

Carbon isotope fingerprinting palaeo fluid inclusion gases using a crushing-trapping technique

Se Gong*
CSIRO Energy
North Ryde, Sydney
Se.Gong@csiro.au

Stephen Sestak
CSIRO Energy
North Ryde, Sydney
Stephen.Sestak@csiro.au

Stephane Armand
CSIRO Energy
North Ryde, Sydney
Stephane.Armand@csiro.au

Tania Vergara
CSIRO Energy
North Ryde, Sydney
Tania.Vergara@csiro.au

SUMMARY

Carbon isotope fingerprinting has been widely used to study gas origin, maturity and gas-source correlations. However, natural gas accumulation in gas reservoirs can be affected by secondary alteration processes. In contrast, palaeo gases trapped in fluid inclusions (FIs) are free of any secondary alterations that may have occurred in the reservoir. FIs are normally less than 10 μm in diameter, hence the gases trapped are at trace level amounts. An online crushing-trapping system has been developed in this study which enabled carbon isotope analyses of hydrocarbon gases which are normally in low concentrations. The crushing-trapping system mainly comprises of a gas-tight crusher and a gas concentrator interface module. The micro-trap is a critical part of the gas concentrator as it collects and concentrates all the released FI gases which results in sharp chromatographic peaks. This novel design is very sensitive, making it an increased challenge to obtain an acceptable blank before running samples. A clean blank is very important for such trace-level gas analysis. System blank results show that there are no hydrocarbon gases but trace amounts of CO_2 (20 mV) detected in the blank. These trace amounts of CO_2 in the blank have no influence on the carbon isotope calculation. It was found that no isotope fractionation was attributable to the cryo-trapping and subsequent thermal release from the trap but there is fractionation due to re-absorption onto the freshly crushed rock matrix (quartz or calcite) powder. Compound specific carbon isotope analysis of hydrocarbon gases (C_1 - C_5 except n - C_4) and CO_2 released from a FI sample from the Cooper-Eromanga Basin was achieved for the first time as a proof of concept of the technique. Preliminary research on FI gases has been carried out in the Browse Basin, Australia.

Key words: fluid inclusion gas; fingerprinting; carbon isotopes

INTRODUCTION

Carbon isotope fingerprinting has been widely used to study gas origin, maturity and gas-source correlation (Schoell, 1980; Dai et al., 2005). Generally, the carbon isotope of natural gas in the current reservoir is influenced not only by the type and maturity of the source rocks but also by various geological processes that took place after reservoir-forming processes such as mixing sources, reservoir seepage, water washing or biodegradation. Hence, it is difficult to distinguish the gas source and migration using the current reservoir gas alone. Fluid inclusions (FIs) preserve geochemical signatures of paleo fluids; hydrocarbon-bearing FIs are often formed soon after the charge to the reservoir which are free of any secondary alterations that may have occurred in the reservoir. FIs are normally less than 10 μm in diameter, hence the gases trapped are at trace level amounts. Due to the analytical challenges involved in obtaining carbon isotopic signatures from such trace levels of gases trapped in FIs, very few papers have been published regarding carbon isotope of FI gases. Karlsen et al. (1993) analysed carbon isotope of FI gases (C_1 - C_3) using off-line crushing and Gong et al. (2008) analysed carbon isotope of methane in FIs using a similar off-line crushing method but the off-line method was limited by large dead volumes in the crusher and abundance of released FI gases being analysed. An On-line method described by Plesson and Lüders (2012) reported the carbon isotope analysis of N_2 , CH_4 and CO_2 in FIs but this method was limited by the maximum sample amount (1g) that could be crushed. Neither the off-line nor the on-line method mentioned above are suitable for samples with low abundances of fluid inclusions.

An on-line crushing-trapping system has been developed in this study which enabled carbon isotope analyses of hydrocarbon gases which are normally in low concentrations.

METHOD AND RESULTS

Sample and analytical method

The on-line crushing-trapping system developed in this study mainly comprises of a gas-tight crusher and a gas concentrator interface module. The designed gas tight crusher enables helium, at a high flow rate, to carry all the released gases from the crusher to the micro-trap. The micro-trap is a critical part of the gas concentrator which results in sharp chromatographic peaks, making carbon isotope analysis of hydrocarbon gases (C_1 - C_5) more achievable. In order to analyse FI gases, quartz grains need to be treated successively with hydrogen peroxide, chromic acid, aqua regia and solvents (methanol and dichloromethane) to remove carbonate cements and organic matter from the surfaces of the quartz grains.

Carbon isotope analysis of the FI gases was conducted on a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-IRMS) connected with the on-line crushing-trapping system. FI gases were released by a short duration (~15s) using a reciprocating crusher with the pre-cleaned quartz grains loaded, and cryo-trapped for 4 mins by liquid nitrogen. The FI gases were then released to the GC-C-IRMS, via the GC injector, by heating the trap to 250°C and measured for their carbon isotopic composition. A system blank was run before each crush to ensure that there was no contamination from the system. Duplicate analyses were performed on each sample.

System blank

This crushing-trapping system is very sensitive, requiring very little amounts of sample (less than 100 mg of clean quartz depending on the abundances of FI in the sample) to achieve the carbon isotope of methane and making it a greater challenge to obtain an acceptable blank before running samples. However system blank is critical for trace level gas measurements because high backgrounds in the blank affects isotope results. In this study, system blank was performed with no sample in the crusher but all other procedures replicated running a real quartz sample. The results showed that there were no hydrocarbon gases but trace amounts of CO₂ (about 20 mV) detected in the blank but such trace amounts of CO₂ do not influence the carbon isotope values of sample released CO₂ in the FIs (typically > 1000 mV).

Isotope fractionation

Carbon isotopes get fractionated easily due to inappropriate sampling, unsuitable gas containers and gas handling processes which then result in biased interpretation. Hence it is critical to identify whether there is any fractionation during the crushing-trapping process. Cryo-trapping and gas absorption on freshly crushed quartz powders are the two possible processes which could potentially cause carbon isotope fractionation.

The micro-trap was tested by injecting gas standards (100% CH₄, 100% CO₂, 50%:50% CH₄:CO₂) into a GC inlet which then swept through the micro-trap (with and without) cryo-trapping. The results showed that there were no apparent fractionations due to the cryo-trapping process.

Absorption effects were tested by injecting a gas standard into a GC inlet on the gas concentrator where the gas standard passed through freshly crushed (400°C pre-cleaned) sand powder in the crusher and subsequently cryo-trapped in the micro-trap. Different quantities of freshly crushed quartz powder in the crusher were also checked due to the exponential concentration profiles in progressing from methane to heavier hydrocarbon gases. 40 mg and 1 g of crushed quartz powder was tested to check for isotope fractionation of methane and C₂₊ hydrocarbon gases, respectively. Results showed that there was no carbon isotope fractionation for methane during the crushing-trapping process. Based on the current data we have, carbon isotopes of C₂₊ hydrocarbon gases and CO₂ were indeed fractionated to varying degrees for different compounds, hence calculated offsets should be applied for the final results accordingly.

Proof of concept of the technique

A quartz sample containing high abundances of FIs (GOI = 24%; GOI stands for Grains containing Oil Inclusions) from Cooper-Eromanga Basin was the first real sample being test as proof of concept of the technique. Since this system is so sensitive, only 43 mg of samples were used to obtain carbon isotopes of methane and CO₂ and 1 g was used to analyse C₂₊ hydrocarbon gases. Hence, at least two crushes were required to get the carbon isotope data for all the hydrocarbon gases and CO₂. Compound specific carbon isotope analysis of all hydrocarbon gases (C₁-C₅ except *n*-C₄) and CO₂ released from the FIs was achieved successfully for the first time in this study.

Application in the Browse Basin

The Browse Basin, located offshore in the North West Shelf in Australia, is highly prospective for hydrocarbons with giant natural gas accumulations. Although there is extensive ongoing exploration activities, the charge history of the gas accumulations within Caswell sub-basin remains a matter of debate with gases originating from multiple sources (Brincat et al., 2004). Evidence for palaeo-oil columns in many gas zones further complicates the filling history of the gas reservoirs (Volk et al., 2005). This newly developed technique allowed the compound specific carbon isotope analysis of palaeo gases trapped in FIs to be measured. Samples from Upper and Lower Vulcan Formation and Plover Formation were analysed.

The results showed that hydrocarbon gases trapped in FIs were of thermogenic origin ($\delta^{13}\text{C CH}_4$: -37 ‰ to -41 ‰) and trapped CO₂ (-5.8 ‰ to -0.8 ‰) was mainly from an inorganic origin. Carbon isotopes of methane and ethane in one of the FI samples from Upper Vulcan Formation is around 4 to 6.5 ‰ heavier than those in the current reservoir gases but carbon isotope of C₃-C₅ hydrocarbon gases are similar to the current reservoir gases (Figure 1). Carbon isotopes of methane in one of the FI sample from Lower Vulcan Formation is similar to the methane in the current gas reservoir while carbon isotope of other hydrocarbon gases is 2.5 to 4.4 ‰ lighter than the current reservoir gases (Figure 1). The reason for the differences between the FI gases and reservoir gases remains unclear. Further study is needed.

CONCLUSIONS

A novel, very sensitive system has been developed to fingerprint the palaeo gases trapped in the fluid inclusions. The developed crushing-trapping technique achieved compound specific carbon isotope analysis of hydrocarbon gases (C₁-C₅ except *n*-C₄) and CO₂ for the first time.

This new technique enabled carbon isotope analysis of FI gases in the Browse Basin which provided extra information for studying the complicated gas origin and charge history of the basin.

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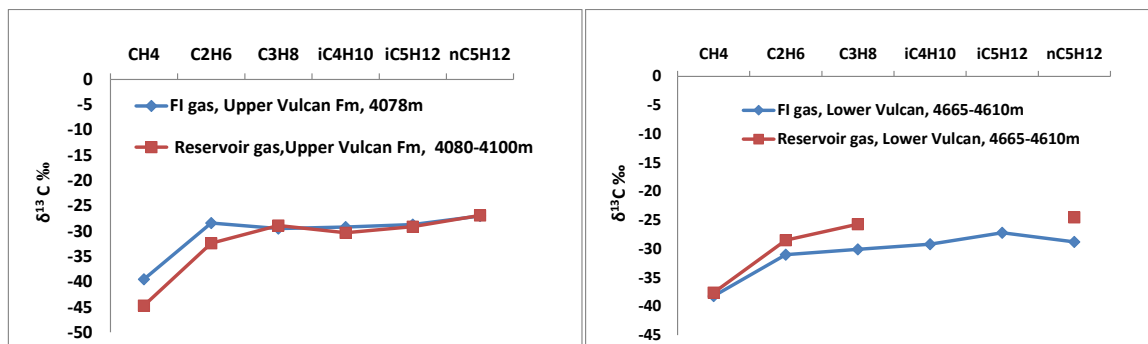


Figure 1 Comparison of carbon isotopes of hydrocarbon gases in fluid inclusions and current gas reservoirs.