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LIGHT HYDROCARBONS IN SOILS UNDERLAIN BY EXCLUSIVELY CRYSTALLINE ROCKS AND IN SEDIMENTARY BASINS: EXPLORATORY IMPLICATIONS

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ABSTRACT

The ubiquity of light hydrocarbons (both saturated and unsaturated) in soils of sedimentary basins is well known. Concentrations above a certain background level in soil gas surveys are considered indicative of seepage of hydrocarbons from possible oil and gas fields in the subsurface. However, for obvious reasons, little attention has been given to regions outside sedimentary basins. The main purpose of this investigation was to ascertain the presence or absence of light hydrocarbons in areas of exclusively igneous and metamorphic rocks. It was concluded that the same light hydrocarbons found in soils of sedimentary basins are also present in soils of areas containing exclusively crystalline rocks. Consequently, light hydrocarbons concentration anomalies in sedimentary basins are not necessarily evidence of thermogenic hydrocarbons accumulations in the subsurface. Considering that only saturated hydrocarbons are present in petroleum and natural gas, the author suggests the use of ratios between saturated and unsaturated light hydrocarbons for characterizing oil and gas seeps and microseeps. Examples of exploration applications of this approach are presented in this paper.

RESUMO

A ubiquidade dos hidrocarbonetos leves (tanto saturados como insaturados) em solos de bacias sedimentares é bem conhecida. Concentrações acima de determinado *background* em levantamentos gasométricos são consideradas como indicativas de exsudações de hidrocarbonetos provenientes de possíveis acumulações petrolíferas existentes na subsuperfície. Entretanto, por razões óbvias, pouca atenção tem sido dada às regiões situadas fora das bacias sedimentares. O objetivo principal desta investigação era verificar a presença ou ausência de hidrocarbonetos leves em áreas exclusivamente de rochas ígneas e metamórficas. Concluiu-se que os mesmos hidrocarbonetos leves encontrados em solos de bacias sedimentares estão também presentes em solos de áreas contendo exclusivamente rochas cristalinas. Conseqüentemente, anomalias de concentração de hidrocarbonetos leves em bacias sedimentares não são necessariamente evidências de acumulações de hidrocarbonetos termoquímicos em subsuperfície. Considerando que no petróleo e no gás natural somente estão presentes hidrocarbonetos saturados, o autor sugere o uso de razões entre hidrocarbonetos saturados e insaturados para a caracterização de exsudações e microexsudações relacionadas a acumulações petrolíferas em subsuperfície. Exemplos de aplicações exploratórias desse enfoque são apresentadas neste trabalho.

INTRODUCTION

The author has been studying the occurrence and origin of light hydrocarbons in soils and recent sediments since 1974, aiming at establishing more effective and reliable methods and equipments for characterizing microseeps of thermogenic hydrocarbons. This paper summarizes some conclusions regarding the application of light hydrocarbon gases as an exploration tool for oil and gas.

The ubiquity of light hydrocarbons (paraffins and olefins) in soils of sedimentary basins is well known. The paraffins are ascribed to seepage from petroleum deposits and source rocks and the olefins (and part of the methane) to biosynthesis by bacteria and other organisms. On the other hand, little attention has been given to regions outside sedimentary basins, due mainly to the lack of attactiveness of those areas from the exploration viewpoint. The presence and distribution of light hydrocarbons in those regions, consequently, are poorly known.

PURPOSE OF THE INVESTIGATION

The main purpose of the present investigation was to ascertain if the same light hydrocarbons usually found in sedimentary basins are also present in soils of areas underlain by exclusively igneous and metamorphic rocks. This being the case, they can not be attributed to seepage of thermogenic hydrocarbons, since in this geologic setting neither petroleum accumulations nor source rocks are present in the subsurface. This is certainly an important information, since concentration anomalies of light hydrocarbons in soils of sedimentary basins are considered evidence of petroleum and natural gas in the subsurface and, therefore, are used as an auxiliary exploration tool.

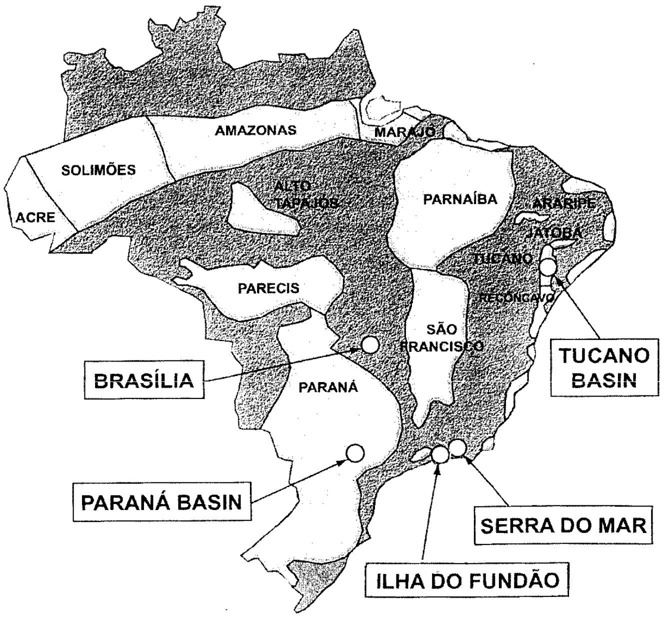

Figure 1 – Map of the onshore Brazilian sedimentary basins and areas of crystalline rocks. Open circles indicate the sites where samples were collected: Brasília, Serra do Mar and Ilha do Fundão (metamorphic areas) and sedimentary basins (Paraná and Tucano).

SAMPLING AND ANALYTICAL PROCEDURE

Three areas of highly metamorphosed rocks - where certainly neither oil fields nor source rocks exist - were selected for sampling soils specifically for this investigation: Brasília (Federal District), Serra do Mar (Rio de Janeiro State) and Ilha do Fundão (Rio de Janeiro State). For comparison purposes, samples were also collected in the Paraná Basin (São Paulo State) and data already available from the Tucano Basin (Bahia State) were integrated with the more recent data.

Figure 1 shows the onshore Brazilian sedimentary basins and areas where the soil is underlain by crystalline rocks. Open circles indicate the sites where soil samples were collected for the present investigation.

The soil was sampled at the bottom of 1 meter deep auger drilled holes and immediately stored in conventional 300cm^3 tin cans. A saturated NaCl solution and a bactericide were added to the cans to stop bacterial action, leaving a headspace equivalent to 1/3rd of the can height. The cans were kept upside down to prevent gas leakage through the lids. For comparison purposes, the soil in the Ilha do Fundão area was also sampled directly, using a special device developed by the author at PETROBRAS' Research Center (CENPES).

Headspace hydrocarbon gases and vapors were analysed in a HP 5890 gas chromatograph equipped with flame ionization detectors and a 50m fused silica column with Al_2O_3/KCl stationary phase. The same equipment and analytical procedure were employed for analyzing soil gases sampled directly for comparison purposes.

RESULTS AND DISCUSSION

Brasília soils (Ferreira, 1998) were found relatively rich in light hydrocarbons. Gas concentrations varied between 60 and 114 ppm. Methane, ethane, ethene, propane, propene, *iso*-butane, *n*-butane, 1-butene, *n*-pentane and some non-identified hydrocarbons were detected in all samples. The olefins are slightly more abundant than the paraffins and an excellent linear correlation exists between ethane and ethene. The same results were obtained from samples collected in the Serra do Mar region (Ferreira, 1999) and in the Ilha do Fundão (CENPES area) (Ferreira, 2000). Methane predominates in all cases, representing 55 to 75% of the total light hydrocarbons (C_1 to C_5).

Figure 2 (A, B and C) shows gas chromatograms of representative samples from Brasília, Serra do Mar and Ilha do Fundão areas. Notice that the analytical results are very similar, despite the fact that Brasília is more than 1,000 kilometers from Rio de Janeiro. This figure also includes ethane *versus* ethene plots, which show the excellent linear correlation above mentioned.

Figure 3 (A and B) presents the analytical results, for comparison purposes, of samples from two far apart Brazilian sedimentary basins (Paraná and Tucano). Notice the impressive similarity between the gas chromatograms obtained from samples collected in the igneous and metamorphic regions (Basília, Serra do Mar and Ilha do Fundão, Figure 2) and those from the sedimentary basins (Paraná and Tucano): (1) The same light hydrocarbons (paraffins and olefins) are present; (2) the paraffin/olefin ratios are approximately the same; (3) the olefins, similarly, predominate slightly over the paraffins; and (4) an excellent correlation exists between ethane and ethene.

Recently a new detailed gas survey was performed in the Serra do Mar area. Fifteen wells were drilled to depth of up to 28 meters in soils developed in this highly metamorphosed region. Samples were collected every meter from the surface to the bottom of the wells. *All 195 samples presented analytical results identical to those obtained from samples already collected in this and other areas of crystalline rocks and in sedimentary basins* (Ferreira, 2001).

It is opportune to remark that Smith and Ellis (1963), almost 40 years ago, detected the same light hydrocarbons in the San Bernardino Mountains (igneous and metamorphic region) and in the Los Angeles sedimentary basin. Our

Light Hydrocarbons in Soils of Metamorphic Areas

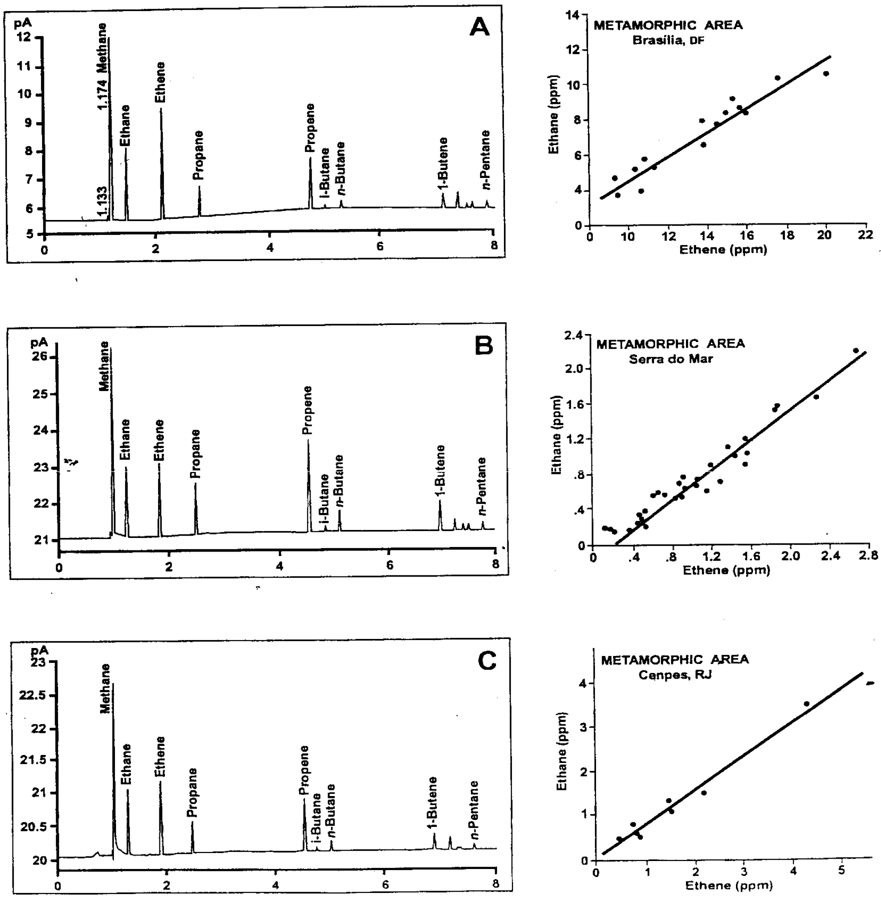

Figure 2 – Gas chromatograms of light hydrocarbons in soils of metamorphic areas and ethane/ethene plots. Notice the composition similarity and the excellent linear correlation between ethane and ethene.

results fully corroborate the findings of those authors.

The above results indicate that the light hydrocarbons found in soils of crystalline regions and in sedimentary basins must have the same origin. Considering that in regions of exclusively crystalline rocks petroleum accumulations and source rocks are absent, the origin of the light hydrocarbons, both saturated and unsaturated, must be biochemical, generated by low temperature chemical reactions. There is no question that methane can be produced by bacteria, and biosynthesis of light hydrocarbons heavier than methane is well documented in the literature (Davis & Squires, 1954; Juranek, 1958; Weber & Turkel'taub, 1960; Malishek *et al.* 1962; Kim & Douglas, 1972; Primrose & Diltworth, 1976; Hunt *et al.*, 1980; Oremland, 1981; Ullom, 1988; Bernard & Brooks, 1999).

In sedimentary basins, occasionally, part

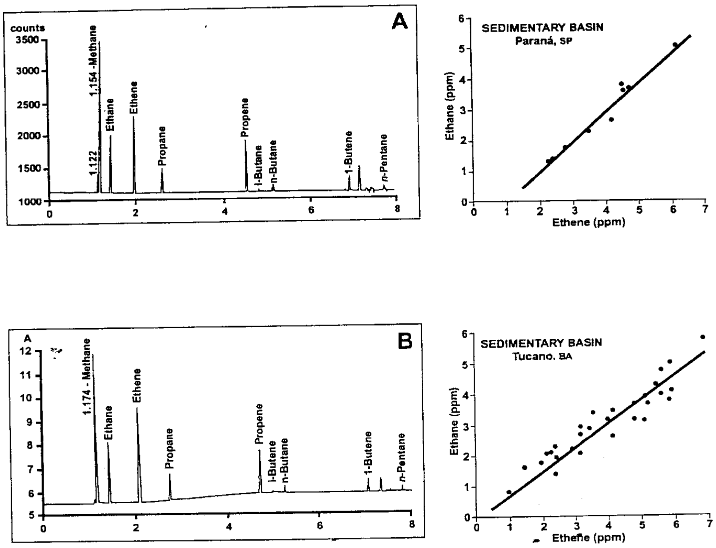

Figure 3 – Gas chromatograms of light hydrocarbons in soils of sedimentary basins and ethane/ethene plots. Notice the similarity of composition with those of metamorphic areas (Figure 2) and the excellent linear correlation between ethane and ethene.

of the *saturated* hydrocarbons in the soil can be thermogenic, from seepages of oil and gas along faults and fractures in the sedimentary column. Since only saturated light hydrocarbons exist in petroleum and natural gas, the ratio between paraffins and olefins increases when the thermogenic hydrocarbons mix with near surface autochtonous biochemical hydrocarbons. This ratio, consequently, can be useful for identifying seeps and microseeps of hydrocarbons related to possible oil and gas accumulations, as proposed by Ferreira (1976). It is interesting to remark that recently Bernard & Brooks (1999) obtained essentially the same conclusion working with piston cores taken from the continental slope offshore Nigeria, Angola and Gabon in western Africa, the southern Caribbean, and western and central Gulf of Mexico. According to those authors, "The natural presence of high levels of C_2+ alkanes serves as a good indicator of migrating thermally sourced gas, because ethane, ethene, propane, propene, the butanes, and the pentanes are not microbially produced at these levels in marine sediments". "We have found that the ethane/ethene ratio in sediments is a particularly robust indicator for surface geochemical exploration", concluded the authors.

EXPLORATORY APPLICATIONS

The ubiquitous nature of light hydrocarbons (paraffins and olefins) in soils, sea water and recent sediments must be considered when interpreting analytical data from soil gas surveys. The concentration of autochtonous light hydrocarbons in soils is not constant, varying within a broad range due to causes not necessarily relatated to seepages of thermogenic hydrocarbons, such as depth of sampling, availability of nutrients, rainy or dry season and so forth. Besides this, as stressed in this paper, the

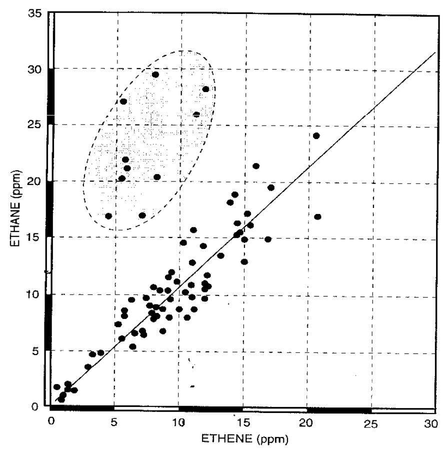

Figure 4 – Ethane/ethene plot of samples collected in a Brazilian onshore sedimentary basin. Notice the excellent linear correlation between ethane and ethene and that 10 samples plot above the line of best fit due to ethane enrichment.

same light hydrocarbons found in sedimentary basins are also present in soils of exclusively igneous and metamorphic regions. Consequently, light hydrocarbons concentration anomalies alone in sedimentary basins are not necessarily evidence of petroleum or natural gas in the subsurface. Ratios between paraffins and olefins in soil gas analyses is probably the most effective tool for identifying thermogenic hydrocarbons in soils, as the following real examples clearly demonstrate.

1 - High ethane/ethene ratios in soil gases above a large gas field

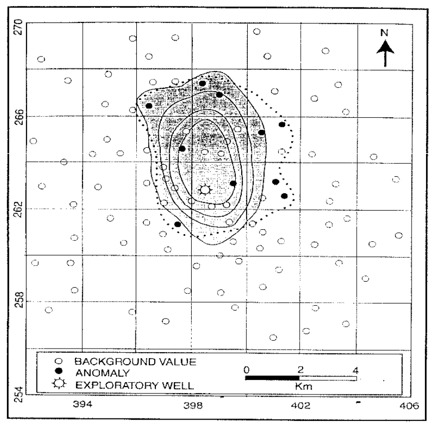

Figure 5 – Map showing the good match between soil samples with anomalous ethane/ethene ratios (Figure 4) and the seismic structure where a large gas field was discovered.

A detailed soil gas survey in a Brazilian onshore sedimentary basin resulted only in background values of light hydrocarbons concentrations and the area was considered as non-attractive for petroleum exploration. Despite this, a wildcat well was drilled in a well defined seismic anticlinal structure in that basin and a relatively large gas field was discovered. Later, a second nearby seismic structure was also drilled and another equally large gas field was discovered.

Figure 4 shows the ethane *versus* ethene plot for all samples colected for soil gas analyses in that area. Notice the excellent linear correlation between ethane and ethene presented by the majority of the samples. Ten of the samples, however, are anomalous, plotting well above the best fit line on the graph, due to enrichment in

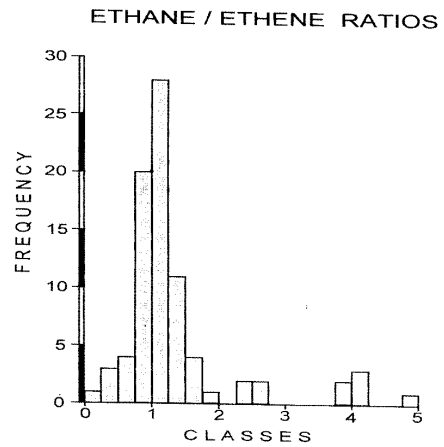

Figure 6 – Frequency histogram of ethane/ethene ratios. Notice the normal distribution of most samples and that the anomalous samples (Figure 5) belong to different populations.

ethane (The gas chromatograms also show enrichment in the other alkanes).

Figure 5 presents a map where the above anomalous samples were represented by solid black circles and background values by open circles. For comparison purposes, the seismic structure (solid contours) was also plotted on the map. Notice the good match between the interpred field outline (dashed line) and the seismic structure. The map also shows the location of the discovery well.

Figure 6 presents a frequency histogram

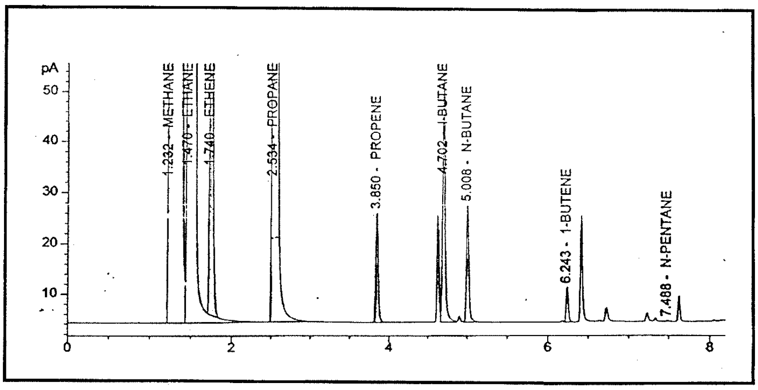

Figure 7 – Gas chromatogram of a sample collected in the water well (see text). The very high ethane/ethene and propane/propene ratios indicate seepage of thermogenic light hydrocarbons from a possible oil or gas accumulation in the subsurface.

of ethane/ethene ratios for all samples collected in the area. Notice the normal distribution of most data. Ten ratios, however, clearly belong to different populations, representing anomalies resulting from enrichment in the paraffin component (ethane). This enrichment was interpreted as evidence of seepage of thermogenic hydrocarbons from the underlying gas field.

The seepage above reported must be along fault and fractures, since normal background values are also found immediately above the field. As a matter of fact, the anomalous values seems to be aligned according to the regional fault pattern of the area (Ferreira, 1999).

2 - Very high ethane/ethane and propane/propene ratios related to a non-commercial gas accumulation

In another Brazilian onshore sedimentary basin, a sample was collected in a shallow water well. The light hydrocarbons from this sample were found highly enriched in paraffins, as evidenced by the gas chromatogram reproduced in Figure 7. The ethane/ethene ratio in this sample is 149 and the propane/propene ratio 55. The same ratios in nearby soil samples presented normal background values of 0.80 and 0.55, respectively. The high ethane/ethene and propane/propene ratios were interpreted as resulting from the mixing of thermogenic light hydrocarbons (seeping from a possible oil or gas accumulation in the subsurface) with autochtonous near surface light hydrocarbons (biogenic, generated by low temperature chemical reactions). This interpretation was corroborated by carbon isotope ratios of methane and ethane (Ferreira & Takaki, 1997a). A wildcat well was subsequently drilled 30m away from the water well and discovered a small non-commercial gas field. The gas, composed entirely of saturated hydrocarbons, was interpreted as thermogenic. This interpretation was also confirmed by carbon isotope ratios (Ferreira & Takaki, 1997b).

3 - First light hydrocarbons survey in Brazil

The author conducted an offshore survey, in 1974, in part of the Campos Basin, Rio de Janeiro, Brazil. By using ratios of saturated/unsaturated light hydrocarbons, three anomalies in the composition of light hydrocarbons were detected, parallel to the main fault pattern of the area. In one of the anomalies PETROBRAS discovered the first oil field of the basin, the Albacora Field (Ferreira, 1976). Later, a large oil field was discovered immediately to the south of the second anomaly and a non-commercial well was completed close to the third anomaly.

CONCLUSIONS

a) The same light hydrocarbons ubiquitously found in soils of sedimentary basins were positively identified in areas of exclusively crystalline rocks;

b) The soil gas is composed of a mixture of saturated and unsaturated light hydrocarbons, with an slight predominance of the latter;

c) The relative proportions of paraffins and olefins are very similar in both sedimentary basins and in areas of exclusively crystalline rocks;

d) The similarity of the light hidrocarbons in soils of sedimentary basins and areas of exclusively crystalline rocks indicates a biochemical origin;

e) When thermogenic gas seeps to the surface, the soil gas is enriched in saturated hydrocarbons, thus increasing the saturated/unsaturated ratio;

f) High saturated/unsaturated ratios detected in soil gas surveys are probably the most effective and reliable indicators of seepages of thermogenic hydrocarbons from oil and gas accumulations in the subsurface;

g) However, high saturated/unsaturated ratios can also be due to thermogenic saturated light hydrocarbons migrating from source rocks not necesssarily related to oil or gas accumulations.

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