OCCLUDED BIOMARKERS OR COVALENTLY BOUND BIOMARKERS?

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Introduction

Recently, more and more geochemists focused on the study and application of bound biomarkers. They have the same origins but quite different evolution histories to their free forms. Bound hydrocarbons (covalently bound and occluded hydrocarbons) are difficult obtained by extraction of conventional organic solvents, but can be effectively released by the decomposition of geological macromolecular network structure. For now, many kinds of methods have been reported to break the macromolecular structure and to obtain bound moieties from geological matrices, including thermal pyrolysis and chemical degradations. Some researchers also thought that the compounds released by various degradation processes were not covalently bonded to macromolecular structure but rather were occluded within it (e.g. Snowdon et al.2016). Actually, it is very difficult to differentiate the bound moieties from occluded species released by the decomposition of macromolecular structure (Snowdon et al., 2016). Thus, the term of bound biomarker (including both covalently bound and occluded biomarkers) was commonly used to represent the biomarkers released from geological macromolecular structures.

Though the release methods and the characteristics of bound biomarkers were well studied, we still know little about the difference between occluded and covalently bound biomarkers and the effect of occluded fraction on bound fraction released by commonly analytical techniques. The aim of this study was to discovery the differences of both gross composition and biomarker distribution between occluded liquid fraction and the corresponding covalently bound fraction within geological matrices. Here, one mature kerogen was conducted oxidation degradation and HyPy experiment. Subsequently, the SARA fractions and biomarkers characteristics released from HyPy, oxidation degradation, and HyPy of oxidized residue were compared and discussed.

Results

Although the solvent extraction with ternary solvent azeotrope was pretreated before HyPy and oxidation degradation experiments, occluded biomarkers are still probably existed in products released from the decomposition of macromolecular network. Thus, BOx-HyPy product should contain both the occluded compounds and the covalently bound compounds. However, the covalently bound compounds released by H_2O_2/CH_3COOH oxidation will contain oxygen atom and exist in the polar fractions oxidation product (Liao and Geng, 2002). In this regard, the saturated fraction in oxidation products (both Ox and AOx-So products) guaranteed to be occluded compounds inside geomacromolecular structures.

It must be borne in mind that we still cannot make sure that all of the occluded compounds were removed by the oxidation degradation and the subsequent solvent extraction procedures. Since the biomarkers in Ox product are significantly different from those in BOx-HyPy and AOx-HyPy product, we can make sure that there are differences between occluded and covalently bound biomarkers. This suggested that if occluded biomarker is the dominated

fraction in the HyPy released bound biomarkers, obviously difference should be observed between the biomarkers released from the geological macromolecule without oxidization degradation and its oxidized residue. However, the distribution of HyPy released biomarkers from the unoxidized sample are still quite similar to those from the corresponding oxidized residue (Figure 1). This phenomenon indicated that occluded biomarkers have only a slight or even no influence on the characteristics of the bound biomarkers released by HyPy.

Conclusions

The occluded fractions and bound fractions (including occluded and covalently bound fractions) were obtained and discussed from a mature kerogen through oxidation degradation and HyPy technique. Based on the comparison of concentration and distributions of biomarkers released by different methods (unreported here), bound biomarkers released by HyPy technique from mature kerogen were dominated by covalently bound forms with only minor amounts of occluded species. Meanwhile it was further confirmed by the phenomena that very similar distributions of bound biomarkers were released from the investigated kerogen before and after oxidation degradation preparation.

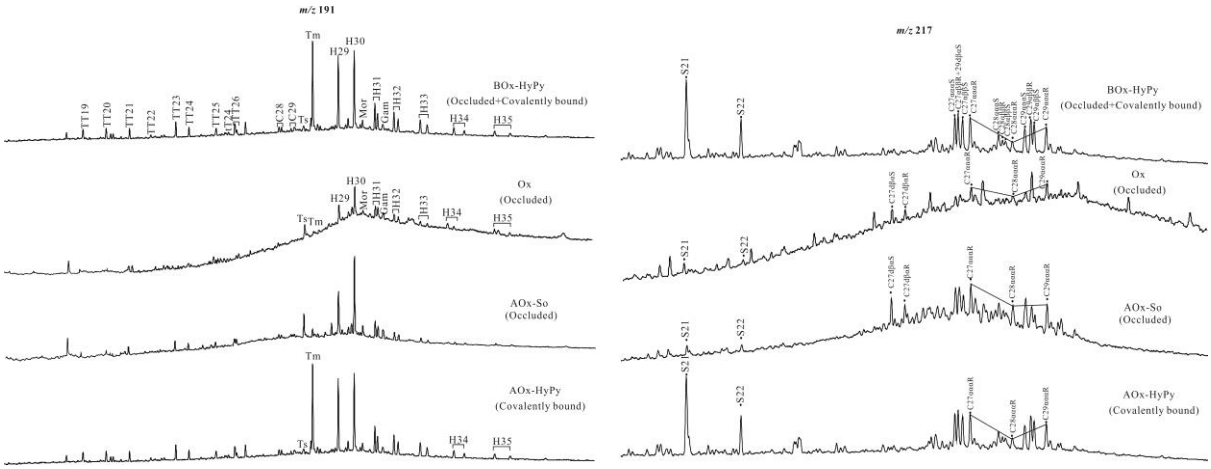

Figure 1 *The m/z 191 and m/z 217 trace of saturated hydrocarbons obtained by H_2O_2/CH_3COOH oxidation from a mature kerogen and by HyPy from the same kerogen with and without H_2O_2/CH_3COOH oxidation. BOx-HyPy means HyPy of kerogen before H_2O_2/CH_3COOH oxidation, AOx-HyPy means HyPy of kerogen after H_2O_2/CH_3COOH oxidation, Ox means H_2O_2/CH_3COOH oxidation, AOx-So means Soxhlet extraction after H_2O_2/CH_3COOH oxidation.*

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