

Carbonaceous Shales in the Araripe Basin, NE Brazil: A Potential Shale Gas Reservoir*

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Abstract

Recent interest in potential Brazilian shale-gas reservoirs (Oyegbile and Narra, 2012) has opened up exploration in a variety of sedimentary basins in the country. The Araripe Basin (8000 km², Pernambuco, Northeast Brazil, [Figure 1](#)) contains a series of Aptian-Albian deposits. We undertake a multi-disciplinary investigation on a series of intercalated carbonaceous pyrobitumen shales underling a sequence of Albian evaporites, in order to characterize their paleodepositional environment and assess the region's potential as a shale-gas reservoir. There are currently over 600 companies involved in the active extraction of the evaporites (the largest such deposits in Brazil) with several expressing interest in the petroliferous potential of the underlying shales.

Geological Setting

Main phase sedimentary deposition in the Araripe Basin occurred between the late Jurassic (Tithonian) and early Cretaceous (up to the Albian). The sediments in this study span the Aptian-Albian boundary (coinciding with oceanic anoxic event 1b) and make up what is locally known as the Santana Group (Neumann et al 2003). The deposition of the Santana Group occurred across a critical interval in the tectonosedimentary evolution of Brazil, namely the initial post-rift phase of the South Atlantic's opening (Ponte, 1992). This sedimentary succession is split into three formations (Crato, Ipubi, Romualdo). These consist of laminated limestones, carbonaceous shales, marls and siltstones (Crato), a large evaporitic sequence of anhydrite and gypsum with clay infillings and a pyrobitumenous shale base (Ipubi), and series of intercalated calciferous silt-mudstones, and limestones (Romualdo).

The carbonaceous pyrobitumen shales of the Ipubi Formation (the focus of this study) occur as a 0.5 - 2 m layer in most of the mines in the region. Further afield, borehole data show that this level can reach up to 15 m in thickness. It is thought that these formed above several 3-4 km diameter paleolakes. Possessing a characteristically pungent scent of hydrocarbons, they usually contain ostracods-rich lenses towards the contact of the overlying evaporites. Sulfur-rich shale levels are also found in many of the mines, formed due to pyrite oxidation.

Methods

Sampling of pyrobitumen shales was undertaken at five gypsum mines in the Araripe Basin. Samples were subsequently split into various aliquots for bulk rock x-ray diffraction (XRD), ICP-MS and phosphorus (inorganic and organic) analysis. Loss on ignition (LOI) was carried out as part of the phosphorus extraction allowing estimates to be made regarding organic matter content. Thermogravimetric analysis using GC-MS and major elemental analysis was used to corroborate the degree of organic matter enrichment. These proxies were selected in order to improve our understanding of paleoenvironmental and -diagenetic processes that led to the formation of this potential shale-gas deposit.

Results and Discussion

Diagenetic Environment

Significant organic matter enrichment is seen using thermogravimetric analysis, with a significant drop in sample weight percentage between 300-500°C ([Figure 2](#)). Elemental and Rock-Eval analyses (the latter from Delgado, 2012) also confirm high organic carbon content with up to 22.2 and 25.7 wt% being measured, respectively.

Despite significant OM, phosphorus analysis reveals low organic phosphorus (P-org) content. There is little difference in P-org content between shale and clay lithologies ([Figure 3](#)). The decoupling of the organic carbon and phosphorus pools is typical of anoxic environments in lacustrine and marine settings (Ingall and Van Cappellen, 1990; Mort et al. 2009).

Barium (up to 2% of BaO), a paleoproductivity indicator, is also elevated during shale deposition. The flux of organic matter to the sediment-water interface was thus probably very high, and would have triggering bottom water oxygen deficiency during organic matter degradation.

Outcrops frequently present a bed of brittle, unconsolidated sulfur-rich shales towards to the top of the shale succession, evidently due to pyrite oxidation (elemental analysis reveals sulfur a content of 5.32%). Nevertheless, its distinctive yellow-orange color suggests intense microbial sulfate reduction (MSR) was active during deposition. Conditions may have even reached euxinic, as seen by high concentrations of Vanadium (up to 817 ppm), which is scavenged by sulfide released during MSR (Emerson and Husted, 1991).

In terms of burial history, X-ray diffraction analysis reveals expansive and interlayered clays with illite/smectite (I/S) values ranging from between 10-30% of illite layers. This is consistent with the moderately deep alteration of smectite at temperatures in the order of 100°C (dry-gas to upper oil window).

Unconventional Reservoir Potential

GC-MS analysis undertaken by a separate study on equivalent material in the Araripe Basin shows that a series of homologous n-alkanes peak at C27 (Delgado, 2012). This chain length is conducive to organic matter derived from type III organic matter (terrestrial plants), traditionally a good source of hydrocarbons in gaseous form (Peters and Moldowan, 1993). The presence of pyrolytic bitumen is confirmed with a

thermogravimetric weight loss from 350-500°C ([Figure 2](#)). Furthermore, Rock-Eval analysis revealed an S2 peak of 125.65 mg HC/g, characteristic of an excellent hydrocarbon generator.

Given the strong scent of petroleum emanating from the rocks, it is clear that the shales of the Araripe Basin contain significant quantities of gas. A very conservative estimation of the occurrence of the oil/gas bearing shale in the western part of Araripe Basin shows an area of approximately 1,200,000 km², along which the shales bed varies in thickness, from few meters to tens of meters. The estimation of its potentially recoverable gas volume depends crucially on rock's permeability natural fracturing system. As most of the clay minerals, which constitute these beds, are expansive, an evaluation of the appropriate exploration strategies is also needed. Further research is needed to provide this information, as well as a better estimation of the total extension of exploitable shale beds and their depths.

Conclusions

The shales of the Araripe Basin were formed under a higher productivity, oxygen deficient regime that favored the preservation of large quantities of organic matter. This hypoxic environment led to the preferential release of phosphorus from organic matter during its degradation resulting in depleted P-org content. It also likely resulted in the formation of pyrite and the scavenging of vanadium by sulfides under anoxic-euxinic conditions. These conditions would have been conducive to the preservation of organic matter. Given the high paleoproductivity, preservation and apparent thermal maturity of the organic matter, we conclude that the shales of the Araripe Basin, likely represent a potentially large shale-gas unconventional reservoir, worthy of further investigation.

Acknowledgements

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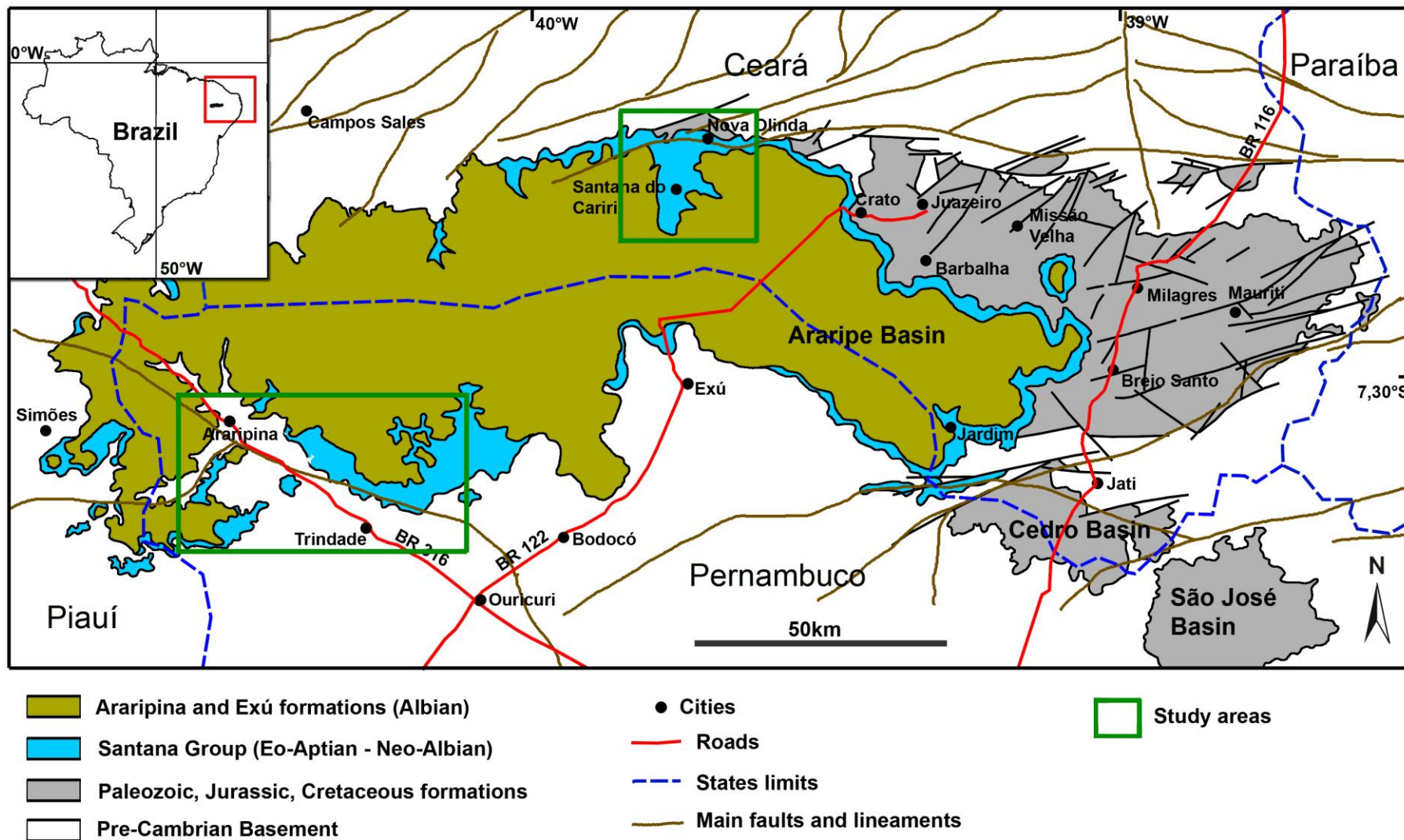


Figure 1. Location of the Araripe Basin (from Miranda et al., in prep).

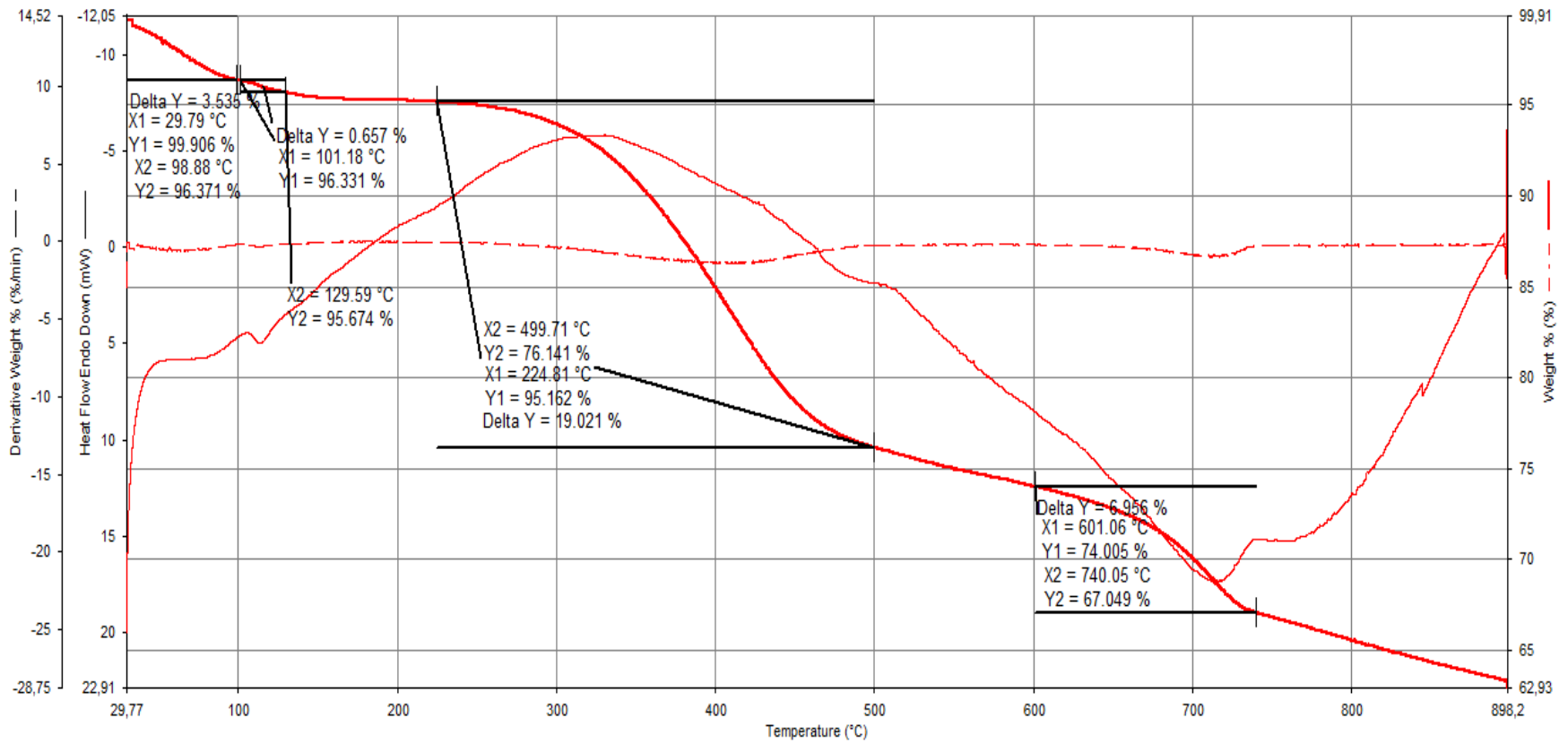


Figure 2. TGA weight loss and derivative curves for shale sample. The weight loss (thick red line) reflects the successive combustion of successively heavier organic compounds. Major weight loss occurs 300 and 500°C.

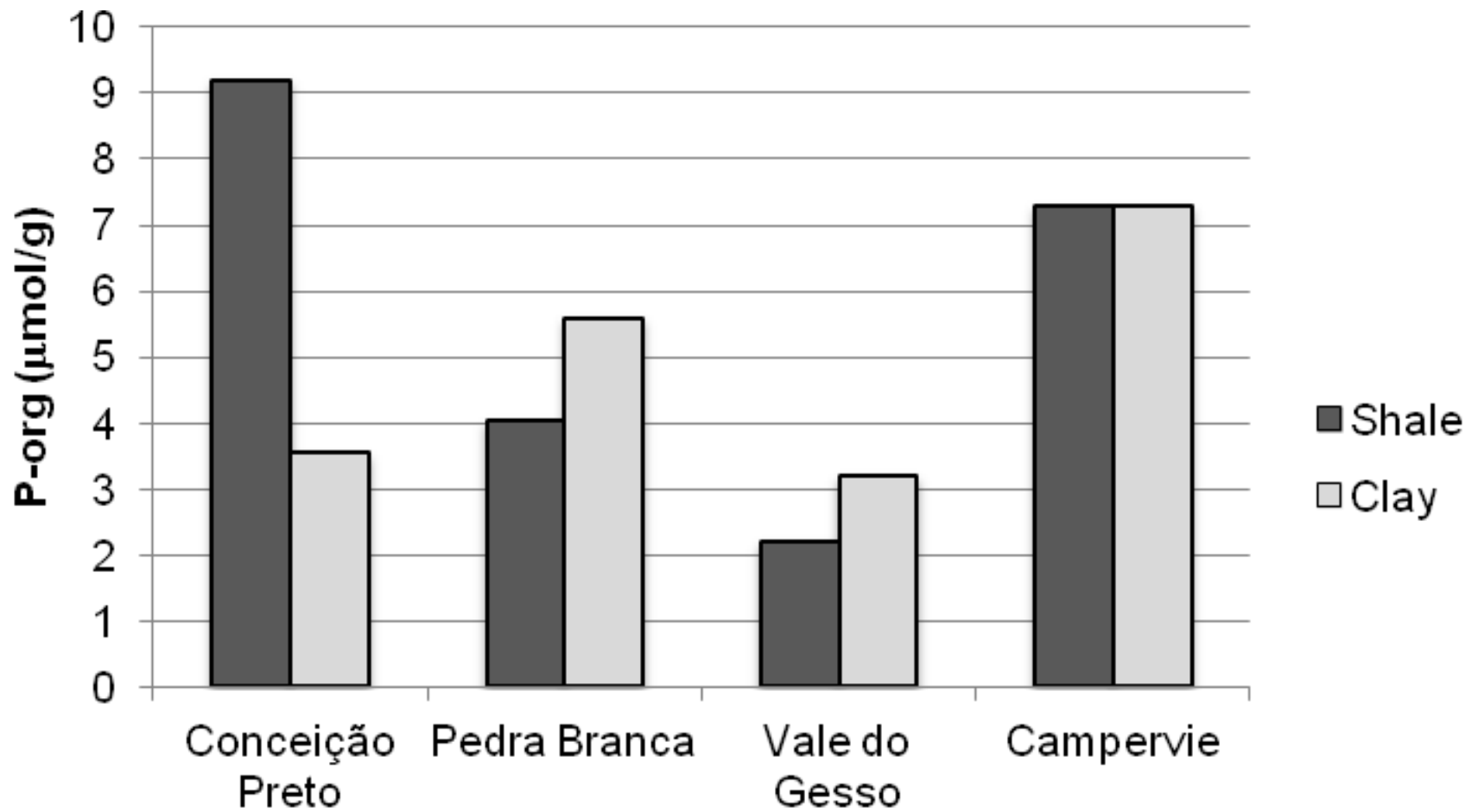


Figure 3. A comparison of organic phosphorus with organic rich (shale) and poor (clay) lithologies in the studied mines.