[PS]Origin of CO_2 in Brazilian Basins*

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Abstract

Carbon dioxide is one of the most common non-hydrocarbon gases found in petroleum reservoirs. However, petroleum accumulations with CO_2 > 20% can be considered relatively rare. The most important source of the large volumes of CO_2 found in petroleum accumulations is the mantle. Commonly, areas with major CO_2 risks are associated with "hot basement" (GG > 30° C/km), deep seated faults, igneous intrusions and basin rifting.

Representative gas samples were collected in petroleum accumulations from 11 Brazilian basins aiming to identify the origin of the produced CO_2. Emphasis was given to the pre-salt basins occurring along the southeastern Brazilian margin. Results used in this investigation include $\delta^{13}C$ of C_1-C_4 and CO_2; percentages of C_1-C_4, CO_2 and other non-hydrocarbons, as well as, concentrations and isotopic ratios of associated noble gases. Data were complemented with $\delta^{13}C$ and $\delta^{18}O$ measured in CO_2 from micropyrolysis experiments using pre-salt carbonates and kerogens.

Regarding the origin of CO_2, results have shown a clear separation in two groups. One represented by almost exclusively CO_2 originated in the mantle ($\delta^{13}C_{CO_2}$ mostly within -7‰ and -5‰, and, relatively high values for $^3He/^4He$ represented by R/Ra up to 5.60). This type of CO_2 can be found in the pre-salt petroleum accumulations with abundances of up to 80%. The second group is represented by CO_2 derived from organic matter originated from microbiological or diagenetic processes (highly enriched or highly depleted in ^{13}C). Many examples of this group have shown a detectable mantle contamination ($0.02 < R/Ra < 1.81$).

The results of this investigation corroborate the worldwide trend that correlates directly CO_2 abundance with intensity of mantle contribution. However, not all of our studied cases have shown a recognizable relationship between CO_2 abundance and deep faults, igneous rocks, or anomalies in the geothermal gradient. These observations suggest that more investigations are necessary to improve our knowledge about the mechanisms and processes of CO_2 generation and migration upwards from mantle to petroleum accumulations in sedimentary basins.

Origin of CO_2 in Brazilian Basins

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Introduction

Carbon dioxide is one of the most common non hydrocarbon gas found in petroleum reservoirs. It can have different origins and petroleum accumulations with CO_2 > 20% can be considered relatively rare (Fig. 1). In those cases invariably mantle is the most important source of the CO_2. Therefore, commonly CO_2 in sedimentary basins is external to petroleum systems, mostly magmatic related (Gilfillan *et al.*, 2008). In the literature, areas with major "CO_2 risk" are associated with "hot basement" (GG > 30ºC/km), deep seated faults, igneous intrusions, crustal thinning associated with basin rifting, type and age of the basement, fault density and reservoir conditions (Clayton, 1995; Thrasher and Fleet, 1995, Imbus *et al.*, 1998; Li *et al*, 2008).

$^{13}C/^{12}C$ is useful to separate organic from inorganic CO_2 (FIG. 2). However, $\delta^{13}C$ of CO_2 originated from different processes can overlap their ranges in variable extensions (Fig. 3). Therefore, a reliable origin of CO_2 can be achieved only when noble gases are used in the interpretation (Sherwood Lollar *et al.*, 1997; Pinti & Marty, 2000).

In this work will be shown part of the results obtained from a study developed together by Petrobras R&D Center and IFPEN that aimed to identify the origin of CO_2 in the prolific Brazilian basins. Emphasis in the research was given to the presalt reservoirs found in offshore southeastern Brazilian basins.

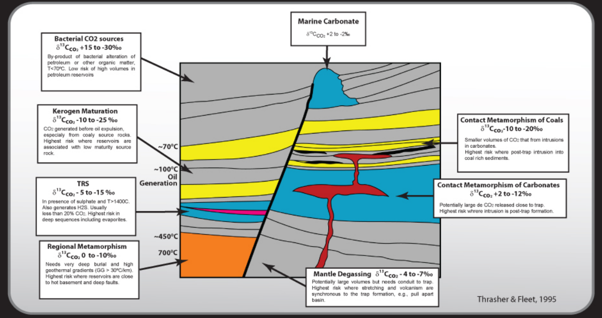

Fig. 1 – Stable carbon isotopic composition of CO_2 accordingly to origin.

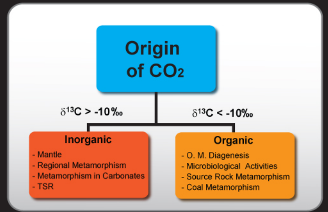

Fig. 2 – Origin of CO_2 based on $^{13}C/^{12}C$ variations.

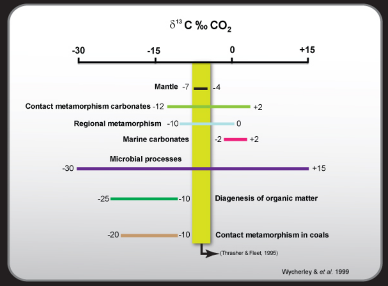

Fig. 3 – Range of $\delta^{13}C$ of CO_2 with different origins.

Methods and Materials

Representative gas samples from 11 Brazilian basins were collected directly from well heads or separated as aliquots of PVT samples (Fig. 4). Great care was devoted in order to avoid any kind of contamination. Emphasis was given to the presalt reservoirs concentrated along the southern offshore Brazilian basins.

Results used in the investigation include $\delta^{13}C$ of C_1-C_4 and CO_2; percentages of C_1-C_4, CO_2 and other non-hydrocarbons, as well as, concentrations and isotopic ratios of noble gases. Data were complemented with $\delta^{13}C$ and $\delta^{18}O$ measured in CO_2 from micropyrolysis experiments (MSSV, see details of the method in Horsfield *et al.*, 1989) using presalt carbonates and kerogens (Results not shown here).

Noble gases were separated and concentrated from gas samples. The quantification of each measurable isotope allowed to calculate ratios diagnostic of mantle and crustal signatures. Details about the integrated use of hydrocarbon and noble gas methodology can be found in Battani *et al*. (2000) and Prinzhofer *et al*. (2010).

Geochemical results were used integrated to the geological and geophysical data in order to achieve the interpretation of CO_2 origin and for improvements in the knowledge of petroleum systems used in this study.

Fig. 4 – Basins used in this study

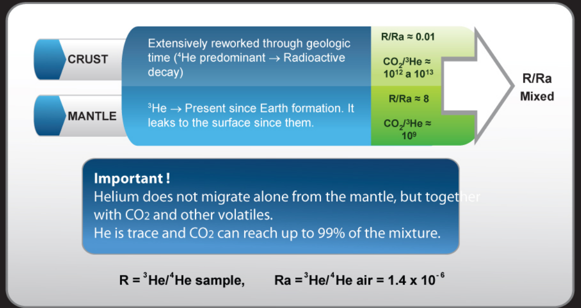

Fig. 5 – Relationship between R/Ra and $CO_2/^3He$ in gases from crust and from mantle.

Results

Among the studied basins, the largest variation in CO_2 content (≈1% < CO_2 <≈80%) and the strongest mantle signature have been found in the Santos Basin. In the Campos Basin CO_2 is less abundant than in Santos however the strong mantle signature is evident (Table I, Fig. 6).
R/Ra values of each sample allow the calculation of percentages of mantle helium (Figs. 7 and 8). Using the known values for the CO_2/He for the mantle and crust it is possible to infer the relative amount of CO_2 derived from the mantle. As example one sample with R/Ra 4.8 has approximately 60% of helium from the mantle. Following the model about 97% of the associated CO_2 was sourced by the mantle (Fig. 9).

The relationship between CO_2 abundance and the mantle signature (R/Ra) is conspicuous (Fig. 10). $\delta^{13}C$ of CO_2 in accumulations with the most significant percentages of CO_2 are clustered preferentially between -5‰ and -10‰ (Fig. 11), and corroborates the mantle as source for the carbon dioxide. The Campos Basin has also a strong mantle signature (Table I), values of $\delta^{13}C$ for CO_2 between ≈-2‰ and ≈-5‰, however CO_2 is lower than 5% in the sampled fields.

In the Potiguar offshore, Solimões, Ceará, Espírito Santo onshore, Recôncavo, Tucano Sul, Camamu and Sergipe-Alagoas CO_2 is less than 4%. The origin of CO_2 in these basins is mostly organic, as suggested by the relatively low $\delta^{13}C$. However, R/Ra values are relatively small and variable indicating that occurred mantle contaminations in basin fluids within the Potiguar offshore, Ceará, Espírito Santo onshore, and Sergipe-Alagoas basins (Table I).

R = $^3He/^4He$ (Sample) Ra = $^3He/^4He$ of the air (standard) ≈ 1.4 x 10^{-6}

Basin	R/Ra min	R/Ra max
Recôncavo-Tucano Sul	0.012	0.029
Sergipe-Alagoas	0.013	0.075
Solimões	0.015	0.026
Espírito Santo	0.15	0.70
Ceará	0.06	1.81
Potiguar onshore	0.01	1.26
Potiguar offshore	0.37	1.61
Campos	0.08	2.26
Santos	1.81	5.60
Neuquén	0.80	4.60

Table I – R/Ra minimum (min) and maximum (max) of the helium found in gas samples from different Brazilian basins used in this study and in the Neuquén Basin, Argentina (from Prinzhofer et al., 2009).

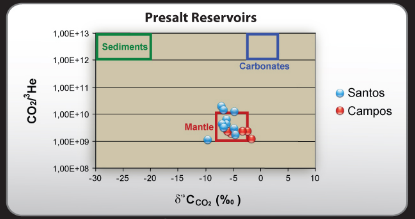

Fig. 6 – Relationship between $CO_2/^3He$ and $\delta^{13}C$ of CO_2 in gases from crust and from mantle. Notice the clustering of the studied samples collected in Santos and Campos basins.

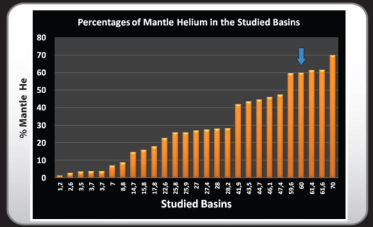

Fig. 7 – Percentage of helium from mantle in gas samples from the studied basins.

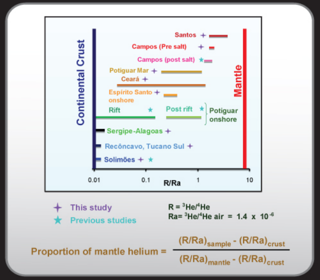

Fig. 8 – R/Ra of helium from gas samples of Brazilian basins.

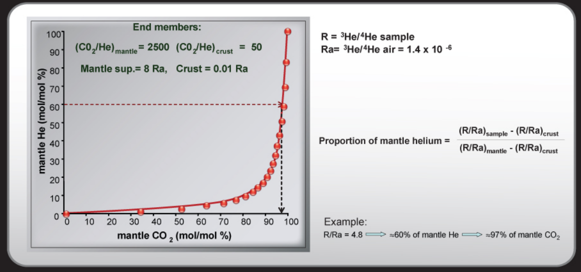

Fig. 9 – Estimation of the CO_2 contribution from mantle.

Presalt - Santos Basin

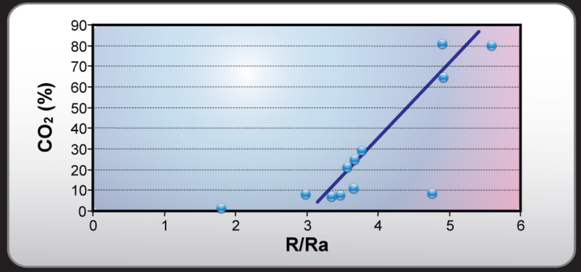

Fig. 10 – Relationship between abundance of CO_2 and intensity of mantle influence.

Santos Basin

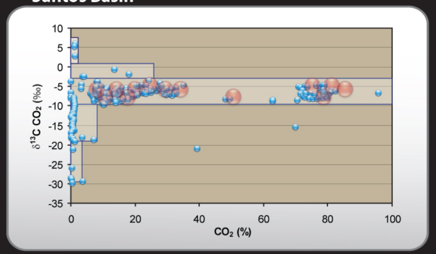

Fig. 11 – Relationship between $\delta^{13}C$ and abundance of CO_2 in gas phase of samples from the Santos Basin (presalt reservoirs). Notice the clustering of the CO_2 most enriched gases within the range of about -10‰ and -5‰.

Conclusions

Among the study cases, the Santos Basin has the most significant occurrences of CO_2, with up to 80% in gas phase, that are concentrated in presalt reservoirs and have isotopic mantle signature. This evidence suggests that deep fluids may have had a significant influence on petroleum systems.

Other basins used in this study have relatively low CO_2 abundance (less than 4%) and were derived predominantly of organic processes with virtually nill or relatively minor contributions of mantle CO_2. In these cases, CO_2 is relatively depleted in ^{13}C (decarboxylation of organic matter or contact methamorfism in organic rich rocks) or extremely enriched in ^{13}C (association of oil biodegradation and methanogenesis), but in these cases R/Ra ratios varies between 0.012 to than 1.61.

Overall results of this investigation are compatible with most of the data published in the literature that show a direct correlation between the abundance of CO_2 and an origin related to the mantle. However, the relationship between deep faults, magmatic activity, crustal thinning or anomalies in the geothermal gradient and CO_2 abundance is not clear, suggesting that other variables can be important to govern the distribution of CO_2 within a basin.

These results suggest that more systematic investigations are necessary to improve our knowledge on the "CO_2 risk" in petroleum systems.

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