







Application of ¹²⁹I/¹²⁷I to define the source of hydrocarbons of the Pol-Chuc, Abkatún and Taratunich–Batab oil reservoirs, Bay of Campeche, southern Mexico

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Abstract

Homogeneous $^{129}I/^{127}I$ ratios from $6.51\pm1.36\times10^{-14}$ to $12.6\pm1.49\times10^{-14}$ were measured in formation brine at the Pol-Chuc, Abkatún, Taratunich—Batab off-shore oil reservoirs, Bay of Campeche in S-Mexico. Cosmogenic production could account for a homogeneous, Late Cretaceous/Paleocene time period $(71.3\pm5.3 \text{ to } 56.3\pm2.9 \text{ Ma})$ for the sedimentation and burial of organic material in the source formation. As the actual reservoir column is formed by Paleocene to Kimmeridgian sediments, the lower part of the lithological column must have received hydrocarbons that migrated downward from an initial source rock (Upper Cretaceous?) during a post-Paleocene event, probably during Miocene. Cosmogenic production from Tithonian shales can be excluded, as ^{129}I would have been decayed. As an alternative or complementary process, the subsurface, radiogenic production of $^{129}I/^{127}I$ by 238 U-fission in Uranium-enriched sediments should also be considered to explain the present, low $^{129}I/^{127}I$ ratios. © 2006 Elsevier B.V. All rights reserved.

Keywords: 129I/127I isotope ratio; Hydrocarbon expulsion; Formation water; Source age

1. Introduction

In most petroleum reservoirs, the formation of hydrocarbons is attributed to a secondary migration process from a primary source rock towards the actual reservoir horizon. In the case of oil reservoirs in the Mexican Gulf coast, the maturation and expulsion of organic matter from Jurassic source sediments — mainly shales — towards overlying permeable layers is assumed to have occurred during the Tertiary period

This article presents the use of the isotope ratio ¹²⁹I/
¹²⁷I as a geochronological tool to answer questions concerning the formation of petroleum reservoirs. It is an attempt to determine and to interpret ¹²⁹I/¹²⁷I ratios in deep formation water in order to reconstruct the source and pathway of organic iodine. Age dating by ¹²⁹I/¹²⁷I-method is used as a potential method to reconstruct the

⁽mainly during Miocene). A variety of Upper Jurassic to Lower Tertiary sediments, such as breccia, packstone, wackestone, and dolomite, form the principal reservoir rocks to be exploited. In order to expand the recent oil production, a quantitative determination of the origin of organic sources was undertaken, as well as the age of hydrocarbons in order to define the potential and dimensions of future reservoirs.

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time of crude oil expulsion from a primary source rock and its migration towards the present reservoir formation.

2. Principles of 129 I

The cosmogenic isotope 129 I ($t_{1/2}$ =15.7 Ma) is produced by the spallation of atmospheric xenon (cosmogenic production) and by the spontaneous fission of ²³⁸U in crustal rocks (Subsurface radiogenic production) (Fabryka-Martin et al., 1985). Its large ionic radius prevents its incorporation into minerals, and contributions from the mantle are negligible (Muramatsu and Wedepohl, 1998). Its long half-life time permits its application for groundwater age estimations on the order of 3 to 80 Ma (Fabryka-Martin and Davis, 1987). Based on geochemical modeling, a steady-state isotope ratio $^{129}I/I$ between 3×10^{-13} to 3×10^{-12} is produced for the atmosphere, biosphere and oceans (Kocher, 1981; Fabryka-Martin et al., 1985). Recent marine sediments without anthropogenic input have a \$^{129}I/\$ ¹²⁷I-ratio of $1.5 \pm 0.15 \times 10^{-12}$ (Fehn et al., 1986; Moran et al., 1995). Nuclear bomb tests in the atmosphere and thermonuclear reactors form a third, artificial source for anthropogenic ¹²⁹I input (Paul et al., 1987). The presence of anthropogenic ¹²⁹I is evident in the surface layer of marine sediments (Fehn et al., 1986; Schink et al., 1995). The current isotopic ratio for precipitation ranges in the order of 10^{-12} to 10^{-10} , depending upon location and time of year (Brauer and Strebin, 1982; Fehn et al., 1986; Paul et al., 1987). Iodine is strongly biophilic and is concentrated by one hundred times or more in marine organic material relative to its concentration in seawater (Moran et al., 1995). Therefore, the biophilic affinity of iodine can be used to trace the fate of organic material.

3. Location of the study area

The Pol-Chuc reservoir, together with the Abkatún, Batab, Caan, and Taratunich oil fields, form part of the continental platform in the Gulf of Mexico (S-Mexico), located approximately 80 km offshore from the town Ciudad de Carmen, State of Campeche. Hydrocarbon resources are hosted in a carbonate reservoir of calcareous breccia with dolomitized and fractured clastics (Lower Paleocene to Upper Cretaceous), marine carbonates (Middle–Lower Cretaceous), and Kimmeridgian wackestone and packstone. Production intervals in the mentioned reservoirs are located at depths from 2900 to 4800 m.b.s.l. Recently, continuing extraction of oil caused the rise of the original water/oil contact from a depth of 3961 towards 3750 m in the Pol-Chuc reservoir.

4. Methods

After separation from the petroleum phase, a volume between 500 and 1000 ml of formation water was sampled at the wellhead from 26 production wells. Four reference samples (baseline) were taken from surface systems, including seawater (Gulf of Mexico), treated seawater for injection, precipitation, and river water. About 1 to 3 mg of silver iodide is required as target material for ¹²⁹I/I determination. ¹²⁹I/I ratio measurements were performed on the accelerator mass spectrometry system (AMS) of the Department of Nuclear Physics at the Australian National University, Canberra. The techniques have been described in detail by Elmore et al. (1980) and Kubik et al. (1987).

5. Results

The measured $^{129}\text{I}/^{127}\text{I}$ ratios of the oilfield brines are extremely low, ranging between $6.51\pm1.36\times10^{-14}$ (Tara-TF52) and $12.6\pm1.49\times10^{-14}$ (Caan-C-79). Iodine concentrations are elevated $(1.77-69.21\,\text{mg/L})$ in comparison to seawater $(0.068\,\text{mg/L})$, therefore most of the I in these brines must have been derived from decomposing organic material. The relatively small concentration range of the brines supports a common origin for the dissolved iodine. The isotopic ratios are very close to the detection limit of the AMS method, and also to the lowest environmental $^{129}\text{I}/^{127}\text{I}$ ratio of 2.0×10^{-14} ever determined in natural material (Fehn et al., 1987).

An initial $^{129}I/^{127}I$ ratio of $1.5\pm0.15\times10^{-12}$, assuming a constant pre-anthropogenic ratio for the entire hydrosphere and for marine iodine, was applied to calculate the cosmogenic component of the iodine source material. An Upper Cretaceous (71.3±5.3 Ma) to Upper Paleocene time span (56.3±2.9Ma) was determined by the $^{129}I/^{127}I$ decay equation (Fig. 1). The calculated ages represent minimum ages for I in these waters, as neither subsurface production of 129I nor anthropogenic 129I input has been taken into account. As the elevated concentrations of iodine in hypersaline waters must be derived from marine organic material — as a precursor of crude oil — the calculated time reflects the moment when iodine was buried beyond the layer of bioturbation, so that exchange between sediments and the overlying seawater no longer occurred. The extreme differences between low $^{129}I/^{127}I$ -ratios in formation water (6.5– 12.6×10^{-14}) and elevated ratios in seawater from the Gulf of Mexico (3.5×10^{-11}) , precipitation water from the Pol-A Platform (46.0×10^{-11}) and runoff systems from the State of Tabasco (15.9×10^{-11}) exclude the

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