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Research paper

Contribution of siderite–water interaction for the unconventional generation of hydrocarbon gases in the Solimões basin, north-west Brazil

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ABSTRACT

Hydrocarbon gases with unconventional carbon isotopic signatures were observed in the Solimões sedimentary basin in north-west Brazil. Siderite contents measured with a new Rock-Eval methodology in the drill-cuttings samples of the Famenian source rock were found to decrease with the increase of gas maturity and with the occurrence of the gas isotopic anomalies. Triassic diabase intrusions induced heating of the source rock, which likely resulted in the gradual oxidative dissolution of siderite as suggested by the observation of etch pits on the siderite surfaces. It is proposed that ferrous iron from the carbonate was involved in a redox reaction with water producing ferric iron and H_2, then reducing CO_2 and yielding an inverse correlation between siderite content and gas maturity. Alternatively, hydrogenation of highly mature kerogen by H_2 derived from siderite could explain the production of ^{13}C-rich CH_4. Mass balance considerations suggest that these mechanisms may account for a significant fraction of the hydrocarbon gases generated from the Famenian source rock in the Solimões basin.

1. Introduction

Natural hydrocarbons are most often formed either by microbial processes (Whiticar et al., 1986), or by thermal decomposition of organic matter following a kinetic law dependent on both time and temperature (Tissot et al., 1987). Both processes lead to an isotopic fractionation of the produced hydrocarbons with respect to their source, due to the preferential breaking of bounds containing ^{12}C (Des Marais et al., 1981). Thereby, thermal generation of hydrocarbons results in an enrichment of the products in ^{12}C, i.e., a decrease of the $\delta^{13}C$ with a decrease in carbon number (Chung et al., 1988; Prinzhofer and Huc, 1995). This implies that there is a so-called “normal isotopic trend” for hydrocarbon gas compounds, with $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \ldots$ where C_1, C_2 and C_3 … stand for the number of carbon atoms in the molecule.

Increasing demand for natural gas has led petroleum exploration toward unconventional gas accumulations such as tight gas sands, fractured reservoirs, coalbed methane and shale gas. Reversal from the normal sequence of isotopic compositions ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$) has been reported in few conventional gas accumulations, but becomes more common in unconventional accumulations (e.g., Jenden et al., 1993; Laughrey and Baldassare, 1998; Burruss and Ryder, 2003; Dai et al., 2004, 2005). In shale gas accumulations, isotopic inversion has been proposed to be a fair indicator of the quality of the resource (Tang and Xia, 2010; Zumberge et al. 2012).

Reversals in isotopic compositions can result from different processes such as the oxidative destruction of hydrocarbon gases by either thermochemical sulfate reduction (Krouse et al., 1988) or microbial activity (James and Burns, 1984; Hunkeler et al., 1998; Katz, 2011), or the mixing between gases from sources at different levels of maturity and different origins including abiotic sources (Jenden et al., 1993; Dai et al., 2004, 2008; Huang et al., 2004; Xia et al., 2013). Prinzhofer and Huc (1995) showed that isotopic reversals can also be explained by partial diffusive leakage

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from gas reservoir involving the most diffusive molecules, i.e., the ^{13}C-depleted compounds. Rayleigh fractionation of ethane and propane driven by redox reactions with transition metals and water at high temperatures (>250 °C) were proposed by Burruss and Laughrey (2010) to explain the isotopic inversions reported in hydrocarbons from the northern Appalachian basin.

During the study of mineral exploration boreholes in crystalline Precambrian rocks, Sherwood Lollar et al. (2002, 2006) reported alkanes presumably generated from abiotic processes showing $\delta^{13}C_1 > \delta^{13}C_{2-4}$. Such patterns could result from kinetically controlled synthesis of high-molecular-mass alkanes from smaller ones (polymerization) in which the lighter $^{12}CH_4$ reacts faster than the heavier $^{13}CH_4$ to be incorporated into larger hydrocarbon chains (Des Marais et al., 1981; Yuen et al., 1984). To explain abiogenic gas production, Sherwood Lollar et al. (2002, 2006) suggested either heating or metamorphism of graphite-carbonate-bearing rocks (Giardini et al., 1968; Holloway, 1984), or a Fischer-Tropsch-Type process, consisting of surface catalyzed reduction and polymerization of CO or CO_2 into CH_4 and larger hydrocarbon gases. Abiotic generation of hydrocarbons through the Fischer-Tropsch-Type process is commonly evoked in geothermal systems associated with ultramafic rocks at mid-oceanic ridges (e.g., Holm and Charlou, 2001; Kelley et al., 2001; Charlou et al., 2002) or in ophiolites (e.g., Abrajano et al., 1988; Hosgormez et al. 2008; Etiope et al., 2011). In this context, the serpentinization of olivine induces the production of H_2-rich fluids from redox reactions between ferrous iron and water:

$$Fe^{2+}{}_{(Olivine)} + H_2O \rightarrow Fe^{3+}{}_{(Magnetite)} + OH^- + 0.5\,H_2 \tag{1}$$

The produced H_2 subsequently reduces the CO_2 transported in the hydrothermal fluids to produce hydrocarbons including CH_4. In fluids from the Lost City hydrothermal vents, Proskurowski et al. (2008) report the formation of alkanes from C_2 to C_4 depleted in ^{13}C relative to CH_4. Polymerization of light $^{12}CH_4$ into longer alkanes during a Fischer-Tropsch-Type process was proposed to explain the inverse isotopic trend.

The generation of H_2- and CO_2-rich fluids enabling the Fischer-Tropsch-Type process can also be achieved through reaction between water and siderite ($FeCO_3$). Experimental decomposition of siderite in the presence of vapor at 300 °C by McCollom (2003) produced mainly magnetite along with CO_2 and H_2 in the gas phase. Small amounts of organic compounds including CH_4 also formed suggesting an overall reaction written as

$$\underset{\text{siderite}}{3\,FeCO_3} + w\,H_2O(l) = \underset{\text{magnetite}}{Fe_3O_4} + x\,CO_{2(g)} + y\,CO_{(g)} + z\,H_{2(g)} + \underset{\text{compounds}}{\text{organic}} \tag{2}$$

(McCollom, 2003), where w, x, y and z are stoichiometric coefficients. Milesi et al., 2015 conducted laboratory experiments between siderite and water in gold containers at 200–300 °C and 50 MPa, which yielded mostly magnetite, condensed carbonaceous material, CO_2, H_2 and CH_4. Thermodynamic calculations indicate that CO_2 and H_2 are close to equilibrium with the siderite – magnetite – graphite mineral assemblage and that CH_4 can be produced by reduction of CO_2. In nature, siderite has been invoked to explain the occurrence of reduced carbon in metamorphic rocks (e.g., Perry and Ahmad, 1977; Ueno et al., 2002). van Zuilen et al. (2003) suggested that, in the carbonate-rich metasomatic rocks of the 3.8 Ga Isua Supracrustal Belt (Greenland), the presence of graphite was due to thermal decomposition of siderite. Zolotov and Shock (2000), McCollom (2003) and Steele et al. (2012) also proposed the decomposition of Fe-bearing carbonate as a source of reduced carbon in Martian meteorites.

In the present work, hydrothermal dissolution of siderite is proposed to generate hydrocarbon gases with unconventional carbon isotopic signature in the Solimões sedimentary basin in north-west Brazil. Hydrocarbon gases show inverse isotopic trends in the western part of the study area, which experienced high paleo-temperatures (see discussion below) related to magmatic activities. The Solimões basin was studied in terms of redox conditions in the source-rocks through the characterization and quantification of the iron-rich mineral phases. In this framework, the Rock-Eval instrument was used with a new methodology (Pillot et al., 2014) to characterize and quantify the different carbonates in rock samples.

2. Regional geologic setting

The Solimões basin is a large, east-west trending, Paleozoic cratonic depression covering an area of approximately 450 000 km^2 of the Amazonas State, northern Brazil (Fig. 1a, modified from Elias et al., 2004). It is limited to the south and north by the Brazilian and Guiana shields, respectively. It is surrounded by the Iquitos Arch of the Acre basin to the west and by the Purus Arch of the Amazon basin to the east. The Solimões basin is divided by the north-south Carauari Arch into two sub-basins: the Jandiatuba sub-basin, in the western area, and the Juruá sub-basin, in the eastern area. Our study focused on the Juruá sub-basin (Fig. 1a).

The tectonic origin of the Solimões basin is under debate. One of the most recent hypotheses suggests that the origin and regional subsidence of the basin occurred in a flexural regime, progressing towards the east, and that it was related to rifting parallel to the western margin of Gondwana during the Ordovician. Basin formation would have become effective during thermo-mechanical subsidence after that rifting stage, synchronous with the formation of other interior sag and marginal basins (Campos et al., 1991).

The Proterozoic basement of the Solimões basin consists of igneous and metamorphic rocks. The Juruá sub-basin is filled with almost 4000 m of sediments ranging from an Upper Proterozoic, siliciclastic sequence deposited in a rift system, to a Quaternary sequence of siliciclastics (Fig. 1b; modified from Eiras et al., 1994). The most important sedimentary sequence is represented by Paleozoic sediments that host a petroleum system, i.e., the Jandiatuba-Juruá formations (Eiras, 1998a). The source rocks are represented by the Upper Devonian marine black shale (Jandiatuba Formation) that can reach a thickness of 40 m with total organic carbon reaching 4 wt.% and vitrinite reflectance (Ro) more than 1% in the northern part of the study area (Eiras, 1998a). Recently, a series of 10 exploratory wells drilled by the HRT Oil and Gas Company (Fig. 1a) showed that the Devonian source rock had three producing intervals of Givetian, Frasnian and Famenian ages. In the study area, the Givetian source rock is not much present, whereas the Frasnian and Famenian source rocks are much more expanded and reach thicknesses of up to 50 and 60 m, respectively (Fig. 2a). Because of magmatic intrusions peculiarly close to the source rock in the study area, all the organic matter shows extremely high maturity, at the end of the gas window, rendering any source characterization quite difficult. However, paleogeographic reconstruction and comparison with the source rocks from the Amazonas basin (Gonzaga et al., 2000) suggest that the Famenian source rocks correspond to a regressive phase representing shallow water and periglacial formations (diamictite). This results for the Famenian in a more gas-prone source-rock whereas the Frasnian black shale contains oil-prone marine type-II kerogen. The gas-prone character of the Famenian source rock suggests a depositional environment less reduced than that of the Frasnian shale, which is supported by a