

Effect of Clay Minerals on Oil Compositional Fractionation during Secondary Migration

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Abstract

The study investigates the compositional fractionation of oil during secondary migration, especially under the interactions between oil and clay minerals. The present work focuses on several di- and tri-aromatic compounds in aromatic fraction. Iran crude oil (API 33.5) reacted with kaolinite, montmorillonite, and illite at 26°C and 80°C respectively, under 1 atm and 3 atm; saline water (20,000 ppm) was also added into the 26°C, 1 atm system. Liquid chromatography was used to separate crude oil into saturate, aromatic, and polar (NSO) fraction before analysis by GC-MS. All the experiments were conducted in duplicate.

The result indicates that different clay minerals lead to distinct aromatic and NSO chromatographic patterns in the contact oil. The isomers of naphthalene, dibenzothiophene, fluorine, and phenanthrene show specific fractionation patterns under the interreaction between oil and different clay minerals, probably resulting from their selective adsorption capability. With the variation of pressure and temperature, isomers such as 1,2/1,5/1,6-DMN (dimethylnaphthalene), MDBT (methyl dibenzothiophene), 1-MP (methylphenanthrene) also slightly change. Our results are consistent with the previous observation that oil compositional fractionation can occur during secondary migration. These useful biomarker patterns can help identify the migration pathways of the petroleum, model the migration distances of petroleum, and correlate the petroleum with their source rock.

Introduction

As index fossils applied in the construction of the geological history, molecular fossils (Eglinton et al., 1964; Eglinton and Calvin, 1967) existed in petroleum also show little or no change in structure from their parent organic matters, so that they can be used to infer original organic types and sources. Molecular fossils, also called biomarkers, are complex organic compounds composed of carbon, hydrogen, and other elements. Since the development of relatively inexpensive gas chromatography-mass spectrometry (GC-MS), petroleum biomarker parameters have been well quantified and applied in oil exploration.

Oil tends to migrate from fine-grained, organic-rich source rock to coarse-grained reservoir rocks. The process of petroleum migration has been divided into two parts by V. C. Illing (1933). Primary migration takes place mainly through fractures at very high pressures, through the pore system (Darcy flow), or by diffusion through the organic matter network, then petroleum continue migrating up to several hundred kilometers from source to reservoir. During secondary migration, compositional fractionation of petroleum accompanying geochromatography can potentially be used to petroleum migration pathways and distances (Larter et al., 2000; B. Bennett, 2002).

Presently, the study of biomarkers can be divided into saturate, aromatic, polar (NSO) fractions and their derivatives. Through their partition coefficients or specific patterns, biomarkers can wildly be used to identify source rock, age, maturity, and extent of biodegradation etc. The relative amount of biomarker may be significantly altered during the migration and have been used to model the migration distance. The reasons for variation of the biomarkers as a function of migration distance have rarely been investigated. It is general believed that the selective adsorption between polar organic compounds and clay minerals may account for the variation because these organic matters are dipoles as a result of the lack of symmetry of electron distribution within individual molecules(Debye,P.,1929). However, few experimental studies investigate the role of clay minerals. The present study aims to compare the different selective capability of clay minerals especially in aromatic and polar fractions (Radke, M., 1987) and list the influenced compounds in oils. We want to eliminate the complication to identify the migration pathways of the petroleum, use relative amount to model the migration distances of petroleum, and correlate the petroleum with their source rock.

Samples and experimental

The Iran crude oil (API gravity 33.5) is offered by CPC Corporation, Taiwan. Kaolinite is KGa-1b CMS reference clay sample from Clay Mineral Society (CMS) Source Clay Minerals Repository. Na-saturated montmorillonite clays were from the

reference clay sample (Swy-2 from CMS). Illite is IMt-2 CMS reference clay sample, treated by grinding and sieving (70 mesh numbers, 0.21mm openings). The specific surface areas of these samples were measured by NOVA 2000TM using the BET method.

The apparatus used for adsorption experiments is a sealed stainless cylinder (13 cm height, 6 cm I.D.) with a sample chamber of 175.4 cm³. The space of the sample chamber can vary by inserting a solid cylinder of different sizes to reduce the sample chamber to the desired volume. Placing in the 80°C water bath, the apparatus is equipped with a pressure sensor connected to a digital pressure gauge to measure the gas pressure within the sample chamber. Under normal pressure and room temperature, several 10ml vials put on the stirrer (MS-100) are used to constantly mix oil and clay minerals.

Using liquid chromatography, the starting and free oils after contacting with clays were fractionated on a silica:alumina column using hexane, dichloromethane, and methanol as eluants to yield the saturate, aromatic, and polar (NSO) fractions, respectively.

Gas chromatographic–mass spectrometric (GC–MS) analysis of the saturated, aromatic and polar (NSO) fractions from all oil samples was performed in a HP6890 GC fitted with a 30 m *0.32 mm i.d. ZB-5 column with a film thickness of 0.25 µm and a carrier gas of nitrogen. The GC oven temperature was held initially at 40°C for 1 min, ramped from 40 to 310 °C at 3 °C/min, and then held at 310 °C.

Result

After reacting for 8 days, kaolinite decolored the black crude oil to brown color while montmorillonite swelled then reduced the amount of oil. Similar chromatograms after oil reacting 3 days and 8 days with kaolinite suggest equilibrium sorption-desorption process during secondary migration.

All oil and clay minerals were interacted for 8 days and their GC-MS chromatograms are shown in Figure 1. Only slight differences are among total saturate fraction patterns, comparison of sterane, terpane, pristane/C₁₇, and phytane/C₁₈ also shows no substantially detectable variation. In contrast, total aromatic and polar (NSO) fraction patterns show attracting differences. Isomers of alkyl-naphthalene, dibenzothiophene, phenanthrene, and fluorine presented in distinct ways may help identify the interacted clay types. Pressure change also affects some peak appearances in the chromatograms. Figure 2 shows the normalized peak area ratio of alkyl-naphthalene/C₁₇. Kaolinite, most common 1 : 1 clay mineral, reacted most intensely with oil in both 1atm and 3atm system than montmorillonite and illite. Naphthalene and isomers of methylnaphthalene (MN), dimethylnaphthalene(DMN), trimethylnaphthalene(TMN) demonstrate selective adsorption of different clay

minerals as illustrated in Fig. 2. The adsorption behaviors of kaolinite and montmorillonite are similar under 3 atm. 1-EN, 2-EN, 1,6-DMN, and TMN are strongly adsorbed when illite existed in the rock formation. Under 1 atm, 80°C closed water bath system, montmorillonite and illite show no big different mass chromatograms with crude oil, but the dramatic removal of 1-MN, 2-MN and some TMN isomers are found in the kaolinite pattern.

Conclusions

Different kinds of clay minerals do reveal distinct selective adsorption capability. The duplicate experiment clearly shows that relative amount of biomarker partition is related to adsorption properties of the carrier system. Therefore, applying these partition coefficients of polar compounds to model the migration distance is valid and some obvious variations can be useful to identify the migration pathways.

References

- Adri C.T. van Duin, S. R. L. (2001). Molecular dynamics investigation into the adsorption of organic compounds on kaolinite surfaces. *Organic Geochemistry* **32**: 143-150.
- B, N. (1960). Review of the chromatographic plate theory with reference to fluid flow in rocks and sediments. *Geochim Cosmochim Acta* **19**(289).
- B. Bennett, M. C., D. Brincat, F.J.P. Gelin, S.R. Larter (2002). Fractionation of benzocarbazoles between source rocks and petroleums. *Organic Geochemistry* **33**: 545-559.
- Changchun Pan, J. F., Yuming Tian, Linping Yu, Xiaoping Luo, Guoying Sheng, Jiamo Fu (2005). Interaction of oil components and clay minerals in reservoir sandstones. *Organic Geochemistry* **36**: 633-654.
- Eglinton, G. a. C. M. (1967). Chemical fossils. *Scientific American* **216**: 32-43.
- Illing, V. C. (1933). Migration of oil and natural gas. *J. Inst. Petrol.* **19**(114): 229-274.
- Mackenzie, A. S. (1984). Applications of Biological Markers in Petroleum Geochemistry. *Academic Press Volume 1*: 115-214.
- Radke, M. (1987). Organic Geochemistry of Aromatic Hydrocarbons. **Volume 2**: 141-208.
- Steve Larter, B. B., Ed Clarke, Colin Wilson, Brian Moffatt, Barry Bennett, Gareth Yardley and Dan Carruthers (2000). An experimental investigation of geochromatography during secondary migration of petroleum performed under subsurface conditions with a real rock. *Geochemical Transactions*
- Trevor P. Bastow, B. G. K. v. A., Geoff E. Chidlow, Robert Alexander, Robert I. Kagi (2003). Small-scale and rapid quantitative analysis of phenols and carbazoles in sedimentary matter. *Organic Geochemistry* **34**: 1113-1127.

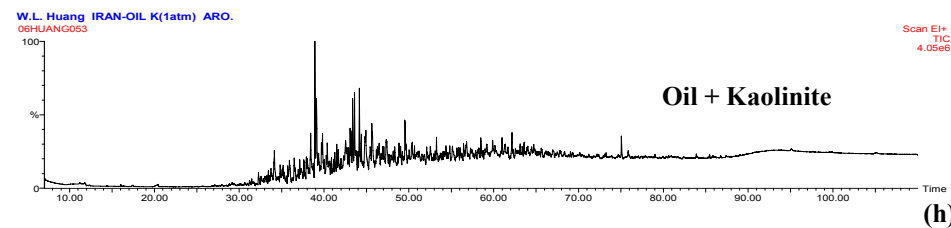
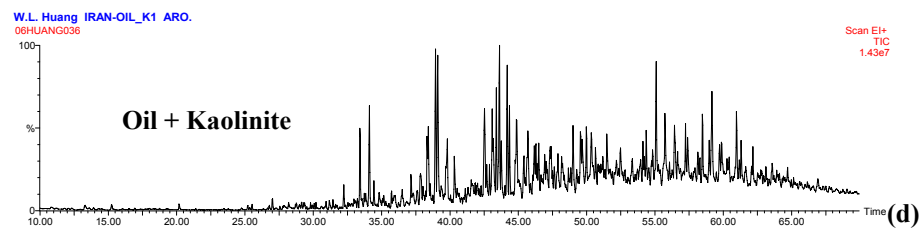
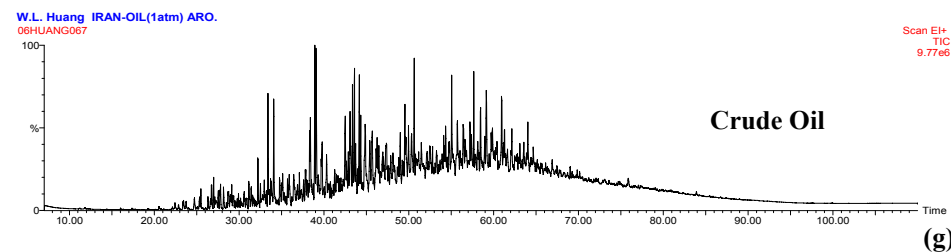
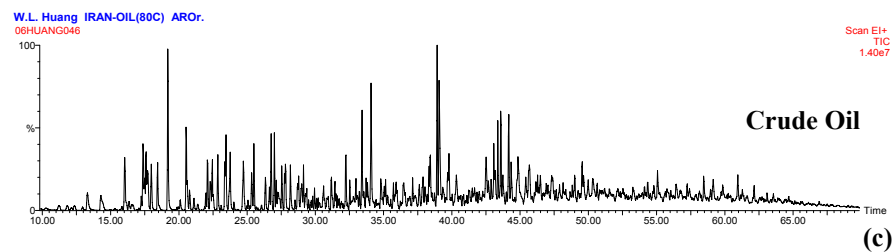
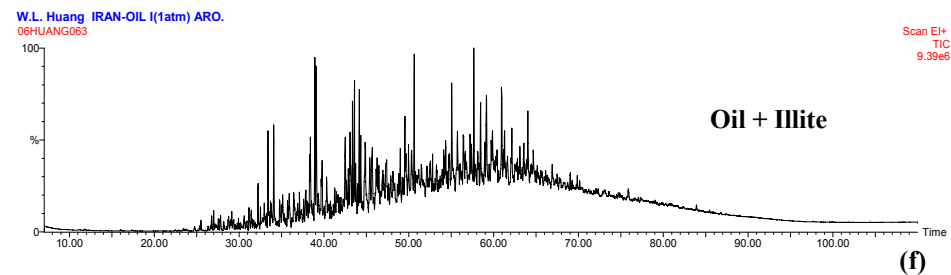
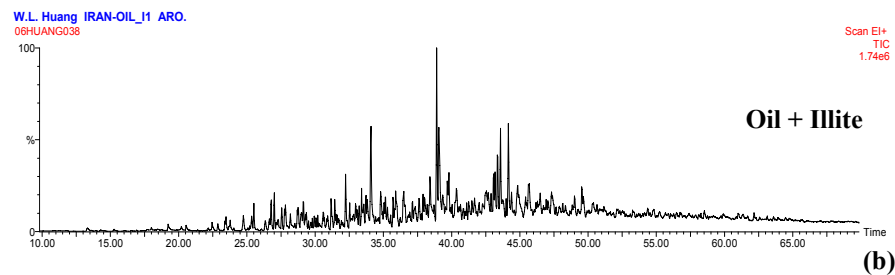
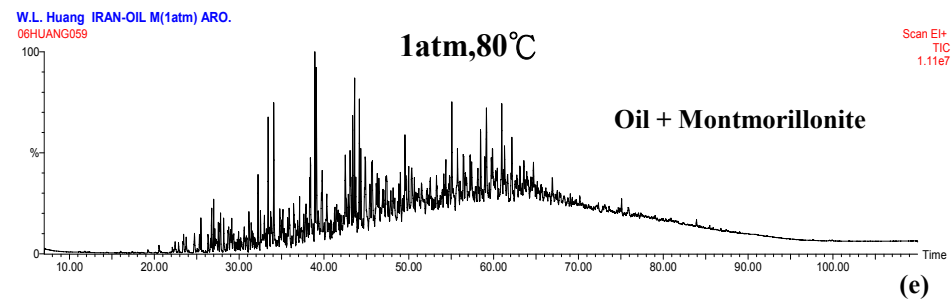
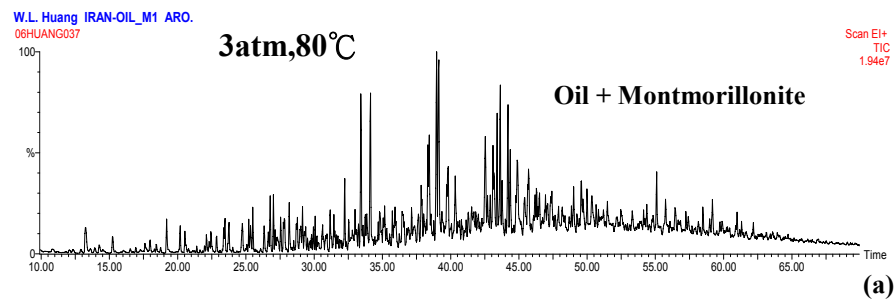


Figure 1. Capillary column gas chromatograms of aromatic fractions. (a)-(d) samples are conducted in the 3atm, 80°C water bath. (e)-(h) samples are conducted in the 1atm, 80°C water bath.

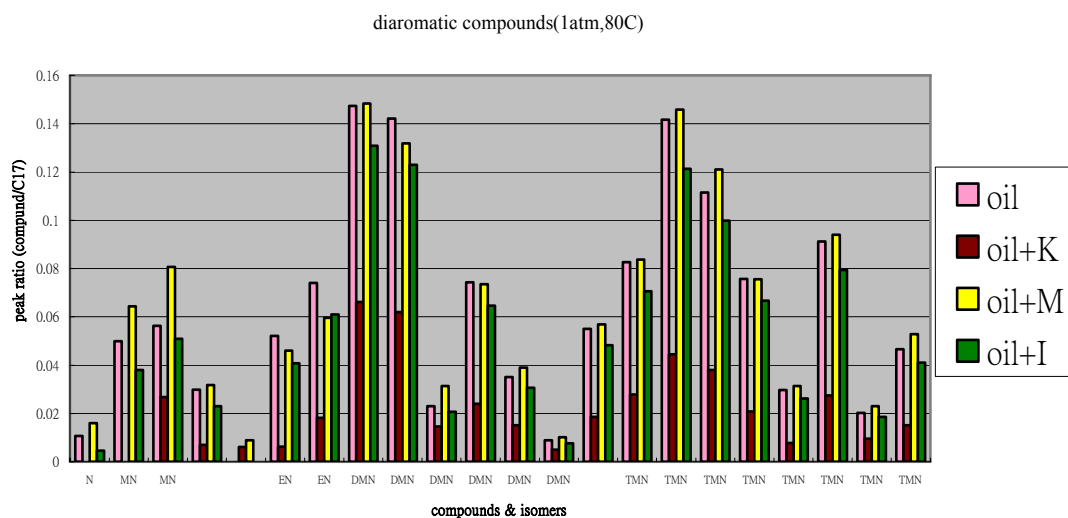


Figure 2. Standard bar diagram shows the distribution and comparison of selected diaromatic subfractions of the crude oil and clay-contacted oil. Peak ratios are obtained from the gas chromatograms presented in Fig.1. Abbreviations : N = naphthalene; MN = methylnaphthalene; EN = ethylnaphthalene; DMN = dimethylnaphthalene; TMN = trimethylnaphthalene.