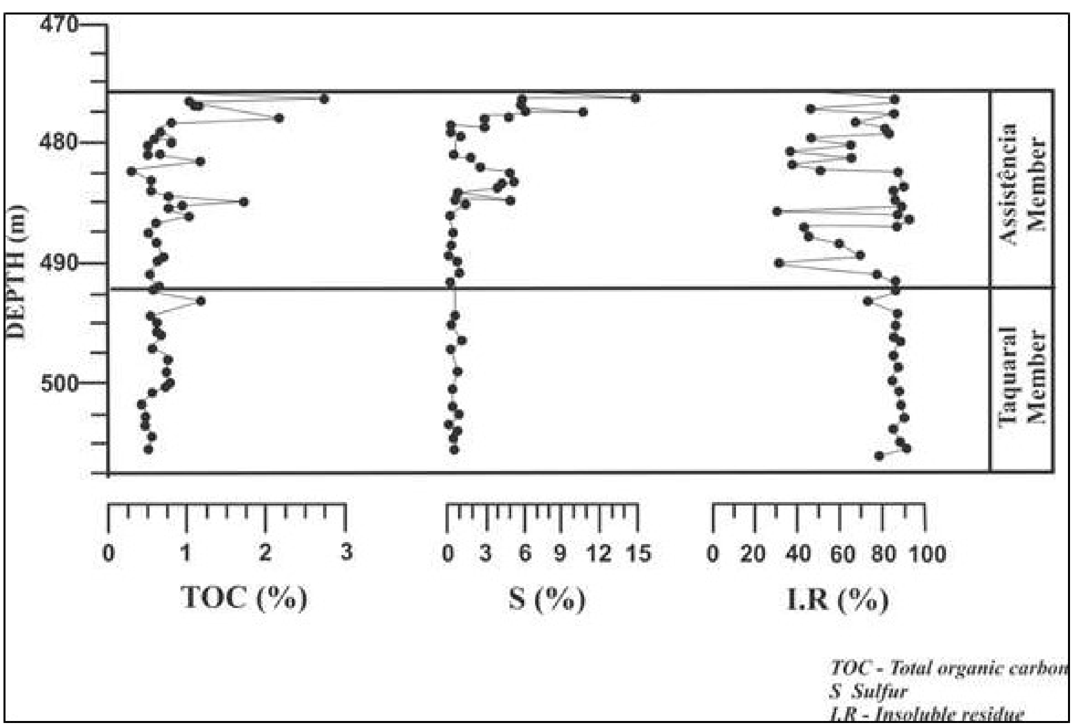

Figure 2 Data on total organic carbon (TOC), sulfur (S) and insoluble residue of the Irati Formation, well SP-58-PR.

Figure 3 A. Core samples of the Irati Formation from well SP-58-PR; B. Black shale facies; C. Pyrite crystals (Py) parallel to the rock lamination; D. Mesosaurus articulated vertebra.

5 Discussions

The heating of organic matter-rich sedimentary rocks by intrusive rocks may be an important mechanism for the generation of gas and oil in many sedimentary basins (Galushikin, 1997; Meyers & Simoneit, 1999; Gurba & Weber, 2001; Cooper *et al*., 2007). Several studies have already discussed the maturation of intervals that could be potential hydrocarbon generators in Irati Formation, mainly related to the presence of igneous intrusions, characterizing an unconventional generation model (Milani, 1997; Araújo *et al.,* 2000; Correa & Pereira, 2005; Souza *et al.,* 2008; Loutfi, 2011; Costa, 2014, among others). In the Sapopema region, a 60 m thick basic sill intrudes organic-rich shales of Irati Formation, which is one of the most important stratigraphic units for hydrocarbon source rock in the Paraná Basin (Araújo, 2001; Milani *et al.,* 2006; Reis *et al*., 2018, among others). Geochemical investigation and SEM images across the contact between the igneous and the sedimentary rocks revealed organic matter changes induced by thermal effects.

Holanda *et al*. (2018) presented TOC values for Assistência Member in Sapopema region, where the Irati Formation was not in contact with diabase sill. The average TOC values observed in well SP-32-PR (without thermal influence from sills and approximately 5 km of distance to SP-58-PR) was 3.8%, reaching values close to 14%. These values are more expressive than those observed at the same interval in well SP-58-PR (TOC average value of 0.68%, reaching a maximum value of 2.1%). Thus, the relatively low TOC values recorded in well SP-58-PR are likely residuals, associated with the depletion of organic carbon, caused by the thermal effect from the overlying intrusive rock, which promoted the cracking of the organic matter and reduced those values in relation to the original ones.

Organic carbon and sulfur ratio can be used to help understand recent and ancient depositional environments

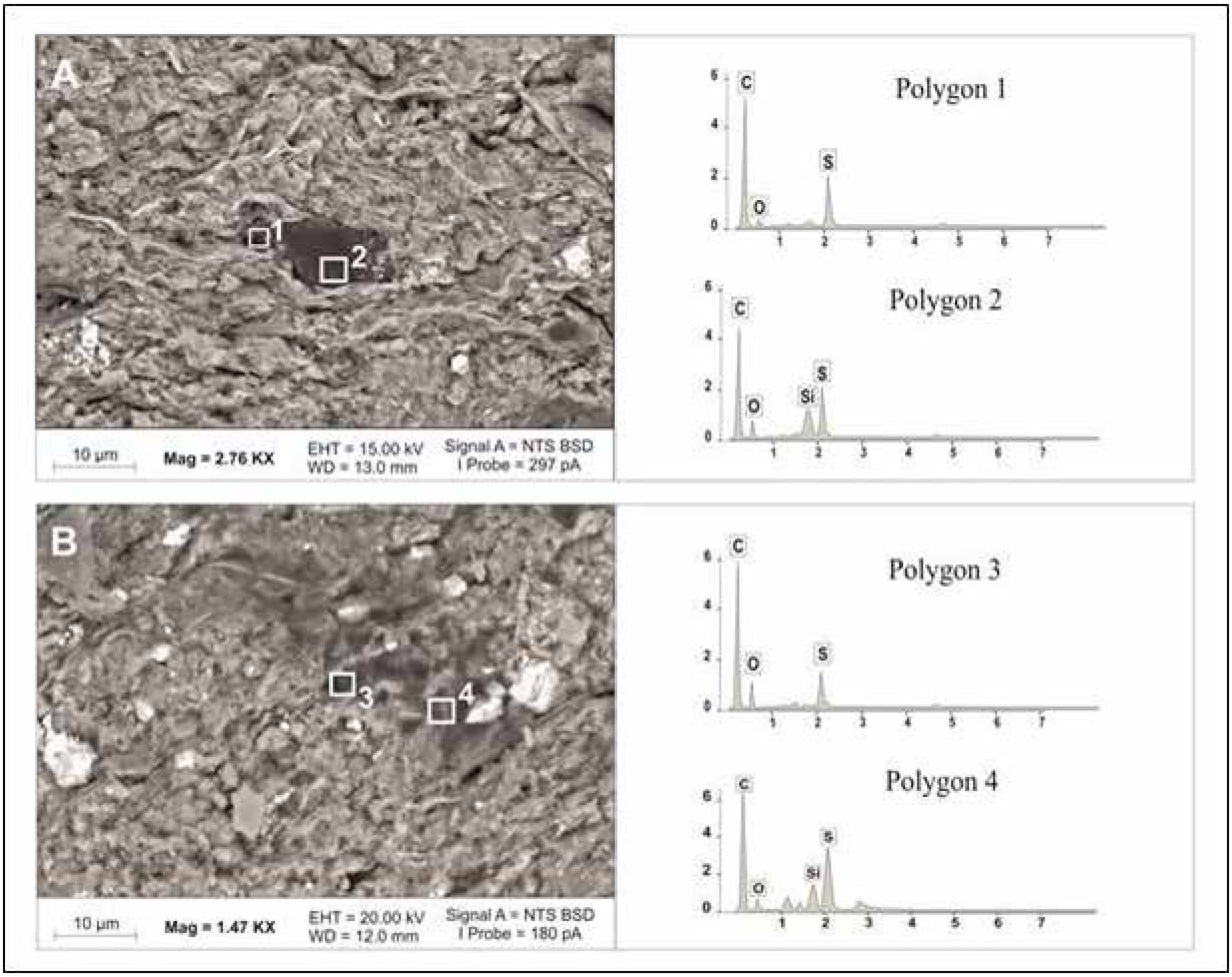

Figure 4 A. Organic matter patter in Taquaral Member; B. Organic matter patter in Assistência Member.

and diagenetic processes (Leventhal, 1983). Usually, C/S ratio is useful to recognize nonmarine/marine environments or oxic/anoxic depositional environments (Leventhal, 1995). According to Berner & Raiswell (1984) marine rocks are characterized by low C/S values (0.5-5) and freshwater rocks by high C/S values (>10). However, the application of these methodologies, in the current study, would not evidence the paleoenvironmental conditions of the Irati Formation. We interpret that TOC values had been depleted due to the heat transfer from the intrusive rock.

Figure 5 correlates the main peaks where the TOC and S maximum values are recorded. We analyzed the set of logs and select the TOC max 4 as a datum. This is a marker which can be traced through all data points. Jahn *et al*. (1998) state that organic-rich shales represent a good datum correlation. Since shales are low energy deposit we may also assume that they have been deposited mostly horizontally, blanketing the underlying sediments thus creating a true datum plane.

Previously studies suggested that the deposition of Irati rocks occurred in a restrict marine environment with saline and anoxia fluctuations (Araujo, 2001; Rodrigues *et al.,* 2010; Alferes *et al.,* 2011; Rodrigues *et al.,* 2019; Holanda *et al.,* 2019a and others). Moreover, the organic-rich shales from Assistência Member are the section originally with higher TOC (Milani & Zalán,1999; Araújo *et al.,* 2000; Araújo, 2001; Milani *et al.,* 2006; Loutfi, 2011;). The high levels of TOC are directly related to the organic facies observed in this interval, as described by Araújo (2001), Gama (2011), Dos Santos (2017) and Reis *et al.,* (2018). There is a large difference between original values of TOC (well SP-32-PR) and the values modified by the presence of the intrusive rock (well SP-58-PR). Table 1 shows that the heat transfers from volcanic rock to the Assistência Member were responsible for a loss of 80.7% to 84.0% of the original TOC. It is important to note that while TOC is being depleted, S is apparently being kept

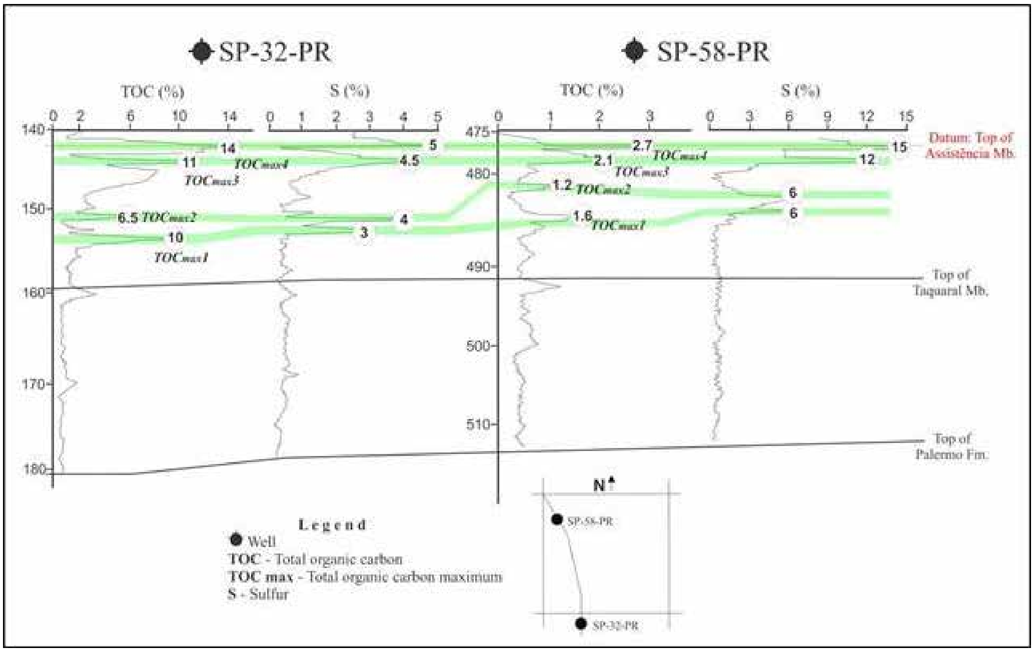

Figure 5 Correlation between TOC values of the Irati Formation without thermal influence from sills (SP-32-PR) and with thermal influence from sills (SP-58-PR).

TOC	SP-32-PR	SP-58-PR	TOC relative loss
TOC max 4	14%	2.7%	80.7%
TOC max 3	11%	2.1%	80.9%
TOC max 2	6.5%	1.2%	81.5%
TOC max 1	10%	1.6%	84%

Table 1 Correlation between TOC values.

unchanged; these two parameters usually go together in anoxic sediments.

Stewart *et al*. (2005) studied geochemically an igneous intrusion and the effects it had on the Springfield coal bed in southern Illinois. Coal closest to the intrusion was coked and heating at the contact volatilized sulfides near the contact, mobilizing volatile elements associated with pyrite. Quaderer *et al*. (2016) studied alterations experienced by the clastic sediments adjacent to the Springfield Coal. The authors observed that TOC in the shale is depleted near the intrusive contact and the temperature was insufficient for pyrite decomposition. Santos *et al*. (2009) investigated the geochemical effects induced by thermal effect of basic sill intruded on black shale of the Irati Formation in north of the Paraná Basin. The presence of organic matter films associated with stylolites and pyrite nodules at location up to 5 m from the lower contact suggested that organic matter was remobilized to various extents. Moreover, mineralogical studies from Irati Formation have demonstrated the formation of pyrite nodules close to the contact zones with the intrusive rock (Dos Anjos & Guimarães, 2008; Dos Anjos *et al.,* 2010; Holanda *et al.,* 2019b). These researches show similar results with the current work. Despite the depletion of TOC, the S content apparently keeps its original values. Thus, the heat transfer may have mobilized volatile elements associated with the formation of pyrite.

Souza *et al*. (2008) analyzed the thermal effects of the igneous intrusions on a potential source rock from Irati Formation. The data showed higher values of TOC close to the contact with the intrusive rock, which gradually decreased with the distance. The biomarker data indicated a low degree of thermal evolution for the extract sampled in the wet gas/dry gas zone, suggesting the presence of migrated hydrocarbons. In this case, there was no depletion of the TOC, on the contrary, the heat transfer helped to generate hydrocarbons. However, it is noteworthy that the maximum thickness of the igneous rock (25 m) is less than that analyzed in the current study (60 m), which indicates that the thickness of the intrusive rock can influence the amount of heat transferred. Souza *et al*. (2008) conclude that the thickness of the section affected by igneous intrusions depends not only of the temperature of the igneous body, but also of the depth of intrusion and thermal conductivity, which could explain the differences between maturation logs.

Galushkin (1997) has compiled several geochemical and petrological studies of host rocks that are thermally affected by igneous intrusion in different regions of the world. The author concludes that thermal influence usually extends from the contact to 50-90% of the intrusive thickness. According to these parameters, in well SP-58-PR, thermal influence has reached the full extent of the Irati Formation. However, some important studies have shown that the extent of the thermal effect also depends on other factors, including thermal conductivity, volume of pore water, and development of a convection cell, time, and maturation of the organic matter (Suchy *et al*., 1997; Barker *et al*., 1998).

Organic matter is easily identified from the analysis of SEM. Figure 4B exhibits organic matter with cloudy visual aspect, filling small fractures and being disseminated over mineral grains. According to Bernard *et al*. (2013) it is characteristic of a thermally evolved material, such as bitumen. However, Camp (2016) alerts that such methodology is not appropriate for the description of such parameters as kerogen, bitumen, pyrobitumen, etc.

6 Conclusions

Geochemistry organic data reveals important changes induced by thermal effects of igneous intrusion: SP-58-PR, where Irati Formation is in contact with diabase sill, presented low TOC values compared to the well without thermal influence of volcanic rocks. Thus these values are residuals and associated with a depletion of organic carbon brought about by heat transfer from the overlying diabase sill, causing cracking of the organic material, and thus lowering TOC levels until 84%. The heat transfer of the igneous rock may have assisted in the mobilization of volatile elements causing the formation of pyrite nodules.

The comparison with data from the bibliography shows that the thickness of the intrusive rock is not the only factor responsible for causing changes in the organic content of the Irati Formation.

SEM reveals an organic matter with cloudy visual aspect, filling small fractures and being disseminated over mineral grains, characteristic of a thermally evolved material in the Assistência Member.

7 Acknowledgements

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