

# Diamondoids and molecular biomarkers generated from modern sediments in the absence and presence of minerals during hydrous pyrolysis

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## Abstract

Experimental work involving artificial maturation of modern sediments was carried out to determine if diamondoids can be generated from biosynthetic precursors abundant in modern sediments. Mineral catalysts of distinctive properties, including montmorillonite K10, acidic aluminosilicate and CaCO<sub>3</sub> were used in the hydrous pyrolysis of organic-rich modern sediments to examine which type of catalyst is active and effective in the production of diamondoids. Our results show that diamondoids are absent from modern sediments lacking petroleum contamination. Hydrous pyrolysis at 340 °C indicates that they are created coincidentally with the formation of biomarkers, as the artificial maturation of organic matter proceeds. The generation of diamondoids is more significant in the presence of montmorillonite K10 and acidic aluminosilicate. This suggests that these clay minerals have a significant catalytic effect on the formation of diamondoids, and may catalyze diamondoid synthesis via carbonium ion mechanisms resulting from Lewis acid sites available on their surface. In contrast, CaCO<sub>3</sub> has an inhibitive effect on the generation of diamondoids as well as on published diamondoid maturity parameters such as MAI and MDI. The formation of 3,4-dimethyldiamantane (DMD), 4,8-DMD, and 4,9-DMD is demonstrated to be source related. The sediment mineralogy can change the composition and distribution of both triterpanes and steranes by either catalyzing isomerization of biomarkers or cracking of side chains. Source biomarker parameters (e.g., C<sub>24</sub>Tet/C<sub>23</sub>TT, C<sub>30</sub><sup>\*</sup>/C<sub>29</sub>Ts, C<sub>27</sub>:C<sub>28</sub>:C<sub>29</sub> steranes) are more sensitive to the addition of minerals including montmorillonite K10, acidic aluminosilicate and CaCO<sub>3</sub> than are maturity indicators. Our results also suggest that CaCO<sub>3</sub> has a remarkable effect on the isomerization of hopanes at the ring system. Isomerization of steranes is probably not clay-mediated, as indicated by only minor variations in isomerization ratios, including C<sub>29</sub> stigmastane ββ/(ββ + αα) and C<sub>29</sub>ααα-sterane 20S/(20S + 20R) observed in the presence of clay minerals.

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## 1. Introduction

Diamondoids are cage-like hydrocarbons possessing extremely rigid structures that can be superimposed upon a diamond crystal lattice (McKervey, 1980). The structures endow diamondoid hydrocarbons with high stability. In addition, diamondoids

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occur naturally in petroleum in various amounts and are generally dominated by substituted and unsubstituted lower members, including adamantanes, diamantanes and triamantanes (Landa and Machacek, 1933; Landa, 1959; Petrov et al., 1974; Wingert, 1992; Dahl et al., 1999, 2003). A wealth of information can be extracted from their distributions. For example, the extent of thermal cracking can be determined by comparing biomarker and diamondoid concentrations in oils (Dahl et al., 1999). Moldowan et al. (2004) reported that the compound specific isotopic analysis of diamondoids (CSIA-D) isolated from oils could be used in oil-source correlations, especially for oils from late catagenetic sources. The relative abundance of dimethyl adamantanes was successfully employed to differentiate source rock facies by Schulz et al. (2001). Chen et al. (1996) and Li et al. (2000) also proposed two diamondoid maturity parameters for use in the assessment of the thermal maturity of highly mature condensates. Moreover, diamondoids have been suggested to characterize biodegraded oils due to their resistance to microbial attack (Williams et al., 1986; Wingert, 1992; Grice et al., 2000). They also are resistant to destruction by thermochemical sulfate reduction, which under the most severe conditions can destroy all other hydrocarbons, thereby producing diamondoid-rich petroleum (Rooney, 1995). Therefore, they are of substantial importance and interest in petroleum geochemistry.

In the laboratory, they can be synthesized by the reaction of an organic precursor and a super acid catalyst via rearrangement of carbocation intermediates (McKervey, 1980; Schleyer et al., 1980; Schleyer, 1990). However, it is not clear how they are formed naturally in petroleum. Although Petrov et al. (1974) speculated that rearrangement of polycyclic hydrocarbons in the presence of a Lewis acid might be responsible for the occurrence of diamondoids in petroleum, there is no compelling evidence for an acid-catalyzed rearrangement mechanism in their formation under conditions characteristic of

petroleum formation. Diamondoids are not known to be natural products derived from any living organism. Modern sediments, however, contain a variety of compounds of biogenic origin that ultimately form petroleum. Hence, investigation of a series of modern sediments through artificial maturation upon heating might help determine if diamondoids can be created from biosynthetic precursors (e.g., *n*-alkenes, fatty acids, cholesterol, etc.) present in modern sediments. More importantly, adding minerals, specifically those naturally occurring in sedimentary rocks, to a pyrolysis system with modern sediments may give some clues as to which catalysts are active and effective in the formation of diamondoids.

In this study, hydrous pyrolysis was performed on modern sediments in the absence and presence of different minerals. The objectives were to: (1) investigate the formation of diamondoids through the thermal maturation of modern sediments; (2) determine if the presence of different minerals has any catalytic effect on the generation of diamondoids; (3) examine if previously proposed diamondoid parameters are influenced by the presence of specific minerals that are common in sedimentary rocks. In parallel, the composition, distribution and geochemical parameters of biomarkers produced from hydrous pyrolysis of modern sediments are determined and discussed.

## 2. Samples and experimental

### 2.1. Samples

Three modern mud samples were collected at 20–35 cm below surface from the San Francisco Bay salt marsh, the Santa Barbara Basin, and Elkhorn Slough at Monterey, CA, USA (Table 1). In addition, one modern pristine carbonate sediment was collected from the mangrove-dominated Celestun Lagoon, which is a shallow coastal lagoon located on the western shore of the Yucatan Peninsula, Mexico. All samples are relatively organic-rich and

Table 1  
Bulk geochemical data for modern sediments

| Sample                    | Environment        | Depth (cm) | TOC (%) | %N   | EOM <sup>a</sup> (mg/g sed) |
|---------------------------|--------------------|------------|---------|------|-----------------------------|
| San Francisco Bay mud     | Salt marsh         | 20–25      | 8.0     | 0.20 | 0.44                        |
| Elkhorn Slough mud        | Marsh              | 25–35      | 5.0     | 0.30 | 0.29                        |
| Santa Barbara Basin mud   | Continental Margin | 20–35      | 7.0     | 0.20 | 0.78                        |
| Celestun Lagoon carbonate | Mangrove Lagoon    | 20–27.5    | 6.0     | 0.30 | 0.15                        |

<sup>a</sup> EOM is the extractable organic matter.

the organic matter is well preserved due to the anoxic environment of these sediments. The organic matter sources are, however, expected to be different. Specifically, San Francisco Bay marsh is dominated by *Spartina* and pickleweed (*Salicornia pacifica*), Santa Barbara Basin sediment organic matter is mostly of marine origin, and the Elkhorn Slough marsh land is dominated by pickleweed vegetation. The Celestun Lagoon sample is characterized by extensive algae, mangrove leaves, and seagrass (*Chara fibrosa*, *Batosphora oerstedii*, *Chaetomorpha linum*, *Halodule wrightii*, *Ruppia* sp.) and contains abundant microfossil debris. The total organic matter content of all four samples is quite similar (between 7% and 8%), with N being around 0.2% (Table 1).

## 2.2. Extraction of sediments

The sediments (ca. 20 g) were dried under a nitrogen flow at 30 °C and ground to <100 µm. The powdered sediments were extracted ultrasonically using a 1:1 mixture of methanol:dichloromethane (200 mL) for 24 h. The extracts were decanted to a 125 ml separatory funnel containing deionized water (50 mL) after the extraction solvent was removed by rotary evaporation. Pentane:dichloromethane (10 mL, 2:1 v:v) was subsequently added to the funnel and the mixture was shaken vigorously for a few minutes. Two distinctive layers formed after 10 min. The upper layer, containing pentane and dichloromethane, was transferred to a 32 mL vial. The aqueous bottom layer was extracted ×3 with 30 mL pentane:dichloromethane (2:1 v:v) and the extract fractions were combined. Treating the extracts with anhydrous sodium sulfate (5 g) removed any residual water. The organic solvent was evaporated under a nitrogen flow and the final extracts were weighed.

## 2.3. Mineral catalysts

Montmorillonite K10 and calcium carbonate (CaCO<sub>3</sub>) were obtained from the Aldrich Chemical Company. The chemical composition of montmorillonite K10 is reported to be SiO<sub>2</sub> (43.77%), Al<sub>2</sub>O<sub>3</sub> (18.57%), CaO (1.02%), Na<sub>2</sub>O (1.13%) and H<sub>2</sub>O (36.09%). Its cation exchange capacity (CEC) is about 80–120 meq/100 g and it has a surface area of 220–270 m<sup>2</sup>/g. CaCO<sub>3</sub> (>99.99% pure) was obtained from Mallinckrodt Baker, Inc. Acidic aluminosilicate (Al<sub>2</sub>O<sub>3</sub> 23.2%, SiO<sub>2</sub> 76.4% and nominal amounts of Na<sub>2</sub>O and SO<sub>4</sub>, etc.) was provided by

Dr. Larry McDorman at the Grace Davison in Columbia, Maryland. It is also defined as “MS-25”, with a surface area of 408 m<sup>2</sup>/g.

## 2.4. Hydrous pyrolysis

Hydrous pyrolysis experiments under isothermal conditions were conducted following the method described by Lewan (1993). Dried modern sediments (ca. 30 g), either natural or well mixed with different minerals (5 g) were loaded into T316 stainless steel vessels. The minerals include CaCO<sub>3</sub>, montmorillonite K10 and acidic aluminosilicate. The steel vessels were filled with 15 mL of deionized water, and purged with argon for 1 min to remove air before sealing. The sealed vessels were placed in a gas chromatography (GC) oven, which was programmed to reach 340 °C within 30 min. The pyrolysis temperature was held constant for 72 h. The expelled pyrolysates, floating free on the water surface or adsorbed on the surface of the sediments and inner sides of the reactors, were recovered by washing the heated sediments and vessels with 1:1 methanol:dichloromethane (100 mL).

## 2.5. GC

GC analysis was performed on the pyrolysates and extracts diluted 100-fold with toluene using a Hewlett Packard 5890, equipped with a flame ionization detector (FID) and a 24 m methyl silicone DB-1 capillary column with 0.2 mm i.d. and 0.33 µm film thickness. The oven temperature was programmed to rise from 80 °C to 320 °C at 10 °C/min and held at 320 °C for 15 min. Hydrogen at 20 psi head pressure was the carrier gas.

## 2.6. GC–mass spectrometry (GC–MS)

Diamantoid analysis was carried out on the saturate fraction of hydrous pyrolysates and sediment extracts that were spiked before fractionation with 5β-cholane and deuterated diamantoid standards synthesized in the laboratory. The saturate fraction was obtained by eluting pyrolysates and extracts with pentane through a silica gel column. GC–MS analysis was performed on the saturates using a Hewlett Packard 5890 Series II GC interfaced to a Micromass Autospec-Q MS, operating in a selected ion detection (SIR) mode. The ions are monitored at *m/z* 135, 136, 149, 163, 177, and 191 for adamantanes, *m/z* 187, 188, 201, and 215 for diamantanes,

$m/z$  239, 240, 244, 253, and 267 for triamantanes and  $m/z$  292 for tetramantanes. The ionization was by electron impact at 70 eV. The GC was equipped with an HP-1 MS fused silica capillary column (60 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m thickness of methyl silicone film). Hydrogen was the carrier gas with a head pressure of 15 psi. Samples were injected at 50 °C while holding constant temperature for 1 min; the oven was programmed to rise to 80 °C at 15 °C/min, then to 290 °C at 2.5 °C/min and finally to 320 °C at 25 °C/min, where it was held for 25 min. The quantification of adamantanes, diamantanes and triamantanes was achieved by the integration of their peak heights with respect to their corresponding standards, D<sub>3</sub>-1-methyladamantane, D<sub>3</sub>-1-methyldiamantane and D<sub>4</sub>-triamantane, respectively. The quantification of tetramantanes was accomplished using the D<sub>4</sub>-triamantane standard and D<sub>5</sub>-1-ethyladamantane was used to quantify ethyl adamantanes. Duplicate hydrous pyrolysis experiments indicated that the standard deviation was typically less than 8% for diamondoid measurements.

For biomarker analysis, ZSM-12 molecular zeolite with a pore size of 6 Å was used to remove *n*-alkanes from other saturates. The silicalite-sieved saturate fractions were analyzed using SIR-GC-MS for terpanes by monitoring ions at  $m/z$  163, 177, 191, 205, 217, 219, 233 and 247. Steranes were analyzed using metastable reaction monitoring of 330  $\rightarrow$  217, 372  $\rightarrow$  217, 386  $\rightarrow$  217, 386  $\rightarrow$  231, 400  $\rightarrow$  217, 414  $\rightarrow$  217, 414  $\rightarrow$  231 and 414  $\rightarrow$  259 transitions. The ionization energy was 70 eV. Biomarker analysis involved a GC temperature program that was isothermal at 80 °C for 1 min, then increased at 2 °C/min–320 °C and held there for 20 min. The injection port and transfer line temperatures were held at 325 °C. Full scan GC-MS analysis was also performed on the extracts and saturate fractions to obtain mass spectra for compound identification. The scan time was set at 1 s for a mass range of 50–500. The same GC program used for the biomarker analyses was used for full scan runs. Quantification of biomarkers was aided by comparing peak areas to that of the 5 $\beta$ -cholane standard.

### 3. Results and discussion

#### 3.1. Chemical composition of sediment extracts

The total extractable organic matter (EOM) was obtained by ultrasonic extraction with metha-

nol:dichloromethane (1:1, v:v). As shown in Table 1, the non-carbonate sediments, especially Santa Barbara Basin mud, have relatively high EOM, ranging from 0.29 to 0.78 mg/g compared with the Celestun Lagoon carbonate sediment. A variety of organic compounds were detected in the total EOM, e.g., saturated and unsaturated hydrocarbons, oxygen-functionalized compounds, cyclic hydrocarbons, steroids, terpenoids and organic sulfur compounds, as shown in Fig. 1. Of particular interest are the differences between the major compounds in the total extracts of these modern sediments. The mud extract from San Francisco Bay is characterized by the predominance of even *n*-alkenes (C<sub>20</sub>–C<sub>30</sub>), branched alkenes, *n*-alkanes (C<sub>16</sub>–C<sub>33</sub>), 9-(4-methylcyclohexyl)nonanoic acid and some unknown compounds marked by “■” symbols (Fig. 1). In addition, Elkhorn Slough marsh mud extract include alkyl thiophenes and phyta-2,4-diene. The GC trace of the Santa Barbara Basin sediment shows that *n*-alkenes (C<sub>20</sub>–C<sub>34</sub>), *n*-alkanes (C<sub>22</sub>–C<sub>32</sub>), low molecular weight branched alkenes, 9-(4-methylcyclohexyl)nonanoic acid, phyta-2,4-diene and some unidentified compounds are prominent. In the Celestun Lagoon sediment, *n*-alkenoic acids, methyl heptadecanoate, 9-(4-methylcyclohexyl)nonanoic acid, sesquiterpenes and alkyl thiophenes are very abundant, while *n*-alkanes, branched alkenes and phyta-2,4-diene are present in relatively low amounts.

It is worth noting the similarity in the composition and distribution of molecular fossils (e.g., tricyclic terpanes, hopanes, C<sub>27</sub>–C<sub>29</sub> diasteranes and regular steranes), which are enriched in the saturated hydrocarbons from the extracts of both San Francisco Bay and Santa Barbara Basin muds. The high abundance of *n*-C<sub>27</sub>, *n*-C<sub>29</sub>, and *n*-C<sub>31</sub> alkanes in both muds indicates organic matter input from terrigenous higher plants (Fig. 2a and c). The saturated fraction from the Elkhorn Slough mud is characterized by an odd/even predominance of *n*-alkanes (C<sub>17</sub>–C<sub>35</sub>) and a relatively high abundance of C<sub>20</sub> highly branched isoprenoids (HBIs, e.g., 2,6,10-trimethyl-5-(3-methylbutyl)dodecane and 2,6,10-trimethyl-7-(3-methylbutyl)dodecane) and methyl alkyl cyclohexanes (Fig. 2b), which have been reported to originate from the green alga *Enteromorpha prolifera* (Rowland et al., 1985). Interestingly, the Elkhorn Slough mud extract also contains relatively low concentrations of hydrocarbon biomarkers, among which 24-ethylcholest-2-ene, C<sub>30</sub>hop-17(21)-ene, C<sub>29</sub>17 $\beta$ ,21 $\beta$ (H)-

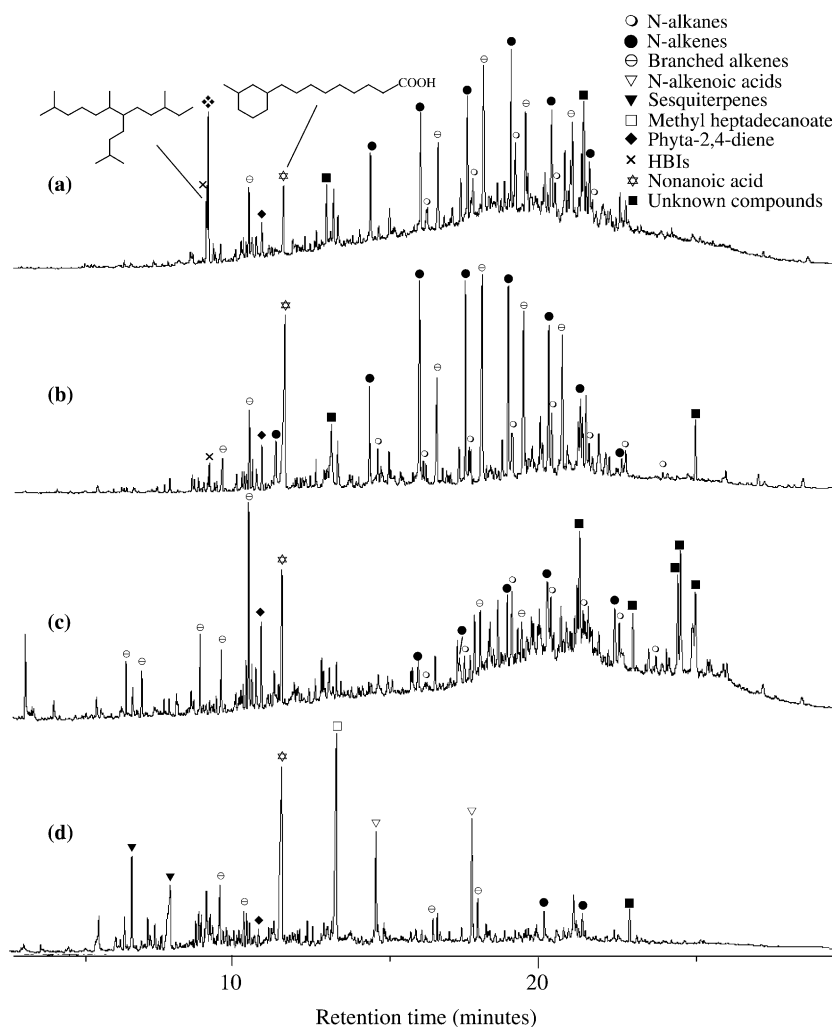


Fig. 1. GC-FID traces of total extracts of modern sediments showing differences in composition. (a) San Francisco Bay marsh mud. (b) Elkhorn Slough marsh mud. (c) Santa Barbara Basin marine mud. (d) Celestun Lagoon carbonate.

30-norhopane,  $C_{30}17\beta,21\beta(H)$ -hopane, and  $C_{31}17\beta,21\alpha(H)$ -moretane are the most abundant (Fig. 2c). Moreover, the predominance of  $C_{28}$  over  $C_{27}$  and  $C_{29}$  steranes provides evidence of a marine algal input for these samples. In the Celestun Lagoon sample extract, the patterns of *n*-alkanes are very similar to those of other sediments. The odd/even predominance of *n*-alkanes ( $nC_{21}$ – $nC_{33}$ ) is typically characteristic of thermal immaturity. The corresponding saturated fraction in this sediment consists of a series of triterpenes, such as urs-12-ene, olean-13(18)-ene, hop-17(21)-ene,  $C_{30}17\beta,21\alpha(H)$ -moret-22(29)-ene,  $C_{30}17\beta,21\beta(H)$ -hop-22(29)-ene, and hopanes including  $C_{31}17\alpha,21\beta(H)$ -homohopane (22*R*) and  $C_{31}17\beta,21\beta(H)$ -homohopane (Fig. 2d; peak assignments in Table 2). These biomarkers

indicate input from both higher plants, such as mangroves, and bacteria because olean-13(18)-ene and olean-18-ene are derived from angiosperms (Whitehead, 1973, 1974; Ten Haven and Rullkötter, 1988) and are precursors of oleanane (Grantham et al., 1983; Zumberge, 1987; Moldowan et al., 1994), and olefinic hopanoids originate from bacteria.

### 3.2. Lack of diamondoids in modern sediments

Fig. 3 shows the mass chromatograms of diamondoid species from SIR-GC-MS analysis. The peak identifications are given in Table 3. Our results indicate that trace amounts of diamondoids were detected in San Francisco Bay, Santa Barbara Basin, and Elkhorn Slough muds (Table 4). We

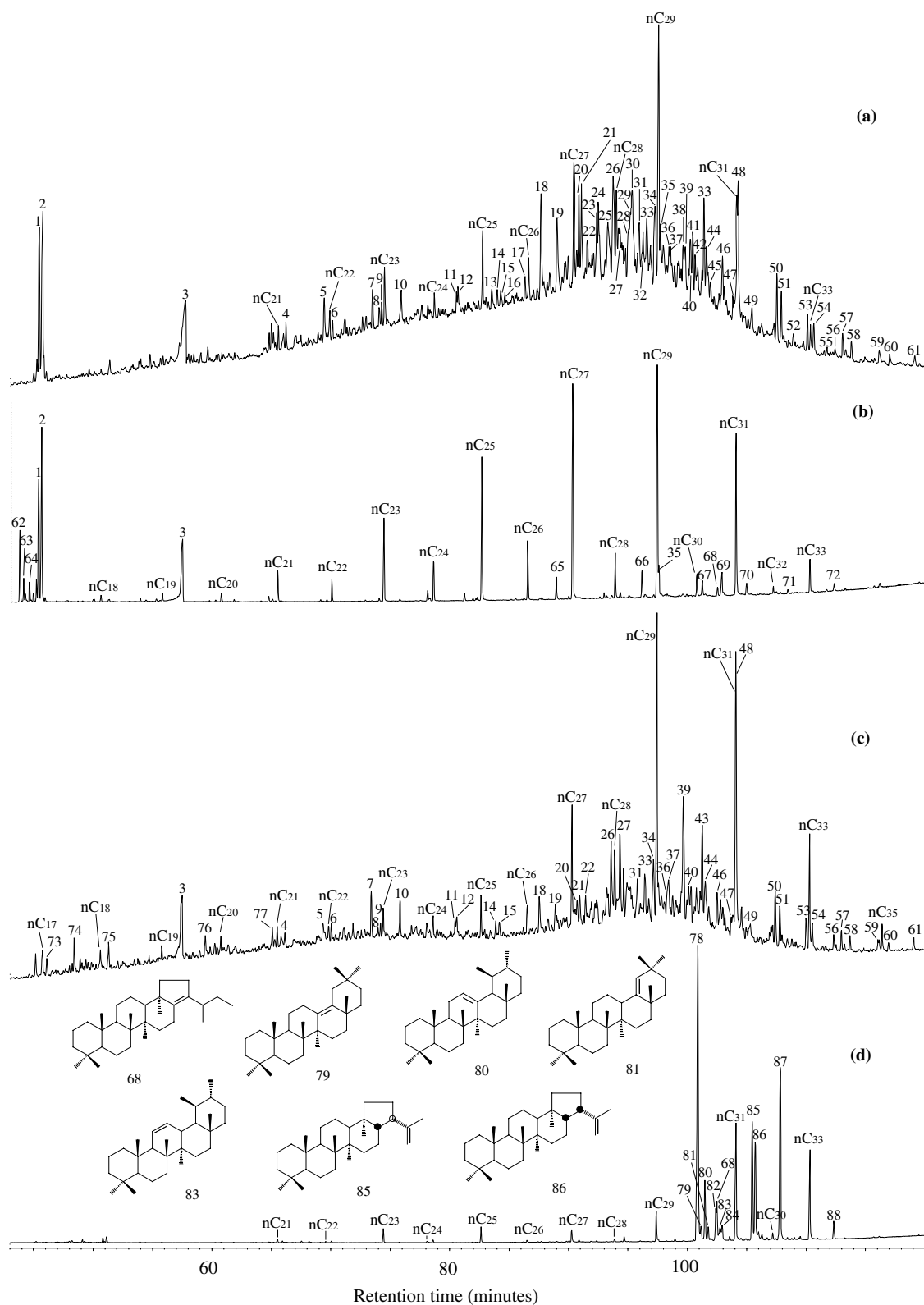


Fig. 2. TIC of saturate hydrocarbon fraction from extracts of modern sediments. (a) San Francisco Bay marsh mud. (b) Elkhorn Slough marsh mud. (c) Santa Barbara Basin marine mud. (d) Celestun Lagoon carbonate. Compounds assignments are listed in Table 1.



Table 2  
Peak assignments for compounds in saturate fraction from total extracts of modern sediments

| Peak no. <sup>a</sup> | Assignment  | Peak no. | Assignment  |
|-----------------------|---|----------|---|
| 1                     | 2,6,10-Trimethyl-5-(3-methyl-butyl)-dodecane  | 45       | C <sub>29</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -stigmastane 20 <i>R</i>     |
| 2                     | 2,6,10-Trimethyl-7-(3-methyl-butyl)-dodecane  | 46       | C <sub>29</sub> 17 $\beta$ ,21 $\alpha$ (H)-normoretane                         |
| 3                     | 256(97), 224(14), 192(100), 160(86), 128(80), 96(85)  | 47       | 18 $\alpha$ - + 18 $\beta$ -oleanane  |
| 4                     | C <sub>21</sub> 5 $\beta$ -pregnane   | 48       | C <sub>30</sub> 17 $\alpha$ ,21 $\beta$ (H)-hopane                              |
| 5                     | C <sub>21</sub> 5 $\alpha$ -pregnane  | 49       | C <sub>30</sub> 17 $\beta$ ,21 $\alpha$ (H)-moretane                            |
| 6                     | C <sub>22</sub> 5 $\beta$ -sterane  | 50       | C <sub>31</sub> 17 $\alpha$ ,21 $\beta$ (H)-homohopane 22 <i>S</i>              |
| 7                     | C <sub>23</sub> tricyclic terpene ( <i>S</i> )  | 51       | C <sub>31</sub> 17 $\alpha$ ,21 $\beta$ (H)-homohopane 22 <i>R</i>              |
| 8                     | C <sub>23</sub> sterane   | 52       | C <sub>31</sub> 17 $\beta$ ,21 $\alpha$ (H)-moretane                            |
| 9                     | C <sub>22</sub> 5 $\alpha$ -sterane   | 53       | C <sub>32</sub> 17 $\alpha$ ,21 $\beta$ (H)-bishomohopane 22 <i>S</i>           |
| 10                    | C <sub>24</sub> tricyclic terpene   | 54       | C <sub>32</sub> 17 $\alpha$ ,21 $\beta$ (H)-bishomohopane 22 <i>R</i>           |
| 11                    | C <sub>25</sub> tricyclic terpene ( <i>S</i> )  | 55       | C <sub>32</sub> 17 $\beta$ ,21 $\alpha$ (H)-moretane 22 <i>S</i>                |
| 12                    | C <sub>25</sub> tricyclic terpene ( <i>R</i> )  | 56       | C <sub>32</sub> 17 $\beta$ ,21 $\alpha$ (H)-moretane 22 <i>R</i>                |
| 13                    | C <sub>26</sub> 13 $\beta$ ,17 $\alpha$ -dia-27-norcholestane 20 <i>S</i>                   | 57       | C <sub>33</sub> 17 $\alpha$ , 21 $\beta$ (H)-trishomohopane 22 <i>S</i>         |
| 14                    | C <sub>26</sub> tricyclic terpene ( <i>S</i> )  | 58       | C <sub>33</sub> 17 $\alpha$ ,21 $\beta$ (H)-trishomohopane 22 <i>R</i>          |
| 15                    | C <sub>26</sub> tricyclic terpene ( <i>R</i> )  | 59       | C <sub>34</sub> 17 $\alpha$ ,21 $\beta$ (H)-tetrakishomohopane 22 <i>S</i>      |
| 16                    | C <sub>26</sub> 13 $\beta$ ,17 $\alpha$ -dia-27-norcholestane 20 <i>R</i>                   | 60       | C <sub>34</sub> 17 $\alpha$ ,21 $\beta$ (H)-tetrakishomohopane 22 <i>R</i>      |
| 17                    | 256(97), 224(14), 192(100), 160(86), 128(80), 96(85)  | 61       | C <sub>35</sub> 17 $\alpha$ ,21 $\beta$ (H)-pentakishomohopane 22 <i>S</i>      |
| 18                    | C <sub>27</sub> 13 $\beta$ ,17 $\alpha$ -diacholestane 20 <i>S</i>                          | 62       | 1-Decyl-3-methylcyclohexane   |
| 19                    | C <sub>27</sub> 13 $\beta$ ,17 $\alpha$ -diacholestane 20 <i>R</i>                          | 63       | 1-Decyl-4-methylcyclohexane   |
| 20                    | C <sub>28</sub> 13 $\beta$ ,17 $\alpha$ -diaergostane 20 <i>S</i> 24 <i>S</i> + 24 <i>R</i> | 64       | 1-Decyl-5-methylcyclohexane   |
| 21                    | C <sub>28</sub> 13 $\beta$ ,17 $\alpha$ -diaergostane 20 <i>S</i> 24 <i>S</i> + 24 <i>R</i> | 65       | 1-Methyl-3-(16-methyl-octadecyl)-cyclohexane                                    |
| 22                    | C <sub>28</sub> tricyclic terpene ( <i>S</i> )  | 66       | 1-Methyl-3-(18-methyl-eicosyl)-cyclohexane                                      |
| 23                    | C <sub>28</sub> 13 $\beta$ ,17 $\alpha$ -diaergostane 20 <i>R</i> 24 <i>S</i> + 24 <i>R</i> | 67       | 24-Ethylcholest-2-ene   |
| 24                    | C <sub>28</sub> 13 $\beta$ ,17 $\alpha$ -diaergostane 20 <i>R</i> 24 <i>S</i> + 24 <i>R</i> | 68       | Hop-17(21)-ene  |
| 25                    | C <sub>27</sub> 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -cholestane 20 <i>S</i>                | 69       | 1-Methyl-3-(20-methyl-docosyl)-cyclohexane                                      |
| 26                    | C <sub>29</sub> tricyclic terpene ( <i>S</i> )  | 70       | C <sub>29</sub> 17 $\beta$ ,21 $\beta$ (H)-30-norhopane                         |
| 27                    | C <sub>27</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -cholestane 20 <i>S</i>                  | 71       | C <sub>30</sub> 17 $\beta$ , 21 $\beta$ (H)-hopane                              |
| 28                    | C <sub>27</sub> 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -cholestane 20 <i>R</i>                | 72       | C <sub>31</sub> 17 $\beta$ ,21 $\beta$ (H)-homohopane                           |
| 29                    | 18 $\alpha$ -22,29,30-trisnorneohopane (Ts)   | 73       | 5-Methyl-hexadecane   |
| 30                    | C <sub>29</sub> 13 $\beta$ ,17 $\alpha$ -diastigmastane 20 <i>S</i>                         | 74       | 3,6-Dimethyl-hexadecane   |
| 31                    | C <sub>29</sub> 13 $\beta$ ,17 $\alpha$ -diastigmastane 20 <i>R</i>                         | 75       | 7-Methyl-nonadecane   |
| 32                    | C <sub>28</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -ergostane 20 <i>R</i>                   | 76       | 10-Methyl-eicosane  |
| 33                    | 17 $\alpha$ -22,29,30-trisnorhopane (Tm)  | 77       | C <sub>21</sub> tricyclic terpene   |
| 34                    | C <sub>28</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -ergostane 20 <i>S</i>                   | 78       | 410(59), 395(74), 286(100), 271(91), 257(63), 218(55), 204(69), 109(65)         |
| 35                    | C <sub>31</sub> tricyclic terpene ( <i>S</i> )  | 79       | Olean-13(18)-ene  |
| 36                    | C <sub>31</sub> tricyclic terpene ( <i>R</i> )  | 80       | Urs-12-ene  |
| 37                    | C <sub>28</sub> 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -ergostane 20 <i>R</i>                 | 81       | Olean-18-ene  |
| 38                    | C <sub>29</sub> 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -stigmastane 20 <i>S</i>               | 82       | 396(3), 286(100) 271(78), 257(9), 218(13), 204(21), 133(40), 109(29), 95(27)    |
| 39                    | C <sub>28</sub> 17 $\alpha$ ,18 $\alpha$ ,21 $\beta$ -bisnorhopane                          | 83       | Urs-11-ene  |
| 40                    | C <sub>29</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -stigmastane 20 <i>R</i>                 | 84       | 408(48), 393(33), 380(40), 271(15), 205(45), 187(63), 175(53), 109(85), 95(100) |
| 41                    | C <sub>29</sub> 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -stigmastane 20 <i>S</i>                 | 85       | 17 $\beta$ ,21 $\alpha$ (H)-moret-22(29)-ene                                    |
| 42                    | C <sub>29</sub> Nor-25-hopane   | 86       | 17 $\beta$ ,21 $\alpha$ (H)-hop-22(29)-ene                                      |
| 43                    | C <sub>29</sub> Tm 17 $\alpha$ ,21 $\beta$ (H)-norhopane                                    | 87       | 17 $\alpha$ ,21 $\beta$ (H)-homohopane 22 <i>R</i>                              |
| 44                    | C <sub>29</sub> 18 $\alpha$ -30-norneohopane (C <sub>29</sub> Ts)                           | 88       | 17 $\beta$ ,21 $\beta$ (H)-homohopane   |

<sup>a</sup> Peak series correspond to those in Fig. 2.

use 3- and 4-methyldiamantanes, monitored using *m/z* 187, to represent the diamondoids since they are less volatile and relatively abundant. Slight contamination from oil spills or oil seeps might be

responsible for the tiny amounts of diamondoids in these samples. The presence of geological epimers (22*S*) for C<sub>31</sub>–C<sub>35</sub> 17 $\alpha$ ,21 $\beta$ (H)-homohopanes in the extracts of these samples, which are usually absent

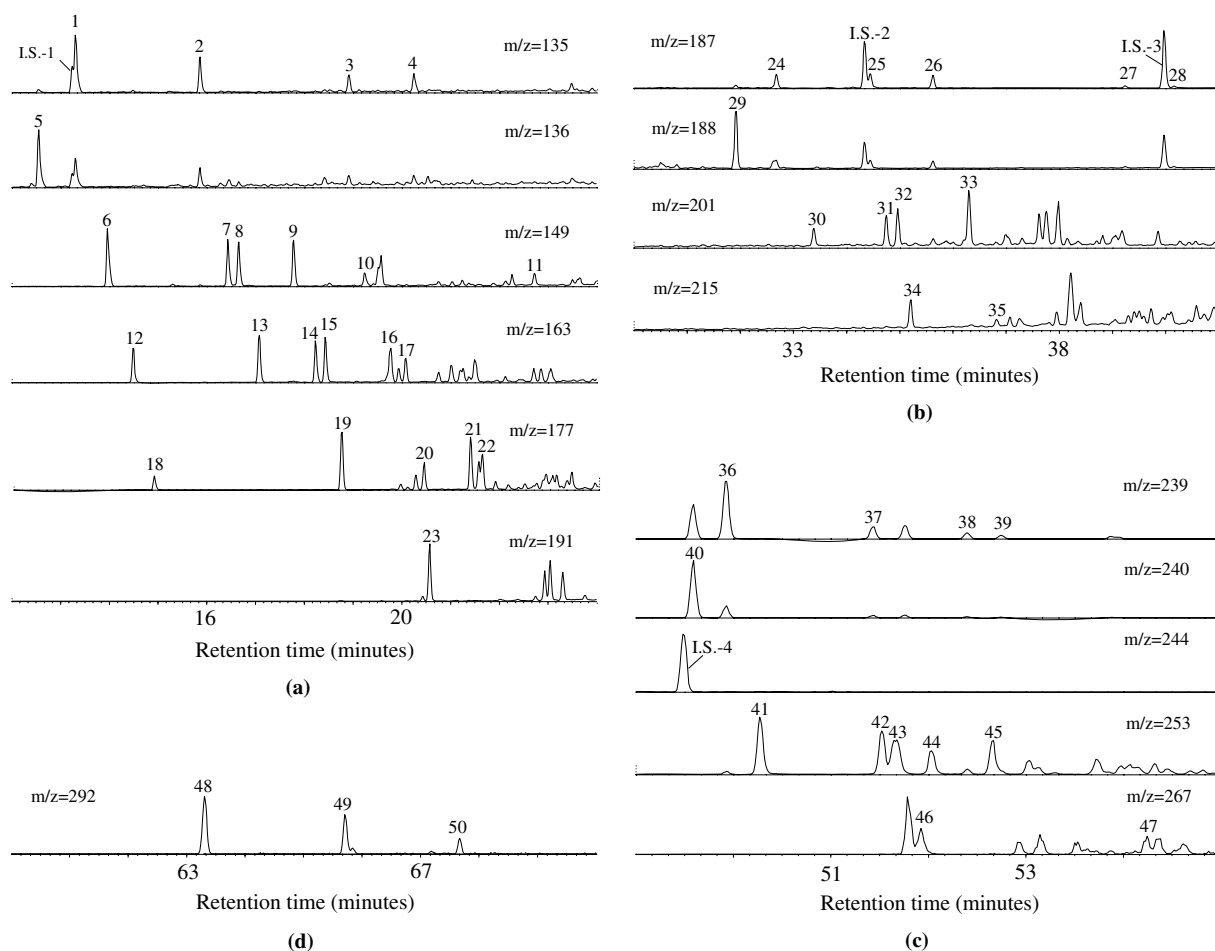


Fig. 3. Mass chromatograms of synthetic deuterated diamondoid standards and diamondoid hydrocarbons in saturate fraction from silica gel chromatography of extracts of modern sediments and hydrous pyrolysates: adamantanes ( $m/z$  135, 136, 149, 163, 177 and 191), diamantanes ( $m/z$  187, 188, 201 and 215), triamantanes ( $m/z$  239, 240, 244, 253 and 267), and tetramantanes ( $m/z$  292).

from modern sediments, supports this conclusion. In addition, the occurrence of other geological epimers such as 20S steranes,  $\beta\alpha$ -diasteranes and 18 $\alpha$ -trisorneohopane (Ts) is indicative of oil contamination. However, diamondoids were not detectable in the Celestun Lagoon sample, which is rich in microfossils but lacks the biological markers with geological configurations. This is consistent with the notion that diamondoids are not natural products of biological origin but rather represent small but measurable petroleum contamination in some of the modern sediment samples.

### 3.3. Diamondoids from thermal maturation of organic matter in modern sediments

Diamondoids are known to be widespread in oil (e.g., Landa and Machacek, 1933; Landa, 1959; Pet-

rov et al., 1974; Dahl et al., 1999). It is assumed that considerable amounts of acids present in sedimentary rocks might promote the chemical reactions of organic compounds, in particular, isomerization and rearrangement, leading to creation of diamondoid cage compounds under favorable conditions during geological processes. One way to test this is through artificial maturation of organic matter in modern sediments. This can be best simulated by hydrous pyrolysis, during which temperature is considered to be of crucial importance (Lewan, 1994). Our experiments used a temperature of 340 °C for 72 h, roughly equivalent to the thermal stress associated with peak oil generation. It is expected that the highest total yield of diamondoids is obtained at this temperature. As illustrated in Fig. 4, various amounts of are generated from all the organic-rich sediment samples, as indicated by the abundance



Table 3  
Peak assignments for diamondoid hydrocarbons

| Peak no.            | Molecular formula                              | Assignment                                    | M <sup>+</sup> (m/z) | Base peak (m/z) |
|---------------------|--|---|----------------------|-----------------|
| I.S.-1 <sup>a</sup> | C <sub>11</sub> H <sub>15</sub> D <sub>3</sub> | D <sub>3</sub> 1-methyladamantane             | 153                  | 135             |
| 1                   | C <sub>11</sub> H <sub>18</sub>                | 1-Methyladamantane                            | 150                  | 135             |
| 2                   | C <sub>11</sub> H <sub>18</sub>                | 2-Methyladamantane                            | 150                  | 135             |
| 3                   | C <sub>12</sub> H <sub>20</sub>                | 1-Ethyladamantane                             | 164                  | 135             |
| 4                   | C <sub>12</sub> H <sub>20</sub>                | 2-Ethyladamantane                             | 164                  | 135             |
| 5                   | C <sub>10</sub> H <sub>16</sub>                | Adamantane                                    | 136                  | 136             |
| 6                   | C <sub>12</sub> H <sub>20</sub>                | 1,3-Dimethyladamantane                        | 164                  | 149             |
| 7                   | C <sub>12</sub> H <sub>20</sub>                | 1,4-Dimethyladamantane ( <i>cis</i> )         | 164                  | 149             |
| 8                   | C <sub>12</sub> H <sub>20</sub>                | 1,4-Dimethyladamantane ( <i>trans</i> )       | 164                  | 149             |
| 9                   | C <sub>12</sub> H <sub>20</sub>                | 1,2-Dimethyladamantane                        | 164                  | 149             |
| 10                  | C <sub>12</sub> H <sub>20</sub>                | 2,6- + 2,4-Dimethyladamantanes                | 164                  | 149             |
| 11                  | C <sub>13</sub> H <sub>22</sub>                | 1-Ethyl-3-methyladamantane                    | 178                  | 149             |
| 12                  | C <sub>13</sub> H <sub>22</sub>                | 1,3,5-Trimethyladamantane                     | 178                  | 163             |
| 13                  | C <sub>13</sub> H <sub>22</sub>                | 1,3,6-Trimethyladamantane                     | 178                  | 163             |
| 14                  | C <sub>13</sub> H <sub>22</sub>                | 1,3,4-Trimethyladamantane ( <i>cis</i> )      | 178                  | 163             |
| 15                  | C <sub>13</sub> H <sub>22</sub>                | 1,3,4-Trimethyladamantane ( <i>trans</i> )    | 178                  | 163             |
| 16                  | C <sub>13</sub> H <sub>22</sub>                | 1,2,3-trimethyladamantane                     | 178                  | 163             |
| 17                  | C <sub>14</sub> H <sub>24</sub>                | 1-Ethyl-3,5-dimethyladamantane                | 192                  | 163             |
| 18                  | C <sub>14</sub> H <sub>24</sub>                | 1,3,5,7-Tetramethyladamantane                 | 192                  | 177             |
| 19                  | C <sub>14</sub> H <sub>24</sub>                | 1,2,5,7-Tetramethyladamantane                 | 192                  | 177             |
| 20                  | C <sub>14</sub> H <sub>24</sub>                | 1,3,5,6-Tetramethyladamantane                 | 192                  | 177             |
| 21                  | C <sub>14</sub> H <sub>24</sub>                | 1,2,3,5-Tetramethyladamantane                 | 192                  | 177             |
| 22                  | C <sub>15</sub> H <sub>26</sub>                | 1-Ethyl-3,5,7-trimethyladamantane             | 206                  | 177             |
| 23                  | C <sub>15</sub> H <sub>26</sub>                | 1,2,3,5,7-Pentamethyladamantane               | 206                  | 191             |
| 24                  | C <sub>15</sub> H <sub>22</sub>                | 4-Methyldiamantane                            | 202                  | 187             |
| I.S.-2              | C <sub>15</sub> H <sub>19</sub> D <sub>3</sub> | D <sub>3</sub> 1-methyldiamantane             | 205                  | 187             |
| 25                  | C <sub>15</sub> H <sub>22</sub>                | 1-Methyldiamantane                            | 202                  | 187             |
| 26                  | C <sub>15</sub> H <sub>22</sub>                | 3-Methyldiamantane                            | 202                  | 187             |
| 27                  | C <sub>16</sub> H <sub>24</sub>                | 1-Ethyldiamantane                             | 216                  | 187             |
| I.S.-3              | C <sub>16</sub> H <sub>19</sub> D <sub>5</sub> | D <sub>5</sub> 2-ethyldiamantane              | 221                  | 187             |
| 28                  | C <sub>16</sub> H <sub>24</sub>                | 2-Ethyldiamantane                             | 216                  | 187             |
| 29                  | C <sub>14</sub> H <sub>20</sub>                | Diamantane                                    | 188                  | 188             |
| 30                  | C <sub>15</sub> H <sub>24</sub>                | 4,9-Dimethyldiamantane                        | 216                  | 201             |
| 31                  | C <sub>16</sub> H <sub>24</sub>                | 1,2- + 2,4-Dimethyldiamantanes                | 216                  | 201             |
| 32                  | C <sub>16</sub> H <sub>24</sub>                | 4,8-Dimethyldiamantane                        | 216                  | 201             |
| 33                  | C <sub>16</sub> H <sub>24</sub>                | 3,4-Dimethyldiamantane                        | 216                  | 201             |
| 34                  | C <sub>17</sub> H <sub>26</sub>                | 1,4,9-Trimethyldiamantane                     | 230                  | 201             |
| 35                  | C <sub>17</sub> H <sub>26</sub>                | 3,4,9-Trimethyldiamantane                     | 230                  | 201             |
| 36                  | C <sub>19</sub> H <sub>26</sub>                | 9-Methyltriamantane                           | 254                  | 239             |
| 37                  | C <sub>19</sub> H <sub>26</sub>                | 5-Methyltriamantane                           | 254                  | 239             |
| 38                  | C <sub>19</sub> H <sub>26</sub>                | 8-Triamantane                                 | 254                  | 239             |
| 39                  | C <sub>19</sub> H <sub>26</sub>                | 16-Triamantane                                | 254                  | 239             |
| 40                  | C <sub>18</sub> H <sub>24</sub>                | Triamantane                                   | 240                  | 240             |
| I.S.-4              | C <sub>18</sub> H <sub>20</sub> D <sub>4</sub> | D <sub>4</sub> triamantane                    | 244                  | 244             |
| 41                  | C <sub>20</sub> H <sub>28</sub>                | 9,15-Dimethyltriamantane                      | 268                  | 253             |
| 42                  | C <sub>20</sub> H <sub>28</sub>                | 5,9-Dimethyltriamantane                       | 268                  | 253             |
| 43                  | C <sub>20</sub> H <sub>28</sub>                | 3,4-Dimethyltriamantane                       | 268                  | 253             |
| 44                  | C <sub>20</sub> H <sub>28</sub>                | 3,9- + 4,9- + 6,9- + 7,9-Dimethyltriamantanes | 268                  | 253             |
| 45                  | C <sub>20</sub> H <sub>28</sub>                | 9,14-Dimethyltriamantane                      | 268                  | 253             |
| 46                  | C <sub>21</sub> H <sub>30</sub>                | 5,9,15-Trimethyltriamantane                   | 268                  | 267             |
| 47                  | C <sub>21</sub> H <sub>30</sub>                | 3,9,15- + 4,9,15-Trimethyltriamantanes        | 268                  | 267             |
| 48                  | C <sub>22</sub> H <sub>28</sub>                | Tetramantane (1)                              | 292                  | 292             |
| 49                  | C <sub>22</sub> H <sub>28</sub>                | Tetramantane (2)                              | 292                  | 292             |
| 50                  | C <sub>22</sub> H <sub>28</sub>                | Tetramantane (3)                              | 292                  | 292             |

<sup>a</sup> Internal standard.

Table 4

Yield, distribution and geochemical parameters for diamondoids in extracts and hydrous pyrolysates of modern sediments with and without different minerals

|                                     | San Francisco Bay mud |                 |                  |                 |                | Elkhorn Slough mud |       |       |        |        | Santa Barbara Basin mud |       |       |        |        | Celestun Lagoon carbonate |       |       |       |       |
|-------------------------------------|-----------------------|-----------------|------------------|-----------------|----------------|--------------------|-------|-------|--------|--------|-------------------------|-------|-------|--------|--------|---------------------------|-------|-------|-------|-------|
|                                     | I <sup>b</sup>        | II <sup>b</sup> | III <sup>b</sup> | IV <sup>b</sup> | V <sup>b</sup> | I                  | II    | III   | IV     | V      | I                       | II    | III   | IV     | V      | I                         | II    | III   | IV    | V     |
| <i>Diamondoid yield<sup>a</sup></i> |                       |                 |                  |                 |                |                    |       |       |        |        |                         |       |       |        |        |                           |       |       |       |       |
| Adamantane                          | 0.04                  | 1.80            | 1.41             | 42.25           | 57.51          | 0.03               | 1.48  | 1.44  | 35.20  | 40.69  | 0.06                    | 2.20  | 2.19  | 21.37  | 12.24  | n.a. <sup>c</sup>         | 0.24  | 0.40  | 1.14  | 4.77  |
| Methyladamantanes                   | 0.24                  | 28.57           | 18.50            | 391.43          | 252.55         | 0.11               | 18.26 | 16.27 | 266.58 | 435.05 | 0.31                    | 36.10 | 31.24 | 232.68 | 166.84 | n.a.                      | 14.39 | 11.69 | 44.72 | 76.52 |
| Dimethyladamantanes                 | 0.31                  | 42.99           | 29.47            | 719.99          | 1010.73        | 0.16               | 20.62 | 21.89 | 306.30 | 599.76 | 0.44                    | 64.44 | 53.48 | 411.35 | 322.02 | n.a.                      | 17.10 | 16.40 | 45.06 | 78.12 |
| Trimethyladamantanes                | 0.27                  | 35.05           | 21.27            | 489.01          | 645.45         | 0.11               | 12.99 | 13.08 | 161.66 | 321.42 | 0.36                    | 51.35 | 41.45 | 289.50 | 177.18 | n.a.                      | 7.79  | 7.78  | 21.26 | 45.80 |
| Tetramethyladamantanes              | 0.12                  | 17.16           | 9.82             | 289.19          | 445.92         | 0.03               | 6.85  | 6.43  | 126.81 | 237.37 | 0.14                    | 21.10 | 16.22 | 90.83  | 108.23 | n.a.                      | 2.25  | 3.51  | 8.02  | 20.27 |
| Pentamethyladamantanes              | 0.01                  | 2.23            | 1.11             | 38.48           | 62.96          | 0.00               | 0.75  | 0.66  | 17.96  | 34.85  | 0.01                    | 1.86  | 1.18  | 7.14   | 10.20  | n.a.                      | 0.04  | 0.05  | 0.54  | 1.59  |
| Other alkyladamantanes              | 0.17                  | 20.94           | 13.01            | 296.07          | 438.62         | 0.08               | 13.27 | 11.59 | 104.62 | 212.55 | 0.30                    | 46.21 | 36.27 | 205.87 | 138.32 | n.a.                      | 8.68  | 6.11  | 30.56 | 40.94 |
| Diamantane                          | 0.03                  | 0.57            | 0.18             | 6.46            | 8.24           | 0.01               | 2.33  | 0.18  | 13.93  | 14.41  | 0.03                    | 0.34  | 0.29  | 3.18   | 1.54   | n.a.                      | 0.04  | 0.03  | 0.13  | 0.45  |
| Methyldiamantanes                   | 0.16                  | 2.61            | 0.94             | 32.57           | 35.77          | 0.03               | 8.22  | 0.70  | 50.10  | 49.31  | 0.10                    | 1.88  | 1.30  | 13.29  | 5.68   | n.a.                      | 0.21  | 0.25  | 0.66  | 2.05  |
| Dimethyldiamantanes                 | 0.18                  | 2.60            | 0.80             | 24.21           | 24.98          | 0.02               | 6.31  | 0.60  | 26.15  | 27.09  | 0.09                    | 1.62  | 1.23  | 11.14  | 5.47   | n.a.                      | 0.21  | 0.48  | 0.54  | 2.20  |
| Trimethyldiamantanes                | 0.04                  | 0.61            | 0.19             | 6.77            | 8.29           | n.a.               | 0.79  | 0.12  | 6.13   | 6.80   | 0.06                    | 0.34  | 0.21  | 2.37   | 1.72   | n.a.                      | 0.03  | 0.10  | 0.06  | 0.44  |
| Other alkyldiamantanes              | 0.04                  | 0.45            | 0.14             | 3.27            | 3.65           | 0.01               | 0.81  | 0.12  | 4.37   | 5.04   | 0.03                    | 0.24  | 0.14  | 1.48   | 0.95   | n.a.                      | 0.04  | 0.03  | 0.13  | 0.42  |
| Triamantane                         | 0.05                  | 0.20            | 0.10             | 0.94            | 1.25           | 0.01               | 0.27  | 0.07  | 0.95   | 0.95   | 0.04                    | 0.09  | 0.07  | 0.74   | 0.22   | n.a.                      | 0.00  | 0.02  | 0.04  | 0.12  |
| Methyltriamantanes                  | 0.18                  | 0.49            | 0.15             | 9.92            | 21.53          | 0.01               | 0.67  | 0.15  | 5.76   | 10.51  | 0.08                    | 0.03  | 0.01  | 2.47   | 5.68   | n.a.                      | 0.04  | 0.03  | 0.09  | 1.01  |
| Dimethyltriamantanes                | n.a.                  | 1.38            | 0.65             | 35.60           | 32.61          | n.a.               | 0.96  | 0.31  | 11.00  | 37.86  | 0.16                    | 0.79  | 0.45  | 15.56  | 9.86   | n.a.                      | 0.13  | 0.17  | 0.62  | 1.16  |
| Trimethyltriamantanes               | 0.02                  | 0.39            | 0.02             | 0.50            | 1.65           | n.a.               | 0.05  | 0.02  | 0.44   | 1.54   | 0.02                    | 0.03  | 0.02  | 0.29   | 1.11   | n.a.                      | 0.03  | 0.03  | 0.08  | 0.17  |
| Tetramantanes                       | n.a.                  | n.a.            | n.a.             | 1.73            | 2.61           | n.a.               | n.a.  | n.a.  | 1.63   | 1.75   | n.a.                    | 0.01  | 0.01  | 0.94   | 1.04   | n.a.                      | n.a.  | n.a.  | 0.04  | 0.36  |
| 3- + 4-Methyldiamantanes            | 0.09                  | 1.84            | 0.55             | 24.07           | 26.63          | 0.02               | 5.80  | 0.48  | 36.17  | 36.32  | 0.07                    | 1.12  | 0.86  | 10.00  | 3.89   | n.a.                      | 0.14  | 0.11  | 0.44  | 1.47  |
| Diamondoids (total) <sup>d</sup>    | 2                     | 155             | 96               | 2339            | 2987           | 0.57               | 91    | 72    | 1089   | 1981   | 2                       | 226   | 183   | 1285   | 954    | n.a.                      | 51    | 47    | 152   | 271   |
| <i>Diamondoid parameters</i>        |                       |                 |                  |                 |                |                    |       |       |        |        |                         |       |       |        |        |                           |       |       |       |       |
| 4-MD/(1- + 3- + 4-MD)               | n.a. <sup>h</sup>     | 0.38            | 0.34             | 0.44            | 0.45           | n.a.               | 0.41  | 0.38  | 0.45   | 0.44   | n.a.                    | 0.34  | 0.37  | 0.45   | 0.37   | n.a.                      | 0.26  | 0.11  | 0.34  | 0.38  |
| 1-MA/(1- + 2-MA)                    | n.a.                  | 0.64            | 0.56             | 0.57            | 0.60           | n.a.               | 0.68  | 0.65  | 0.74   | 0.68   | n.a.                    | 0.51  | 0.47  | 0.54   | 0.58   | n.a.                      | 0.32  | 0.22  | 0.32  | 0.36  |
| 1-EA/(1- + 2-EA)                    | n.a.                  | 0.39            | 0.36             | 0.48            | 0.45           | n.a.               | 0.38  | 0.32  | 0.52   | 0.52   | n.a.                    | 0.48  | 0.51  | 0.36   | 0.33   | n.a.                      | 0.65  | 0.65  | 0.61  | 0.45  |
| 4,9-DMD. %                          | n.a.                  | 22              | 22               | 20              | 20             | n.a.               | 20    | 22    | 22     | 20     | n.a.                    | 23    | 26    | 26     | 24     | n.a.                      | 39    | 37    | 35    | 32    |
| 4,8-DMD. %                          | n.a.                  | 29              | 24               | 29              | 29             | n.a.               | 30    | 27    | 31     | 28     | n.a.                    | 25    | 21    | 21     | 25     | n.a.                      | 16    | 16    | 20    | 22    |
| 3,4-DMD. %                          | n.a.                  | 49              | 54               | 51              | 51             | n.a.               | 50    | 51    | 48     | 52     | n.a.                    | 52    | 53    | 53     | 51     | n.a.                      | 45    | 47    | 46    | 46    |

<sup>a</sup> Diamondoid yield is the amount of diamondoids generated from sediment extraction and hydrous pyrolysis relative to initial dry sediment, ng/g sediment.<sup>b</sup> Experiment series. I = extract from modern sediment; II = hydrous pyrolysis of modern sediment; III = hydrous pyrolysis of sediment:CaCO<sub>3</sub> mixture (6:1); IV = hydrous pyrolysis of sediment:montmorillonite K10 mixture (6:1); V = hydrous pyrolysis of sediment:MS-25 mixture (6:1).<sup>c</sup> Not available due to absence and/or negligible concentration.<sup>d</sup> Total ppm diamondoid species in extract and pyrolysate including adamantanes, diamantanes, triamantanes, and tetramantanes. The negligible amounts of higher diamondoids (e.g., pentamantanes, and hexamantanes) are not included.

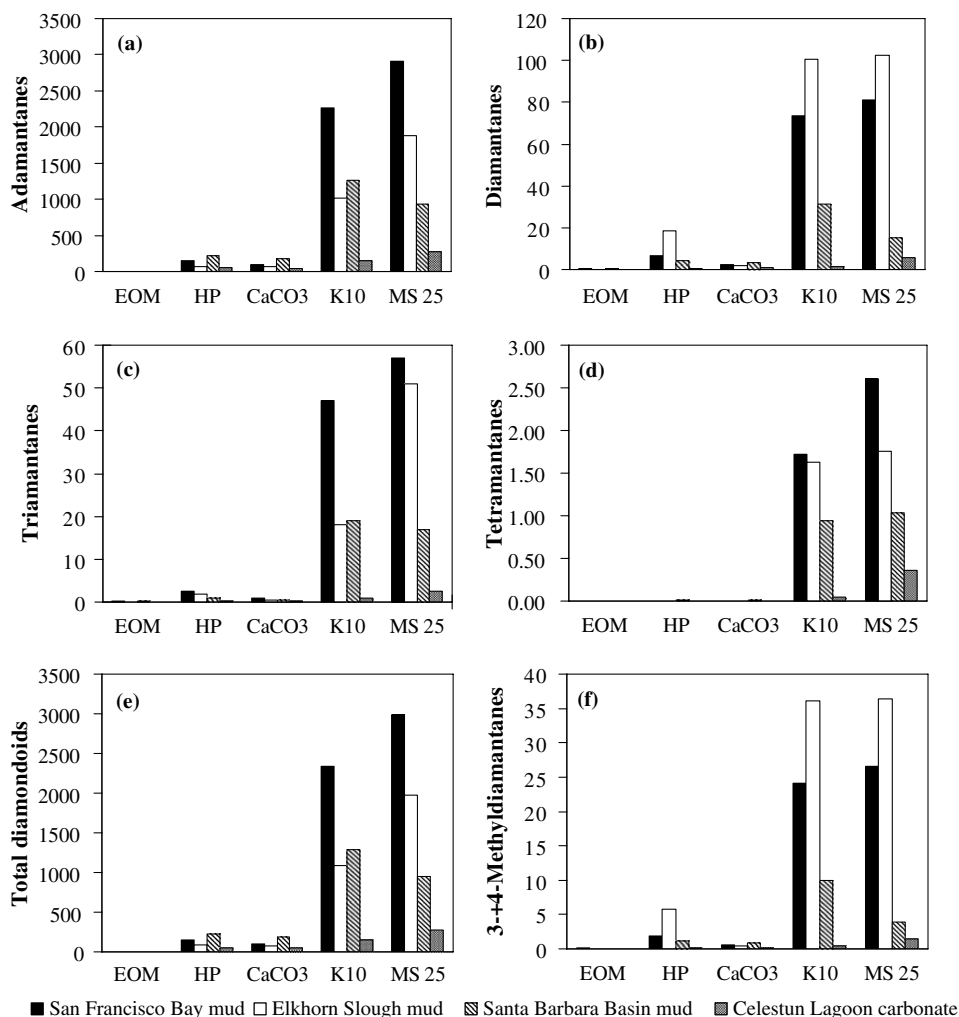


Fig. 4. Yield (ng/g sediment) of each diamondoid cluster (a–d), total diamondoids (e), and 3- + 4-methyldiamantanes (f) in hydrous pyrolysates of modern sediments in presence and absence of minerals including CaCO<sub>3</sub>, montmorillonite K10, and MS-25 [72 h hydrous pyrolysis performed on modern sediments and sediment/mineral mix (6:1) at 340 °C]. HP = hydrous pyrolysis of modern sediments; CaCO<sub>3</sub> = hydrous pyrolysis of sediments:CaCO<sub>3</sub> mixture (6:1); K10 = hydrous pyrolysis of sediments:montmorillonite K10 mixture (6:1); MS-25 = hydrous pyrolysis of sediments:MS-25 mixture (6:1).

in the pyrolysates. Large quantities of terpanes and steranes also are released, such as tricyclic terpanes, C<sub>30</sub>17 $\alpha$ -hopane, Ts, Tm, C<sub>31</sub>–C<sub>35</sub>17 $\alpha$ ,21 $\beta$ (H)-homohopanes (22S and 22R), C<sub>27</sub>–C<sub>29</sub>5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steranes, 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steranes, and diasteranes (Table 5). This suggests that the liberation of diamondoids from a sedimentary rock during diagenesis and catagenesis accompanies the liberation of biological markers and other hydrocarbons such as *n*-alkanes.

The yield of diamondoids varies among different sediments. As shown in Fig. 4, artificial maturation of Elkhorn Slough mud gave the largest quantities of 3- + 4-methyldiamantanes. In contrast, the yield of 3- + 4-methyldiamantanes from

the Celestun carbonate pyrolysate is only 0.14 ng/g (Table 4), probably as a result of the absence of inorganic acids. Only a minor difference exists between the yield of 3- + 4-methyldiamantanes from the San Francisco Bay and Santa Barbara Basin muds. The yield of four diamondoid clusters—adamantanes, diamantanes, triamantanes, and tetramantanes is the lowest in the Celestun Lagoon carbonate sample. However, the highest yield of adamantane, diamantane, and triamantane clusters shifted in the other three sediments (Fig. 4a–d). There are some inconsistencies in total diamondoids, which may be attributable to evaporative losses during sample work up.

Table 5  
Yield of molecular biomarkers and associated geochemical parameters from GC–MS analysis of saturates from extracts and hydrous pyrolysates of sediments with and without minerals

|   | San Francisco Bay mud |                 |                  |                 |                | Elkhorn Slough mud |       |       |       |       | Santa Barbara Basin mud |        |       |        |        | Celestun Lagoon carbonate |        |        |        |         |
|---|-----------------------|-----------------|------------------|-----------------|----------------|--------------------|-------|-------|-------|-------|-------------------------|--------|-------|--------|--------|---------------------------|--------|--------|--------|---------|
|   | I <sup>b</sup>        | II <sup>b</sup> | III <sup>b</sup> | IV <sup>b</sup> | V <sup>b</sup> | I                  | II    | III   | IV    | V     | I                       | II     | III   | IV     | V      | I                         | II     | III    | IV     | V       |
| <i>Biomarker yield<sup>a</sup></i>                                      |                       |                 |                  |                 |                |                    |       |       |       |       |                         |        |       |        |        |                           |        |        |        |         |
| C <sub>28</sub> 17 $\alpha$ ,18 $\alpha$ ,21 $\beta$ (H)-bisnorhopane   | 32.72                 | 1.26            | 14.52            | 46.25           | 136.73         | 1.15               | 0.18  | 0.27  | 0.43  | 0.31  | 143.21                  | 16.29  | 18.69 | 118.01 | 75.03  | 4.55                      | 1.52   | 0.95   | 3.01   | 3.94    |
| C <sub>30</sub> 17 $\alpha$ -diahopane                                  | 8.80                  | 1.79            | 2.58             | 8.04            | 27.35          | 0.13               | 0.08  | 0.07  | 0.15  | 0.14  | 2.08                    | 0.72   | 0.83  | 3.30   | 3.48   | n.d. <sup>c</sup>         | n.d.   | n.d.   | n.d.   | n.d.    |
| 18 $\alpha$ -trisnorneohopane (Ts)                                      | 28.33                 | 60.73           | 53.52            | 165.11          | 329.60         | 1.62               | 5.33  | 11.58 | 45.39 | 59.39 | 10.67                   | 26.26  | 14.90 | 83.25  | 55.08  | 4.76                      | 20.02  | 16.10  | 21.38  | 31.01   |
| 17 $\alpha$ -Trisnorhopane (Tm)   | 36.36                 | 63.97           | 85.77            | 182.69          | 365.50         | 1.94               | 10.34 | 70.65 | 48.68 | 50.58 | 27.27                   | 55.69  | 58.12 | 411.87 | 192.65 | 3.13                      | 325.31 | 414.78 | 329.71 | 620.10  |
| C <sub>29</sub> nor-25-hopane   | 13.70                 | 0.85            | 9.45             | 46.25           | 163.82         | 0.29               | 0.17  | 1.18  | 1.25  | 1.15  | 8.20                    | 2.01   | 3.05  | 31.55  | 13.25  | 2.34                      | 4.75   | 3.83   | 8.71   | 15.75   |
| C <sub>29</sub> 17 $\alpha$ ,21 $\beta$ (H)-norhopane                   | 91.50                 | 11.02           | 121.91           | 326.46          | 760.36         | 2.88               | 12.22 | 57.07 | 52.24 | 54.80 | 92.00                   | 75.63  | 80.78 | 639.71 | 287.33 | 0.00                      | 360.35 | 364.81 | 552.38 | 1284.59 |
| C <sub>30</sub> 17 $\alpha$ ,21 $\beta$ (H)-hopane                      | 126.80                | 61.27           | 83.48            | 230.20          | 620.04         | 7.72               | 4.33  | 15.91 | 13.30 | 12.99 | 193.48                  | 49.50  | 46.67 | 417.71 | 171.51 | 25.06                     | 255.25 | 152.82 | 494.34 | 600.46  |
| $\alpha\beta$ -Homohopanes (C <sub>31</sub> -C <sub>35</sub> )          | 19.56                 | 12.75           | 19.14            | 53.26           | 131.16         | 0.65               | 1.60  | 7.61  | 6.34  | 5.09  | 14.68                   | 15.60  | 18.17 | 214.82 | 81.78  | 17.02                     | 99.61  | 127.92 | 313.45 | 507.05  |
| $\beta\alpha$ -Homomoretanes (C <sub>31</sub> -C <sub>35</sub> )        | 175.84                | 55.10           | 70.50            | 206.03          | 578.01         | 3.42               | 3.38  | 15.20 | 8.02  | 9.74  | 157.28                  | 48.43  | 45.98 | 556.29 | 200.84 | n.d.                      | 216.38 | 215.54 | 585.93 | 866.21  |
| Total triterpanes   | 997                   | 840             | 979              | 3338            | 7867           | 54                 | 133   | 325   | 444   | 471   | 1046                    | 704    | 612   | 5441   | 2443   | 5199                      | 1918   | 1855   | 3705   | 6122    |
| C <sub>27</sub> regular sterane   | 96.47                 | 64.03           | 82.05            | 230.78          | 722.19         | 1.03               | 0.84  | 2.27  | 44.04 | 4.83  | 96.88                   | 81.04  | 83.94 | 580.90 | 322.62 | n.d.                      | 128.43 | 40.62  | 312.21 | 166.63  |
| C <sub>28</sub> regular steranes  | 103.99                | 25.28           | 31.45            | 130.08          | 449.79         | 1.58               | 0.07  | 0.20  | 0.64  | 0.24  | 118.58                  | 14.36  | 26.41 | 197.89 | 112.02 | n.d.                      | 13.01  | 2.14   | 92.21  | 22.96   |
| C <sub>29</sub> regular steranes  | 74.34                 | 20.22           | 23.25            | 109.10          | 348.43         | 0.41               | 0.05  | 0.87  | 1.06  | 0.75  | 66.65                   | 6.15   | 15.09 | 130.86 | 68.71  | n.d.                      | 37.39  | 10.69  | 130.42 | 71.51   |
| C <sub>26</sub> -C <sub>30</sub> diasteranes                            | 385.42                | 431.36          | 426.66           | 1728.75         | 4504.19        | 2.56               | 3.36  | 9.94  | 44.04 | 31.42 | 109.28                  | 144.64 | 61.30 | 714.95 | 379.38 | n.d.                      | 61.78  | 17.10  | 130.42 | 76.75   |
| Total steranes C <sub>26</sub> -C <sub>30</sub>                         | 674                   | 541             | 568              | 2211            | 6082           | 6                  | 4     | 13    | 90    | 39    | 400                     | 247    | 188   | 1647   | 890    | n.d.                      | 243    | 69     | 833    | 342     |
| <i>Biomarker parameters</i>   |                       |                 |                  |                 |                |                    |       |       |       |       |                         |        |       |        |        |                           |        |        |        |         |
| C <sub>24</sub> Tet/C <sub>23</sub> TT <sup>d</sup>                     | 0.15                  | 0.40            | 0.43             | 0.31            | 0.29           | 0.88               | 1.29  | 9.56  | 4.00  | 4.24  | 0.10                    | 0.25   | 0.40  | 0.22   | 0.23   | 0.67                      | 4.11   | 5.73   | 3.02   | 4.89    |
| C <sub>32</sub> 22S/(22S + 22R)   | 0.57                  | 0.59            | 0.58             | 0.58            | 0.58           | 0.50               | 0.51  | 0.56  | 0.55  | 0.55  | 0.53                    | 0.50   | 0.47  | 0.51   | 0.47   | n.d.                      | 0.51   | 0.48   | 0.43   | 0.45    |
| C <sub>30</sub> $\beta\alpha$ -moretanes/ $\alpha\beta$ -hopanes        | 0.08                  | 0.09            | 0.11             | 0.09            | 0.08           | 0.07               | 0.12  | 0.14  | 0.12  | 0.10  | 0.06                    | 0.13   | 0.17  | 0.15   | 0.14   | n.d.                      | 0.20   | 0.23   | 0.20   | 0.20    |
| 18 $\alpha$ /(18 $\alpha$ +18 $\beta$ )-Oleananes                       | 0.42                  | 0.23            | 0.25             | 0.16            | 0.18           | 0.45               | 0.31  | 0.22  | 0.20  | 0.14  | 0.48                    | 0.33   | 0.29  | 0.23   | 0.28   | n.d.                      | n.d.   | n.d.   | n.d.   | n.d.    |
| Ts/(Ts + Tm)  | 0.44                  | 0.49            | 0.38             | 0.47            | 0.47           | 0.46               | 0.34  | 0.14  | 0.48  | 0.54  | 0.28                    | 0.32   | 0.20  | 0.17   | 0.22   | 0.60                      | 0.06   | 0.04   | 0.06   | 0.05    |
| C <sub>30</sub> <sup>e</sup> /C <sub>29</sub> Ts <sup>e</sup>           | 0.18                  | 0.08            | 0.11             | 0.09            | 0.10           | 0.31               | 0.09  | 0.04  | 0.08  | 0.06  | 0.13                    | 0.08   | 0.06  | 0.18   | 0.18   | n.d.                      | n.d.   | n.d.   | n.d.   | n.d.    |
| C <sub>29</sub> 30-norhopane/C <sub>30</sub> hopane                     | 0.11                  | 0.13            | 0.11             | 0.20            | 0.26           | 0.04               | 0.04  | 0.07  | 0.09  | 0.09  | 0.04                    | 0.04   | 0.07  | 0.08   | 0.08   | 0.09                      | 0.02   | 0.03   | 0.02   | 0.03    |
| C <sub>29</sub> $\alpha\alpha$ -sterane 20S/(20S + 20R)                 | 0.55                  | 0.53            | 0.53             | 0.49            | 0.50           | 0.31               | 0.49  | 0.43  | 0.36  | 0.44  | 0.44                    | 0.49   | 0.50  | 0.42   | 0.44   | n.d.                      | 0.43   | 0.36   | 0.36   | 0.35    |
| C <sub>29</sub> sterane $\beta\beta$ /( $\beta\beta$ + $\alpha\alpha$ ) | 0.55                  | 0.75            | 0.74             | 0.71            | 0.67           | 0.20               | 0.53  | 0.71  | 0.82  | 0.88  | 0.48                    | 0.71   | 0.59  | 0.61   | 0.61   | n.d.                      | 0.44   | 0.23   | 0.34   | 0.34    |
| C <sub>29</sub> $\beta\alpha$ -diasterane 20S/(20S + 20R)               | 0.54                  | 0.56            | 0.52             | 0.53            | 0.54           | 0.68               | 0.70  | 0.40  | 0.60  | 0.58  | 0.46                    | 0.39   | 0.30  | 0.38   | 0.36   | n.d.                      | 0.23   | 0.10   | 0.08   | 0.22    |
| Dia/dia + regular steranes  | 0.61                  | 0.76            | 0.70             | 0.77            | 0.72           | 0.60               | 0.75  | 0.30  | 0.68  | 0.74  | 0.35                    | 0.53   | 0.27  | 0.43   | 0.42   | n.d.                      | 0.25   | 0.24   | 0.21   | 0.23    |
| %C <sub>27</sub> /C <sub>27-29</sub> steranes                           | 35                    | 58              | 60               | 49              | 48             | 34                 | 88    | 68    | 96    | 83    | 34                      | 80     | 67    | 64     | 64     | n.d.                      | 72     | 77     | 65     | 64      |
| %C <sub>28</sub> /C <sub>27-29</sub> steranes                           | 38                    | 24              | 23               | 28              | 30             | 52                 | 7     | 6     | 1     | 4     | 42                      | 14     | 21    | 22     | 22     | n.d.                      | 7      | 3      | 9      | 9       |
| %C <sub>29</sub> /C <sub>27-29</sub> steranes                           | 27                    | 18              | 17               | 23              | 23             | 14                 | 5     | 26    | 2     | 13    | 24                      | 6      | 12    | 14     | 14     | n.d.                      | 21     | 20     | 25     | 27      |

<sup>a</sup> Biomarker yield is the amount of biomarker generated from sediment extraction and hydrous pyrolysis relative to the initial dry sediment, ng/g sediment.

<sup>b</sup> Experiment series. I = extract from modern sediment; II = hydrous pyrolysis of modern sediment; III = hydrous pyrolysis of sediment:CaCO<sub>3</sub> mixture (6:1); IV = hydrous pyrolysis of sediment:montmorillonite K10 mixture (6:1); V = hydrous pyrolysis of sediment:MS-25 mixture (6:1).

<sup>c</sup> Not detected.

<sup>d</sup> C<sub>24</sub> tetracyclic terpane/C<sub>23</sub> tricyclic terpane.

<sup>e</sup> 17 $\alpha$ -Diahopane/18 $\alpha$ -30-norneohopane.

The yield variations may be ascribed to the difference in the chemical composition of the extractable organic matter in the samples, as previously discussed. Indeed, Wei et al. (2005a) suggested that almost every organic compound could create diamondoids in the presence of suitable catalysts, but the major products vary on the basis of the original organic matter composition and are dominated by a different distribution. In addition, the yield of diamondoid production changes for different categories of organic precursors. Therefore, the compounds in these natural sediments might make different contributions to the abundance of diamondoids during hydrous pyrolysis. Alternatively, the mineralogical difference between samples might contribute to the variations in the yield in the pyrolysates. In general, the mud pyrolysates contain higher concentrations of diamondoids than the carbonate pyrolysates under the same conditions (Fig. 4), indicating that the presence of clay minerals enhances diamondoid formation, while carbonate may have a repressive effect.

### 3.4. Diamondoids from mineral catalysis of modern sediments during hydrous pyrolysis

Clay minerals usually behave as acidic catalysts in the transformation of organic matter to hydrocarbons since clay catalysis of chemical reactions occurs in sediments after the adsorption of organic molecules (e.g., Johns, 1979; Goldstein, 1983; Alexander et al., 1984; Faure and Landais, 2000). Our previous studies showed that montmorillonite K10, having large surface area, high CEC, and superacidity, is very effective in the production of diamondoids and substantially promotes their formation during pyrolysis of immature kerogens (Wei et al., 2005b). In the present study, montmorillonite K10 and MS-25 are added to investigate if they can catalyze diamondoid formation during the artificial maturation of organic matter in modern sediments upon heating. Table 4 shows hydrous pyrolysis results of modern sediments in the presence of minerals including montmorillonite K10, MS-25, and CaCO<sub>3</sub>. As illustrated in Fig. 4, compared to the hydrous pyrolysis of sediment alone, the yield of 3- + 4-methyldiamantanes increases greatly by about 3–13 times when montmorillonite K10 is added, although the amounts of diamondoids generated from Celestun carbonate through clay-catalyzed pyrolysis are not as high as those from other muds. As an active catalyst, MS-25 acts

very similarly to montmorillonite K10, resulting in relatively equivalent quantities of 3- + 4-methyldiamantanes. Likewise, the generation of other diamondoid species becomes significant compared to non-catalyzed reactions in the presence of montmorillonite K10 and MS-25 due to their superacidity. The catalytic activities of montmorillonite K10 and MS-25 were also demonstrated when the highest yields (6.34 and 4.20 mg/g, respectively) of hydrous pyrolysates were generated from San Francisco Bay mud when heated with MS-25 compared to hydrous pyrolysis with CaCO<sub>3</sub> added, where the product yield (1.69 mg/g) is only slightly improved compared with no mineral addition (1.37 mg/g, Fig. 5).

The acidity of clay minerals (e.g., montmorillonite K10) is generally known to be associated with two types of catalytic sites: Lewis acid sites and Brønsted acid sites, distributed at the interlamellar region and the edge of clay particles, respectively (Johns, 1979). At higher temperatures (ca. 200–300 °C), the Lewis acidity becomes dominant because of the attenuation of the Brønsted acidity of clay minerals (Cseri et al., 1995). Therefore, the Lewis acidic sites can be of importance in the catalytic reactions of organic compounds in modern sediments at 340 °C. These reactions proceed via carbocation mechanisms through which certain strained polycyclic alkane precursors are rearranged to diamondoids. The Lewis acid-catalyzed rearrangements of some organic compounds to alkyl adamantanes have been discussed elsewhere (Schneider et al., 1966; Petrov et al., 1974; Fort, 1976). In general, carbocation mechanisms

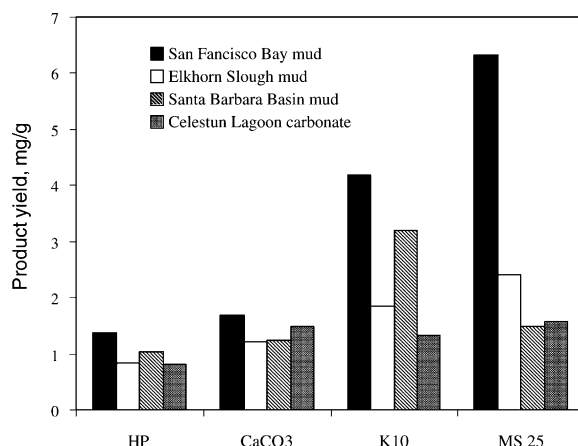


Fig. 5. Yield (mg/g sediment) of hydrous pyrolysates of modern sediments with and without minerals. For abbreviations see Fig. 4.

involving positively charged intermediates would be expected to produce a predominance of branched products. The acyclic and/or branched compounds may crack to form unsaturated compounds that then cyclize. Further fragmentation, alkylation and cyclization eventually yield polycyclic diamondoid precursors and then alkyl diamondoids themselves. Therefore, with the addition of montmorillonite K10 and MS-25, more Lewis acidic sites become available for the rearrangement of organic compounds. As a result, an increasing number of organic precursors are converted to diamondoid compounds via carbocation mechanisms. Based on this, it is most likely that acidic clay minerals pre-exist in these muds, leading to the high abundance of diamondoids in their pyrolysates. As shown in Table 4, the yield of 3- + 4-methyldiamantanes and total diamondoids from hydrous pyrolysates of marsh muds is 3–82 times and 4–15 times, respectively, higher than those for Celestun carbonate pyrolysate.

As shown in Fig. 4,  $\text{CaCO}_3$  appears to largely inhibit the formation of diamondoids because the yield is greatly reduced for all the sediments in the presence of  $\text{CaCO}_3$ . Li et al. (1998) suggested that  $\text{K}_2\text{CO}_3$  could catalyze the decomposition of kerogen via electron transfer mechanisms. If this were the case,  $\text{CaCO}_3$  would be expected to show a behavior similar to clays in catalyzing the thermal maturation of organic matter in the sediments. However, the opposite is observed and  $\text{CaCO}_3$  appears to inhibit the creation of diamondoids. The yield of diamondoids for the hydrous pyrolysis of Celestun Lagoon carbonate in the absence and presence of  $\text{CaCO}_3$  is very similar, suggesting  $\text{CaCO}_3$  addition does not affect experimentally-generated products from this already carbonate rich sediment. Indeed, the presence of  $\text{CaCO}_3$  may lead to the dominance of heavy hydrocarbons in pyrolysates because of its negligible adsorption capacity (Tannenbaum et al., 1986) and the activity of  $\text{CaCO}_3$  is much weaker than that of clay minerals (Taulbee and Seibert, 1987), particularly with increasing temperature (Li et al., 1998). In addition, the mineral acidity of clays may be consumed through reaction with  $\text{CaCO}_3$ , reducing their superacidity and making them catalytically less effective in the reactions of the organic matter. Thus, the presence of  $\text{CaCO}_3$  is expected to have a pronounced inhibitive effect on the occurrence of diamondoids. Our results undoubtedly demonstrate that, while the presence of either montmorillonite K10 or MS-25 is favorable for diamond-

oid formation,  $\text{CaCO}_3$  is an inhibitor of their generation. This observation suggests that the carbocation mechanisms, rather than electron transfer mechanisms, are of major importance in the formation of diamondoids.

### 3.5. Effect of minerals on diamondoid parameters

With the same carbon structures as diamond lattice fragments would have, diamondoids, in general, have extremely high stability. However, methyl adamantane and methyl diamantane isomers exhibit different thermal stability. Bridgehead 1-methyladamantane (1-MA) is thermodynamically more stable than 2-methyladamantane (2-MA). Bridgehead 1-ethyladamantane (1-EA) is more stable than 2-ethyladamantane (2-EA). Bridgehead 4-methyldiamantane (4-MD) is more stable than 1-methyldiamantane (1-MD) and 3-methyldiamantane (3-MD). Accordingly, Chen et al. (1996) defined and used the MDI ( $4\text{-MD}/(1\text{-MD} + 3\text{-MD} + 4\text{-MD})$ ) and MAI ( $1\text{-MA}/(1\text{-MA} + 2\text{-MA})$ ) indices as maturity indicators for overmature crude oils. However, Schulz et al. (2001) found these maturity parameters are also source controlled. Our work also indicates that both parameters appear to be affected by mineralogy, in particular by  $\text{CaCO}_3$  abundance. For instance, MDI and MAI ratios decrease with the addition of  $\text{CaCO}_3$  to the San Francisco Bay mud (Table 4; Fig. 6). Similar trends are observed for the other samples under the same conditions. The EAI ratio ( $1\text{-EA}/(1\text{-EA} + 2\text{-EA})$ ) is also suppressed by  $\text{CaCO}_3$ . In contrast, the presence of montmorillonite K10 or MS-25 may elevate the EAI ratio. For example, the ratio increases from 0.38 to 0.48 for San Francisco Bay mud and from 0.38 to 0.56 for Santa Barbara Basin mud with clay addition. However, it behaves differently for Celestun Lagoon carbonate where the inhibitive effect of  $\text{CaCO}_3$  in the sample overwhelms the catalytic activity of montmorillonite or MS-25. Therefore, lithology should be taken into account when the diamondoid maturity parameters MAI, EAI, and MDI are used to evaluate the thermal maturity of oils and source rocks.

Schulz et al. (2001) suggest that the relative abundance of 3,4-dimethyldiamantane (3,4-DMD), 4,8-dimethyldiamantane (4,8-DMD), and 4,9-dimethyldiamantane (4,9-DMD) can be used to identify different facies within source rocks. Table 4 suggests that the presence of either montmorillonite K10 or MS-25 facilitates 4,8-DMD generation since a



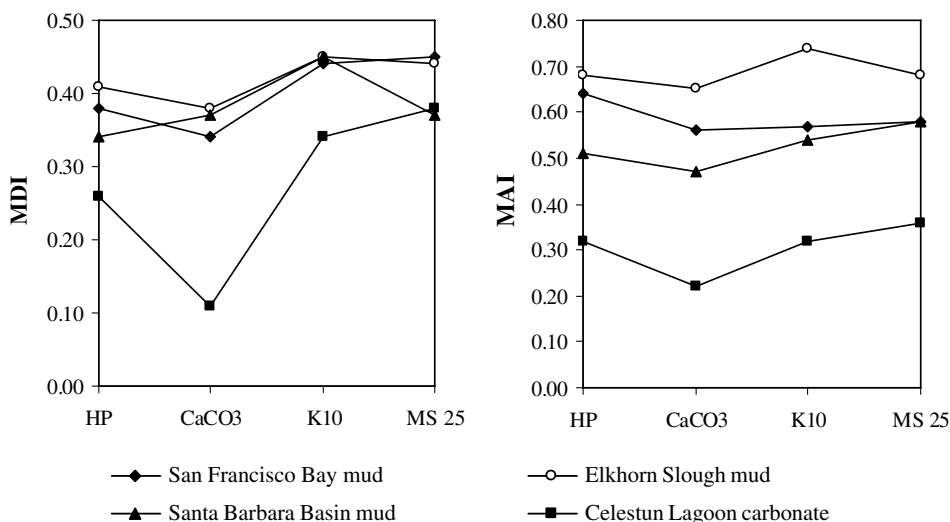


Fig. 6. Change in MDI and MAI ratios as a function of mineralogy in hydrous pyrolysis of modern sediments. For abbreviations see Fig. 4.

4–6% increase in 4,8-DMD is observed for the Celestun Lagoon carbonate sample after clay addition. Fig. 7 shows that the three clay muds can be distinguished from Celestun Lagoon carbonate using the relative abundance of 3,4-DMD, 4,8-DMD, and 4,9-DMD. This indicates that these dimethyl diamantane isomers might be related to organic matter type and/or mineralogy.

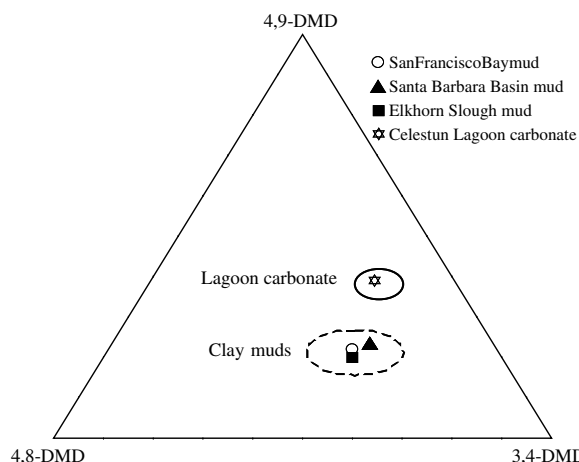


Fig. 7. Ternary plot of dimethyldiamantanes (3,4-DMD, 4,8-DMD and 4,9-DMD) from hydrous pyrolysates of modern sediments showing differentiation of mud from carbonate sediment.

### 3.6. Biomarkers from thermal maturation of modern sediments with and without minerals

Complex mixtures of organic compounds were produced during hydrous pyrolysis of modern sediments. The total concentrations of triterpanes and steranes and the individual concentrations of selected compounds obtained by MeOH:DCM extraction and hydrous pyrolysis in the absence or presence of minerals are listed in Table 5. A suite of the extended  $17\beta,21\alpha(\text{H})$ -moretanes ( $\text{C}_{31}$ – $\text{C}_{35}$ ) is detected in the pyrolysates of all sediments with and without minerals (Fig. 8; Table 5); this may be attributed to the high heating rates in laboratory simulations as well as the nature of the hopane–kerogen linkage in sediments (Seifert and Moldowan, 1980). The mass spectra of moretanes ( $\text{C}_{31}$ – $\text{C}_{33}$ ) are given in Fig. 9. The  $17\beta,21\alpha(\text{H})$  isomers all have a greater relative intensity of the D/E-ring fragment ions than that of the A/B-ring fragment ions (Ensminger et al., 1974; Van Dorselaer et al., 1974; Seifert and Moldowan, 1980; Larcher et al., 1987). The diagnostic D/E-ring fragment ions are characterized by  $m/z$  205, 219, 233, 247 and 261 for  $17\beta,21\alpha(\text{H})$ -moretanes with carbon numbers of 31, 32, 33, 34 and 35, respectively (Larcher et al., 1987). Table 5 shows that the mineral-catalyzed hydrous pyrolysates overall have elevated  $\text{C}_{29}30$ -norhopane/ $\text{C}_{30}$ -hopane ratios compared to those for sediment pyrolysis alone. The presence of minerals also improves the yields of other triterpanes, such as

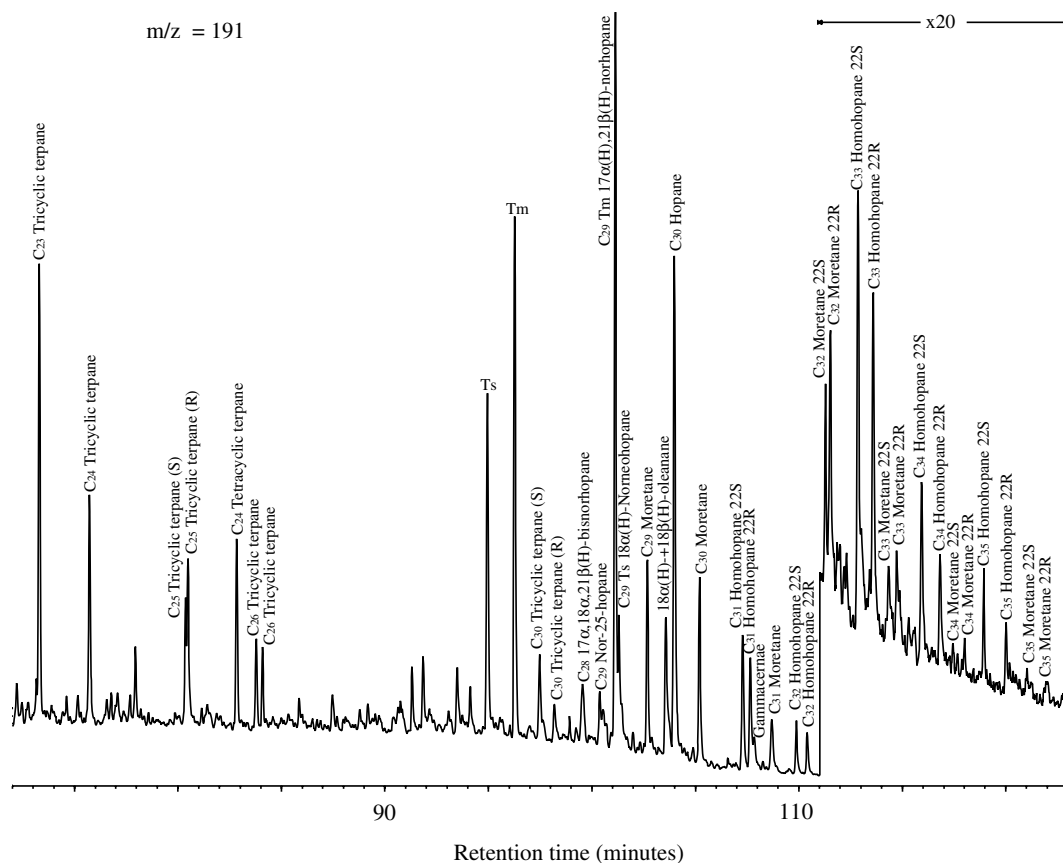


Fig. 8. Mass chromatograms of  $m/z$  191 showing presence of  $17\beta,21\alpha(\text{H})$ -moretanes ( $\text{C}_{31}$ – $\text{C}_{35}$ ) and distribution of triterpanes in hydrous pyrolysates of San Francisco Bay sediment.

tricyclic terpanes ( $\text{C}_{19}$ – $\text{C}_{30}$ ),  $18\alpha$ -trishomohopane (Ts),  $17\alpha,18\alpha,21\beta(\text{H})$ -bishomohopane,  $\text{C}_{29}$ nor-25-hopane,  $\text{C}_{30}17\alpha$ -diahopane,  $17\alpha,21\beta(\text{H})$ -homohopanes ( $\text{C}_{31}$ – $\text{C}_{35}$ ) and  $17\beta,21\alpha(\text{H})$ -moretanes ( $\text{C}_{31}$ – $\text{C}_{35}$ ) compared to hydrous pyrolysis of sediments alone, which is inconsistent with those reported by Eglinton et al. (1986). Our results also show that hopanes with  $\beta\beta$  configuration in the extracts of some sediments are absent from their pyrolysates. The reason is that the  $\beta\beta$ -hopanes in the membranes of bacteria are readily converted to  $\beta\alpha$ -moretane and  $\alpha\beta$ -hopane counterparts upon thermal stress (Seifert and Moldowan, 1980). Most importantly, the presence of either montmorillonite or MS-25 appears to give relatively higher concentrations of individual triterpanes compared to samples with  $\text{CaCO}_3$  (Table 5). The catalysis by clay minerals may accelerate the transformations of triterpanes from either functionalized biomarkers (e.g., sterols, triterpenols, etc.) in these modern sediments or the thermal degradation of kerogen.

Likewise, montmorillonite and MS-25 had pronounced catalytic effects on the generation of steranes at  $340^\circ\text{C}$ , as indicated by a significant increase in the total concentrations of steranes ( $\text{C}_{26}$ – $\text{C}_{30}$ ) in the hydrous pyrolysates in the presence of clay minerals (Table 5) in comparison with sediment pyrolysis without added clay. For sterane homologues, the concentrations of  $\text{C}_{27}$  steranes increase considerably relative to those of  $\text{C}_{28}$  and  $\text{C}_{29}$  steranes in pyrolysates compared to those in the original extracts. The increase in the quantities of  $\text{C}_{27}$  steranes may be related to relatively more abundant organic precursors of  $\text{C}_{27}$  steranes bound to the kerogen in modern sediments. Upon thermal stress,  $\text{C}_{27}$  steranes are released from the kerogen matrix. The formation of secondary  $\text{C}_{27}$  steranes by preferential cracking of the side chain of  $\text{C}_{28}$  or  $\text{C}_{29}$  steranes during hydrous pyrolysis of sediments at  $340^\circ\text{C}$  also is possible (Fowler et al., 1988; Lu et al., 1989). This effect may have been expressed with the addition of montmorillonite K10 or MS-

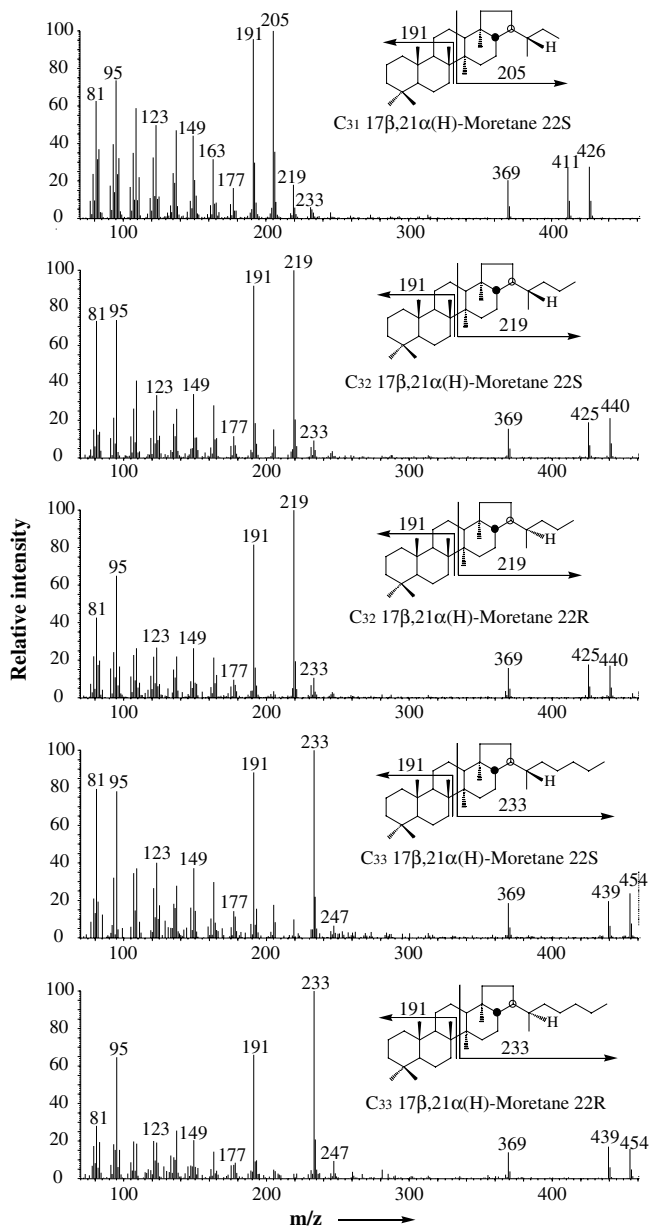


Fig. 9. Mass spectra of  $17\beta,21\alpha(\text{H})$ -moretanes ( $\text{C}_{31}$ – $\text{C}_{33}$ ). Spectra are background subtracted, recorded from GC–MS runs on B/C fractions in full-scan mode.

25 for Elkhorn Slough mud pyrolysis. Our findings are in a good agreement with the results reported by Lu et al. (1989). A similar trend is observed for dias-teranes ( $\text{C}_{27}$ – $\text{C}_{29}$ ).

### 3.7. Variations in biomarker parameters in the presence of minerals

Minerals generally exhibit a strong effect on many chemical reactions (Tannenbaum et al.,

1986; Lu et al., 1989). Of particular interest is the catalytic effect of minerals on the isomerization of terpanes and steranes. The  $\text{C}_{24}$  tetracyclic terpane ( $\text{C}_{24}17,21$ -secohopane;  $\text{C}_{24}\text{Tet}$ ) and the extended series up to  $\text{C}_{30}$  are proposed to be derived from thermal or microbial rupture of the E-ring in hopanes or precursor hopanoids (Peters et al., 2005). High abundance of the  $\text{C}_{24}$  tetracyclic terpane is thought to reflect carbonate or evaporitic depositional environments (Peters et al., 2005). This

was observed in the higher  $C_{24}$  tetracyclic/ $C_{23}$  tricyclic terpane ( $C_{24}Tet/C_{23}TT$ ) values in the extract and hydrous pyrolysates of Celestun Lagoon carbonate compared with the other muds. This ratio increases in the presence of  $CaCO_3$  for all the sediments in our experiments. In contrast,  $C_{24}Tet/C_{23}TT$  appears not to be influenced by montmorillonite or MS-25, except for the Elkhorn Slough sediment (Table 5);  $17\alpha$ -diahopane/ $18\alpha$ -30-nor-neohopane ( $C_{30}^*/C_{29}Ts$ ) behaves differently from  $C_{24}Tet/C_{23}TT$  since  $17\alpha$ -diahopane is formed by rearrangement in the D ring of bacterial hopanoid precursors through clay-mediated acid catalysis (Moldowan et al., 1991). Our results suggested that the presence of montmorillonite K10 or MS-25 might favor the formation of  $17\alpha$ -diahopane due to the access to acid sites, as supported by a slight increase in the  $C_{30}^*/C_{29}Ts$  value for the three clay-dominated sediments (Table 5);  $17\alpha$ -diahopane is not detectable in the extract and pyrolysates of the Celestun Lagoon sample, which is poor in clays. Although  $Ts/(Ts + Tm)$  is maturity dependent due to the lower relative stability of Tm than Ts, it is also controlled to some extent by lithology or oxicity of the depositional environment (Moldowan et al., 1986). Table 5 indicates that  $Ts/(Ts + Tm)$  is relatively sensitive to the presence of either montmorillonite K10 or MS-25, and decreases in the presence of  $CaCO_3$ , which demonstrates that clay minerals may catalyze Ts formation during hydrous pyrolysis of sediments.

The  $22S/(22S + 22R)$  ratios for ( $C_{31}$ – $C_{35}$ ) hopanes can provide useful information about thermal maturity (Peters et al., 2005). However, lithology may influence the rate of isomerization at C-22 in the  $17\alpha$ -homohopanes ( $C_{31}$ – $C_{35}$ ). The  $22S/(22S + 22R)$  ratio may reach equilibrium even in immature carbonates or source rocks deposited under hypersaline environments because of full isomerization (Ten Haven et al., 1986; Moldowan et al., 1992). As shown in Table 5, only very minor variations in the  $22S/(22S + 22R)$  ratio occur for the extracts and pyrolysates of all the sediments, suggesting that the effect of minerals on the  $17\alpha$ -homohopane isomerization at the chiral center is not as significant as suggested by Lu et al. (1989). However, isomerization at the ring system for hopanoids is influenced by minerals such as  $CaCO_3$ , which is illustrated by the ratios of  $C_{30}\beta\alpha$ -moretanes/ $\alpha\beta$ -hopanes and  $18\alpha/(18\alpha + 18\beta)$ -oleanane. Both ratios show a minor increase in the presence of  $CaCO_3$ , which is not seen in the pyrolysates in

the presence of either montmorillonite K10 or MS-25 (Table 5). In addition, the pyrolysates with montmorillonite K10 or MS-25 show higher ratios of  $C_{29}30$ -norhopane/ $C_{30}17\alpha$ -hopane than the pyrolysates with  $CaCO_3$ , suggesting that clay minerals have a significant catalytic effect on the degradation of hopanes, as they have with steranes (Table 5).

The total yields of steranes ( $C_{26}$ – $C_{30}$ ) in the pyrolysates of sediments mixed with montmorillonite K10 or with MS-25 are much higher than those from sediments without added clay (Table 5). However, this is not consistent with similar experiments done with kerogen by Lu et al. (1989). The discrepancy may be due to the different materials used. Clay minerals seem to play an important role in the conversion of sterols to steranes via acid catalysis. In the sediment pyrolysis experiments, montmorillonite K10 and MS-25 are not active in the epimerization of steranes as only minor variations in the ratio of  $C_{29}$  stigmastane  $\beta\beta/(\beta\beta + \alpha\alpha)$  and  $C_{29}\alpha\alpha$  stigmastane  $20S/(20S + 20R)$  are observed. Thus, the catalytic effect of these clay minerals on the isomerization of steranes is not pronounced when compared to the sediment pyrolysis alone, which suggests that sterane isomerization is not clay-mediated. Diasteranes/regular steranes ratios area routinely used source indicator for differentiation of anoxic carbonates from clastic source rocks since the conversion of sterols, sterenes and probably stanols to diasterenes and eventually diasteranes is achieved through the acidic catalysis of clay minerals during diagenesis (Rubinstein et al., 1975; Sieskind et al., 1979). In our study, for the ratios of  $C_{29}\beta\alpha$ -diastigmastane  $20S/(20S + 20R)$  and diasterane/(dia- + regular) steranes, the addition of  $CaCO_3$  impedes the progress of the conversion. In these mud sediments, there is already sufficient clay to catalyze the reactions even without the addition of montmorillonite K10.

#### 4. Conclusions

- (1) Diamondoids are largely absent from modern sediments. Trace amounts of diamondoids observed in some samples are attributed to petroleum contamination from either natural seeps or pollution.
- (2) Diamondoids are produced along with molecular markers from the thermal maturation of organic-rich sediments.

- (3) The yield of diamondoids during hydrous pyrolysis of modern sediments depends on the chemical composition of the sediments as well as the added catalyst added. Due to superacidity, clay minerals, including montmorillonite K10 and MS-25, exhibit strong catalysis in the formation of diamondoids. In contrast, CaCO<sub>3</sub> has an inhibitive effect.
- (4) Diamondoid maturity parameters, such as MAI, EAI, and MDI, which have been used to determine the thermal maturity of source rocks, are influenced by the mineralogy, particularly CaCO<sub>3</sub>, which reduces diamondoid yield relative to experiments performed with clay minerals. Three dimethyldiamantanes including 3,4-DMD, 4,8-DMD, and 4,9-DMD are demonstrated to be source related.
- (5) The presence of minerals may change the composition and distribution of both triterpanes and steranes through catalyzing the isomerization of biomarkers.
- (6) Source parameters of triterpanes are relatively more sensitive to the presence of minerals than are maturity indicators.
- (7) The stereoisomerization of steranes does not appear to be clay-mediated.

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### References

- Alexander, R., Kagi, R.I., Larcher, A.V., 1984. Clay catalysis of alkyl hydrogen exchange reactions – reaction mechanisms. *Organic Geochemistry* 6, 755–760.
- Chen, J., Fu, J., Sheng, G., Liu, D., Zhang, J., 1996. The diamondoid hydrocarbon ratios: novel maturity indices for over-mature crude oils. *Organic Geochemistry* 25, 179–190.
- Cseri, T., Bekassy, S., Figueras, F., Rizner, S., 1995. Benzoylation of aromatics on ion-exchanged clays. *Journal of Molecular Catalysis A: Chemical* 98, 101–107.
- Dahl, J.E., Moldowan, J.M., Peters, K., Claypool, G., Rooney, M., Michael, G., Mellos, M., Kohlen, M., 1999. Diamondoid hydrocarbons as indicators of oil cracking. *Nature* 399, 54–56.
- Dahl, J.E., Liu, S.G., Carlson, M.K., 2003. Isolation and structure of higher diamondoids, nanometer-sized diamond molecules. *Science* 299, 96–99.
- Eglinton, T.I., Rowland, S.J., Curtis, C.D., Douglas, A.G., 1986. Kerogen-mineral reactions at raised temperatures in the presence of water. *Organic Geochemistry* 10, 1041–1052.
- Ensminger, A., van Dorsselaer, A., Spycykerelle, C., Albrecht, P., Ourisson, G., 1974. Pentacyclic triterpanes of the hopane type as ubiquitous geochemical markers: origin and significance. In: Tissot, B., Biener, F. (Eds.), *Advances in Organic Geochemistry 1973*. Editions Technip, Paris, pp. 245–260.
- Faure, P., Landais, P., 2000. Evidence for clay minerals catalytic effects during low-temperature air oxidation of *n*-alkanes. *Fuel* 79, 1751–1756.
- Fort, R.C., 1976. Rearrangements leading to adamantanes. In: *Adamantane: The Chemistry of Diamond Molecules*. Marcel Dekker, Inc, pp. 35–66.
- Fowler, M.G., Snowden, L.R., Brooks, P.W., Hamilton, T.S., 1988. Biomarker characterization and hydrous pyrolysis of bitumens from Tertiary volcanics, Queen Charlotte Islands, British Columbia, Canada. *Organic Geochemistry* 13, 715–725.
- Goldstein, T.P., 1983. Geocatalytic reactions in the formation and maturation of petroleum. *American Association of Petroleum Geologists Bulletin* 67, 152–159.
- Grantham, P.J., Posthuma, J., Baak, A., 1983. Triterpanes in a number of Far-Eastern crude oils. In: Bjoroy, M. et al. (Eds.), *Advances in Organic Geochemistry 1981*. John Wiley and Sons, New York, pp. 675–683.
- Grice, K., Alexander, R., Kagi, R.I., 2000. Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. *Organic Geochemistry* 31, 67–73.
- Johns, W., 1979. Clay mineral catalysis and petroleum generation. *Annual Reviews Earth and Planetary Sciences* 7, 183–198.
- Landa, S., 1959. Adamantane and its derivatives. *Ropa a Uhlie* 1, 5–7.
- Landa, S., Machacek, V., 1933. Adamantane, a new hydrocarbon extracted from petroleum. *Collection Czechoslov. Chemical Communications* 5, 1–5.
- Larcher, A.V., Alexander, R., Kagi, R.I., 1987. Changes in configuration of extended moretanes with increasing sediment maturity. *Organic Geochemistry* 11, 59–63.
- Lewan, M.D., 1993. Laboratory simulation of petroleum formation-hydrous pyrolysis. In: Engel, M., Macko, S. (Eds.), *Organic Geochemistry-Principles and Applications*. Plenum Press, New York, pp. 419–442.

- Lewan, M.D., 1994. Assessing natural oil expulsion from source rocks by laboratory pyrolysis. In: Magoon, L.B., Dow, W.G. (Eds.), *The Petroleum System – from Source to Trap*. American Association of Petroleum Geologists Memoir 60, pp. 201–210.
- Li, S., Guo, S., Tan, X., 1998. Characteristics and kinetics of catalytic degradation of immature kerogen in the presence of mineral and salt. *Organic Geochemistry* 29, 1431–1439.
- Li, Ji., Philp, P., Cui, M., 2000. Methyl diamantane index (MDI) as a maturity parameter for Lower Palaeozoic carbonate rocks at high maturity and overmaturity. *Organic Geochemistry* 31, 267–272.
- Lu, S., Ruth, E., Kaplan, I.R., 1989. Pyrolysis of kerogen in the absence and presence of montmorillonite-I. The generation, degradation and isomerization of steranes and triterpanes at 200 and 300 °C. *Organic Geochemistry* 14, 491–499.
- McKervey, M.A., 1980. Synthetic approaches to large diamondoid hydrocarbons. *Tetrahedron* 36, 971–992.
- Moldowan, J.M., Sundararaman, P., Schoell, M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of S.W. Germany. *Organic Geochemistry* 10, 915–926.
- Moldowan, J.M., Fago, F.J., Carlson, R.M.K., Young, D.C., Duvne, G., Clardy, J., Schoell, M., Pillinger, C.T., Watt, D.S., 1991. Rearranged hopanes in sediments and petroleum. *Geochimica et Cosmochimica Acta* 55, 3333–3353.
- Moldowan, J.M., Sundararaman, P., Salvatori, T., Alajbeg, A., Gjukic, B., Lee, C.Y., Demaison, G.J., 1992. Source correlation and maturity assessment of select oils and rocks from the Central Adriatic Basin (Italy and Yugoslavia). In: Moldowan, J.M., Albrecht, P., Philp, R.P. (Eds.), *Biological Markers in Sediments and Petroleum*. Prentice Hall, Englewood Cliffs, NJ, pp. 370–401.
- Moldowan, J.M., Dahl, J., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., Taylor, D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. *Science* 265, 768–771.
- Moldowan, J.M., Chen, Z., Wei, Z., Fago, F., Dahl, J., Schouten, S., Sinnighe Damsté, J.S., Carrigan, W.J., Jenden, P., Abu-Ali, M.A., 2004. High resolution geochemical technologies (HRGTs) applied to understanding petroleum systems in Saudi Arabia. In: *The 6th International Conference on Petroleum Geochemistry and Exploration in the Afro-Asian Region*, October 12–14, 2004, Beijing, China, abstract book, pp. 108–109.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide Biomarkers and Isotopes in Petroleum Exploration and Earth History*, vol. 2. The University Press, Cambridge, pp. 559–560.
- Petrov, A., Arefjev, D.A., Yakubson, Z.V., 1974. Hydrocarbons of adamantane series as indices of petroleum catagenesis process. In: Tissot, B., Biener, F. (Eds.), *Advances in Organic Geochemistry*. 1973. Editions Technip, Paris, pp. 517–522.
- Rooney, M.A., 1995. Carbon isotopic data of light hydrocarbons as indicators of thermochemical sulfate reduction. In: Grimalt, G.O., Dorronsoro, C. (Eds.), *17th International Meeting on Organic Geochemistry*. AIGOA, San Sebastian, pp. 523–525.
- Rowland, S.J., Yon, D.A., Lewis, C.A., Maxwell, J.R., 1985. Occurrence of 2,6,10-trimethyl-7-(3-methylbutyl)dodecane and related hydrocarbons in the green alga *Enteromorpha prolifera* and sediments. *Organic Geochemistry* 8, 207–213.
- Rubinstein, I., Sieskind, O., Albrecht, P., 1975. Rearranged steranes in a shale: occurrence and stimulated formation. *Journal of the Chemical Society Perkin Transactions I*, 1833–1836.
- Schleyer, P.v.R., 1990. My thirty years in hydrocarbon cages: from adamantane to dodecahedrane. In: Olah, G.A. (Ed.), *Cage Hydrocarbons*. John Wiley & Sons, Inc., pp. 1–38.
- Schleyer, P.v.R., Grubmuller, P., Maier, W.F., Vostrowsky, O., Skattebol, L., Holm, K.H., 1980. An adamantane rearrangement. A new pathway. *Tetrahedron Letters* 21, 921–924.
- Schneider, A., Warren, R.W., Janoski, E.J., 1966. Formation of perhydrophenalenes and polyalkyladamantanes by isomerization of tricyclic perhydroaromatics. *Journal of Organic Chemistry* 31, 1617–1625.
- Schulz, L.K., Wilhelms, A., Rein, E., Steen, A.S., 2001. Application of diamondoids to distinguish source rock facies. *Organic Geochemistry* 32, 365–375.
- Seifert, W.K., Moldowan, J.M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *Physics and Chemistry of the Earth* 12, 229–237.
- Sieskind, O., Joly, G., Albrecht, P., 1979. Simulation of the geochemical transformations of sterols: superacid effect of clay minerals. *Geochimica et Cosmochimica Acta* 43, 1675–1679.
- Tannenbaum, E., Ruth, E., Kaplan, I.R., 1986. Steranes and triterpanes generated from kerogen pyrolysis in the absence and presence of minerals. *Geochimica et Cosmochimica Acta* 50, 805–812.
- Taulbee, D.N., Seibert, E.D., 1987. Comparison of the hydrocarbon pyrolysis products from a Devonian type II kerogen to those from kerogen/mineral blends. *Energy and Fuels* 1, 514–519.
- Ten Haven, H.L., Rullkötter, J., 1988. The diagenetic fate of taxaer-14-ene and oleanene isomers. *Geochimica et Cosmochimica Acta* 50, 853–855.
- Ten Haven, H.L., de Leeuw, J.W., Peakman, T.M., Maxwell, J.R., 1986. Anomalies in steroid and hopanoid maturity indices. *Geochimica et Cosmochimica Acta* 50, 853–855.
- Van Dorsselaer, A., Ensminger, A., Spycykerelle, C., Dastillung, M., Brooks, P.W., Gaskell, S.J., Philp, R.P., Maxwell, J.R., Eglinton, G., 1974. Degraded and extended hopane derivatives (C<sub>27</sub>–C<sub>35</sub>) as ubiquitous geochemical markers. *Tetrahedron Letters* 14, 1349–1352.
- Wei, Z., Moldowan, J.M., Dahl, J., 2005a. Formation of diamondoids from hydrous pyrolysis and their potential in modeling oil and gas generation. *Stanford Molecular Organic Geochemistry Industrial Affiliates Internal Report*.
- Wei, Z., Moldowan, J.M., Dahl, J., 2005b. The catalytic effects of minerals on the formation of diamondoids during kerogen pyrolysis. In: *22nd International Meeting of Organic Geochemistry (IMOG) Seville, Spain*, abstracts book part 1, pp. 260–261.
- Whitehead, E.V., 1973. Molecular evidence for the biogenesis of petroleum and natural gas. In: Ingerson, E. (Ed.), *Proceedings of Symposium on Hydrogeochemistry and Biogeochemistry*, vol. II. The Clarke, Co., pp. 158–211.
- Whitehead, E.V., 1974. The structure of petroleum pentacyclanes. In: Tissot, B., Biener, F. (Eds.), *Advances in*



- Organic Geochemistry 1973. Editions Technip, Paris, pp. 225–243.
- Williams, J.A., Bjorøy, M., Dolcater, D.L., Winters, J.C., 1986. Biodegradation in South Texas Eocene oils-effects on aromatics and biomarkers. *Organic Geochemistry* 10, 451–461.
- Wingert, W.S., 1992. GC–MS analysis of diamondoid hydrocarbons in Smackover petroleum. *Fuel* 71, 37–43.
- Zumberge, J.E., 1987. Prediction of source rock characteristics based on terpane biomarkers in crude oils: a multivariate statistical approach. *Geochimica et Cosmochimica Acta* 51, 1625–1637.