



The catalytic effects of minerals on the formation of diamondoids from kerogen macromolecules

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Received 17 April 2006; received in revised form 27 June 2006; accepted 12 July 2006

Abstract

To investigate the catalytic effects of minerals on the formation of diamondoids, a series of anhydrous and hydrous pyrolysis experiments were conducted at 340 °C for 72 h on six kerogens of four types (I, II, II-S, and III) in the presence and absence of different minerals (montmorillonite K10, acidic aluminosilicate, kaolinite, illite, CaCO₃, CaSO₄, and S⁰) and their mixtures in different ratios. Regardless of the accessibility of water, direct decomposition of kerogen upon thermal stress produces various quantities of diamondoids depending on the type of kerogen. Montmorillonite K10 and acidic aluminosilicate greatly promote the formation of diamondoids at 340 °C during kerogen pyrolysis because they are strong Lewis acids. Rearrangements of polycyclic carbonium ion intermediates at Lewis super-acid sites probably are responsible for the observed relatively large quantities of diamondoids produced at elevated temperatures in the presence of montmorillonite K10 or acidic aluminosilicate. In contrast, CaCO₃ appears to inhibit the formation of diamondoids. Kaolinite is a less active catalyst because the yield of diamondoids is only slightly elevated, while no catalytic effect is observed from illite. The presence of elemental sulfur appears to “poison” the catalytic activity of montmorillonite K10, but it is counteracted to some extent by the presence of CaCO₃. The yield of diamondoids was slightly improved in the anhydrite catalytic reaction with kerogen in the presence of water. The addition of elemental sulfur to the kerogen of any type may initiate the C–C bond cleavage and is not favorable for diamondoid formation. The yield of diamondoids is very sensitive to the amount of montmorillonite K10 mixed with the kerogen up to a montmorillonite K10/kerogen ratio of ca. 15:1. At higher montmorillonite K10/kerogen ratios (≥15:1), the accessible Lewis sites at montmorillonite K10 might be completely saturated with the organic precursors of diamondoids from thermal degradation of kerogen.

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1. Introduction

The carbon structures of diamondoid hydrocarbons can be viewed as tiny chunks of a diamond crystal lattice. These compounds exist in virtually all petroleum (Landa and Machacek, 1933; Landa,

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1959; Landa et al., 1961; Petrov et al., 1974; Dahl et al., 1999), most of which is formed mainly from the thermal degradation of kerogen disseminated in finely-grained sedimentary rocks (Tissot and Welte, 1984). It is accepted that a variety of chemical reactions occur during the maturation of kerogen, e.g., defunctionalization, rearrangement, disproportionation, C–C bond cleavage, condensation, oxidation, and reduction, which can be catalyzed by minerals in sediments due to intimate contact with kerogen macromolecules during diagenesis and catagenesis.

Much effort has been made to investigate the role of minerals in the thermal alteration of organic matter, kerogen and model compounds (e.g., Johns, 1979; Goldstein, 1983; Eglinton et al., 1986; Heller-Kallai et al., 1996; Raimondo et al., 1998; Höld et al., 1998; Hart and Brown, 2004). It has been suggested that clay minerals can adsorb organic compounds on their surface and then catalyze organic reactions (e.g., Eltantawy and Arnold, 1973; Johns, 1979; Johns and McKallip, 1989; Espitalié et al., 1984; Collins et al., 1995; Kennedy et al., 2002; Seewald, 2003). An example of this is alkyl hydrogen exchange reactions catalyzed by acidic clays (Alexander et al., 1984). Clay minerals, particularly montmorillonite, have high surface areas, exposed cations on their surface, and the ability to complex with polar compounds (Fripiat and Cruz-Cumplido, 1974; Johns, 1979; Johns and Ulkus, 1993; Rhodes and Brown, 1994). More importantly, they contain two types of catalytic sites: Brønsted and Lewis acid sites (Solomon et al., 1971; Massam and Brown, 1995; Rhodes and Brown, 1997), where organic reactions are catalyzed. Brown and Rhodes (1997) demonstrated that the strength of Brønsted acidity was largely dependent on the degree of hydration of the clay. In contrast, the Lewis acidity is controlled by the dehydration of clay as well as the presence of exchangeable cations. Therefore, at higher temperature, the loss of water in the interlayer of clay leads to a decrease in Brønsted acidity, but an increase in Lewis acidity (Cseri et al., 1995). Fort and Schleyer (1964) reported that a number of organic compounds (e.g., cholesterol, cyclohexane, and cedrene) produced diamondoids, i.e., alkyladamantanes, when treated with Lewis acids. Thus, it is probable that the presence of Lewis acid sites in clay minerals may favor the formation of diamondoids in organic-rich sediments. Other minerals in sedimentary rocks may include CaCO₃, pyrite, CaSO₄, and quartz. These minerals can change the chemical

composition and yield of oil generated from hydrous pyrolysis of either kerogens or sedimentary rocks (Tannenbaum et al., 1986; Lao et al., 1989; Siskin and Katritzky, 2001). However, the catalytic activity of these minerals is shown to be rather weak compared to acidic clays (Horsfield and Douglas, 1980; Davis and Stanley, 1982; Taulbee and Seibert, 1987; Lao et al., 1989). In addition, the presence of water attenuates their catalytic activity. Although sulfur is thought to play an important role in petroleum formation (Lewan, 1998), the details of the interactions between sulfur and these minerals are not clear. In some cases, sulfur might complicate the catalytic activity of other minerals because of many sulfur-related organic reactions.

In general, diamondoids occur as complex mixtures of compact and caged polycycloalkane molecules. Their lower members such as adamantanes and diamantanes have been successfully synthesized via carbonium ion rearrangements under laboratory conditions by treating a wide variety of organic molecules with super-acid catalysts (e.g., Schneider et al., 1966; Williams et al., 1966; Schleyer et al., 1980; Olah et al., 1989; Sorensen and Whitworth, 1990; Ganter, 1992). However, how these compounds come to be present in petroleum remains uncertain. Also, there is no convincing proof for the formation of diamondoids via acid-catalyzed rearrangement mechanisms either from kerogen or in petroleum.

In the present study, a series of pyrolysis experiments were performed on kerogen macromolecules with and without different minerals and water to understand the role of naturally occurring minerals in the synthesis of diamondoids in petroleum. Here, we report the catalytic activity of different minerals during kerogen pyrolysis, the possible formation mechanisms of diamondoids, the generation of diamondoids from kerogens, the effect of montmorillonite K10/kerogen ratios on the yield of diamondoids, and the interaction of minerals with respect to catalysis.

2. Materials and methods

2.1. Samples

The rock and coal samples used for hydrous pyrolysis and kerogen isolation are characterized in Tables 1 and 2. Samples #24 and #27 are organic-rich limestone (TOC = 2.4 wt%) and oil shale (TOC = 6.96 wt%), respectively, which were

Table 1
Rock-Eval pyrolysis data for selected rock and coal samples

Sample number	Lithology	Location	Formation	Age	R ₀ (%)	TOC (wt%)	T _{max} (°C)	S ₁ ^a	S ₂ ^a	S ₃ ^b	S ₁ + S ₂ ^a	HI ^a	OI ^b	Type of kerogen
#24	Limestone	Southern Brazil	Irati	Permian	0.43	2.40	430	4.70	17.78	0.43	22.48	741	18	I
#27	Shale	Southern Brazil	Irati	Permian	0.45	6.96	422	6.30	33.37	0.77	39.67	479	11	I
Antelope	Shale	San Joaquin Basin, CA	Monterey	Miocene	0.44	2.01	422	0.40	8.8	0.60	9.20	438	31	II
Monterey	Siliceous shale	Naples Beach, CA	Monterey	Miocene	0.20	3.82	409	0.72	16.42	1.57	17.14	430	41	II-S
ML91-17	Shale	Naples Beach, CA	Monterey	Miocene	0.13	16.45	405	5.20	67.82	5.41	73.02	412	33	II-S
Raton	Coal	Raton Basin, New Mexico	Raton	Late Cretaceous	0.90	15.06 ^c	448	0.57	25.39	6.12	25.96	169	41	III

^a Unit: mg HC/g TOC.

^b Unit: mg CO₂/g TOC.

^c TOC value for the solvent-extracted Raton coal.

Table 2
Elemental analysis results of isolated kerogens (normalized ash-free)

Sample number	Atomic H/C	Atomic O/C	Atomic N/C	Atomic S _{org} /C	Type of kerogen
Antelope	1.339	0.207	0.045	0.018	II
Monterey	1.585	0.357	0.037	0.064	II-S
ML91-17	1.338	0.185	0.040	0.058	II-S

taken from the Irati Formation, southern Brazil. Data from Rock-Eval pyrolysis suggest that both rocks contain immature oil-prone type I kerogen with low T_{max} (<435 °C) and high hydrogen index (HI) values. The Antelope shale, which contains type II kerogen, was obtained from the Miocene Monterey Formation, San Joaquin Basin, CA, USA. It is an immature shale, as indicated by low T_{max} = 422 °C and %R₀ = 0.44%. Sample ML91-17 was an immature shale (T_{max} = 409 °C, %R₀ = 0.12%) collected from the Carbonaceous Member of the Monterey Formation, Naples Beach, CA, USA. A siliceous shale was sampled from the Monterey Formation at Naples Beach, CA, USA. Based on the criteria established by Orr (1986), both Monterey shales are rich in type II-S kerogen (S_{org}/C = 0.064, 0.058, respectively) defined as S_{org}/C > 0.04. The Rock-Eval pyrolysis and %R₀ data indicate that the Monterey siliceous shale is also immature. In addition, a gas-prone mature coal was selected from the Raton Formation at the depth of 3 cm below the Cretaceous-Tertiary boundary in the Raton Basin, New Mexico, USA. It is characterized by a low HI value of 169 mg HC/g TOC.

2.2. Mineral catalysts

Montmorillonite K10 and CaCO₃ (>99.99% pure) were obtained from Aldrich Chemical Company. The chemical composition of montmorillonite K10 clay is: SiO₂ (43.77%), Al₂O₃ (18.57%), CaO (1.02%), Na₂O (1.03%), and H₂O (35.61%), its cation exchange capacity (CEC) is about 80–120 meq/100 g, and it has a surface area of 220–270 m²/g. The KGa-2 kaolinite clay (Cretaceous Tuscaloosa Formation, County of Washington, Georgia) and IMT-1 illite clay (Cambrian shale, Silver Hill, Montana) were ordered from The Source Clays Repository at Purdue University, Indiana. The chemical composition of kaolinite is: SiO₂ (44.2%), Al₂O₃ (39.7%), TiO₂ (1.39%), Fe₂O₃ (0.13%), FeO (0.08%), MnO (0.002%), MgO (0.03%), Na₂O (0.013%), K₂O (0.05%), F (0.013%), and P₂O₅

(0.034%). The CEC and surface area of kaolinite are 3.3 meq/100 g and $23.5 \pm 0.06 \text{ m}^2/\text{g}$, respectively. The chemical composition of illite is: SiO_2 (49.3%), Al_2O_3 (24.25%), TiO_2 (0.55%), Fe_2O_3 (7.32%), FeO (0.55%), MnO (0.03%), MgO (2.56%), CaO (0.43%), Na_2O (0), K_2O (7.83%), and P_2O_5 (0.08%). O'Loughlin et al. (2000) reported that the CEC value of the IMt-1 illite clay is 17.0 meq/100 g. Its surface area is $11 \text{ m}^2/\text{g}$. Acidic aluminosilicate ($\text{Al}_2\text{O}_3 = 23.2\%$, $\text{SiO}_2 = 76.4\%$, and nominal amounts of Na_2O and SO_4 , etc.) was provided by Dr. Larry McDorman at Grace Davison in Columbia, Maryland. It is also identified as "MS-25" with a surface area of $408 \text{ m}^2/\text{g}$. Anhydrous calcium sulfate (CaSO_4 , >99% pure) and sublimed sulfur powder were purchased from J.T. Baker Inc.

2.3. Kerogen isolation

Organic-rich rock and coal samples were finely ground, and then ultrasonically extracted for 3 h with methanol (MeOH)/dichloromethane (DCM) (1:1 v:v). The dried and solvent-extracted samples were demineralized in a steam bath (60 °C) after treatment with HCl (aq) (1 g:8 ml; 37%), stirring for 2 h to completely remove mineral carbonates. The suspensions were filtered and the residue washed with hot distilled water (55 °C) until pH neutral. The residues were subsequently treated for 3 h twice with an HF/HCl acidic mixture (1:1 v:v, 1 g:8 ml) for the removal of silicates. During the HF/HCl digestion, to remove complex fluorides formed, concentrated HCl (aq) treatment was subsequently used, followed by rinsing with distilled water until pH neutral. The scanning electron microscopy (SEM) analysis of these kerogen concentrates indicates that most inorganic materials were eliminated as a result of the HF/HCl acid treatment. The kerogen concentrates were re-extracted with MeOH/DCM (1:1 v:v) for 3 h to remove traces of free hydrocarbons bound to the kerogen matrix. The extracted kerogens were finally dried at 60 °C and 18 kPa.

2.4. Bulk measurements

Basic data on the solvent-extracted rocks and coal were obtained from Rock-Eval pyrolysis. It was completed using a Rock-Eval II Plus TOC instrument by progressively heating from 300 to 600 °C at the rate of 25 °C/min (all temperatures are nominal) under an inert atmosphere (helium).

Their maturity was determined by vitrinite reflectance measurements on kerogens isolated from these samples (Table 1). The atomic $\text{S}_{\text{org}}/\text{C}$ ratios of the Monterey and Antelope kerogens were determined by elemental analysis.

2.5. Catalytic pyrolysis of kerogens

A series of catalytic pyrolysis experiments of kerogens were conducted on six kerogens (Table 1) of four different types (type I, II, II-S, and III). Some experiments were repeated for data reproducibility. Typically, 500 mg of kerogen were used in each experiment, except for those involving type III kerogen, where 1 g was used to obtain sufficient liquid hydrocarbons for accurate quantification of targeted organic compounds. For anhydrous pyrolysis, the kerogen samples were loaded into T316 stainless steel vessels, which were then purged with argon for 1 min before sealing. These vessels were heated in a GC oven at 340 °C for 72 h. For hydrous pyrolysis experiments, a fixed quantity of distilled water was added to the reaction vessels containing kerogen only (kerogen/water = 1:20) or kerogen well mixed with various mineral catalysts, including montmorillonite K10, MS-25, kaolinite, illite, CaCO_3 , CaSO_4 , and S^0 (kerogen/mineral/water = 1:20:20), and various mixtures of these minerals. The reaction vessels were then heated at 340 °C for 72 h in a GC oven. Hydrous pyrolysis was also conducted on a montmorillonite K10:kerogen mixture using different ratios (2:1, 5:1, 10:1, 15:1, and 20:1) in the presence of water at 340 °C.

The expelled pyrolysates include generated oil accumulated on the water surface, and free oil sticking to the pyrolyzed kerogens and minerals and inner sides of the reactors. Therefore, after the high-pressure steel reactors cooled down, they were opened and the pyrolysates were obtained by washing the heated kerogen/mineral mix and vessels with 1:1 MeOH/DCM. The water-borne pyrolysates were poured into a 125-ml separatory funnel. After 10 ml of pentane/DCM (2:1 v:v) were added, the mixture was shaken vigorously for 1 min. The funnel was then allowed to stand in a rack for 10 min. The pentane/DCM organic layer was transferred to a 32-ml vial. The aqueous layer was then extracted three times with pentane/DCM (2:1 v:v), and the extracts were combined and stored. Activated copper was used for desulfurization of the pyrolysates obtained from sulfur and CaSO_4 catalytic experiments. In order to remove the residual

water, the pyrolysates were treated with anhydrous sodium sulfate (5 g). The solvents were evaporated with nitrogen flow, and the pyrolysates were weighed.

2.6. Gas chromatography

The kerogen pyrolysates were diluted with toluene by 100 times and analyzed using a Hewlett Packard 5890 Gas Chromatograph, equipped with an on-line injector. A methyl silicone DB-1 capillary column (24 m × 0.2 mm i.d.) was used with hydrogen as the carrier gas at 20 psi head pressure. The samples were injected at 80 °C and the oven was subsequently programmed at 10 °C min⁻¹ to 320 °C where it was held for 15 min.

2.7. Gas chromatography-mass spectrometry (GC-MS)

About 30 mg of each kerogen pyrolysate were weighed and spiked with deuterated diamondoid standards for quantitation of any generated diamondoid compounds. These synthetic internal standards (I.S.) included D₃-1-methyladamantane, D₄-adamantane, D₅-diamantane, D₃-1-methyldiamantane, D₅-2-ethyldiamantane, and D₄-triamantane. The saturate fraction was separated using flash column chromatography through Pasteur pipettes filled with silica gel (Baker 40 μm silica gel, activated at 250 °C overnight). The saturates were analyzed directly by GC-MS using a Micromass Autospec-Q run in selective ion recording (SIR) mode for ions *m/z* 135, 136, 140, 149, 187, 188, 191, 192, 201, 217, 239, 240, 244, and 292. The GC was an HP 5890 Series II equipped with an HP-1 MS 60 m column with 0.25 mm i.d. and 0.25 μm phase thickness. Hydrogen carrier gas was used at a constant pressure of 15 psi. The temperature program was 50 °C for 1 min, 50–320 °C at 3 °C min⁻¹ and 320 °C for 20 min.

The parent diamondoids including adamantane, diamantane, and triamantane were analyzed using the molecular ions *m/z* 136, 188, and 240, respectively. They were quantified against the isotopically labeled diamondoid I.S., D₄-adamantane, D₅-diamantane, and D₄-triamantane, which were measured at their respective *m/z* molecular ions, 140, 192, 244, respectively. Similarly, the 1-, 3-, and 4-methyldiamantanes were analyzed quantitatively at the same time, using D₃-1-methyldiamantane as the I.S. These compounds were all measured at *m/z* 187. Other alkylated adamantanes, diaman-

tan, and triamantanes were all measured by the same method above using the appropriate isotopically labeled I.S., which have the most similar volatility and chemical characteristics.

3. Results and discussion

3.1. Diamondoid generation from pyrolysis of kerogen

Thermally immature kerogens are metastable macromolecules (Tissot and Welte, 1984), and they release a variety of petroleum-like hydrocarbons from their structures upon heating (Larter and Horsfield, 1993; Grasset and Amblés, 1998; Wei et al., 2005). This can be best simulated by hydrous and anhydrous pyrolysis during which temperature is considered to be of crucial importance (Lewan, 1994). Thus, the kerogen concentrates were heated in the presence and absence of water at 340 °C for 72 h, which is approximately equivalent to the peak of oil generation. The SEM analysis showed that the inorganic materials are dominated by pyrite in most of the isolated kerogens and a trace quantity of titanium oxide (<1%) is also present. A few hydrous pyrolysis experiments were performed on the pyrite and kerogen mix. However, the yield of diamondoids was similar to that from kerogen hydrous pyrolysis alone. This suggests that pyrite is inactive in the formation of diamondoids. For the purposes of this study we assume that titanium oxide has no catalytic effect on kerogen maturation.

A typical mass chromatogram of methyl- and ethyl-diamantanes, monitored by the fragment ion *m/z* 187, is shown in Fig. 1. Fig. 2a shows that the pyrolysis of kerogens of various types produces diamondoids with or without the presence of water. The interaction of the kerogen with possible mineral catalysts in the rock matrix may aid the formation of diamondoid groups or moieties in the kerogen network via the rearrangements of organic molecules. Wei et al. (2006) suggested that numerous organic compounds and even those containing functionalized groups (e.g., stearic acid, abietic acid, phytol, stigmastanol, and cholesterol) could rearrange into diamondoids in the presence of suitable catalysts such as aluminum chloride and montmorillonite through carbonium ion mechanisms. The Lewis acid-catalyzed rearrangements of potential precursors to polyadamantanes have also been discussed elsewhere (e.g., Fort and Schleyer, 1964; Schneider et al., 1966; Petrov et al., 1974).

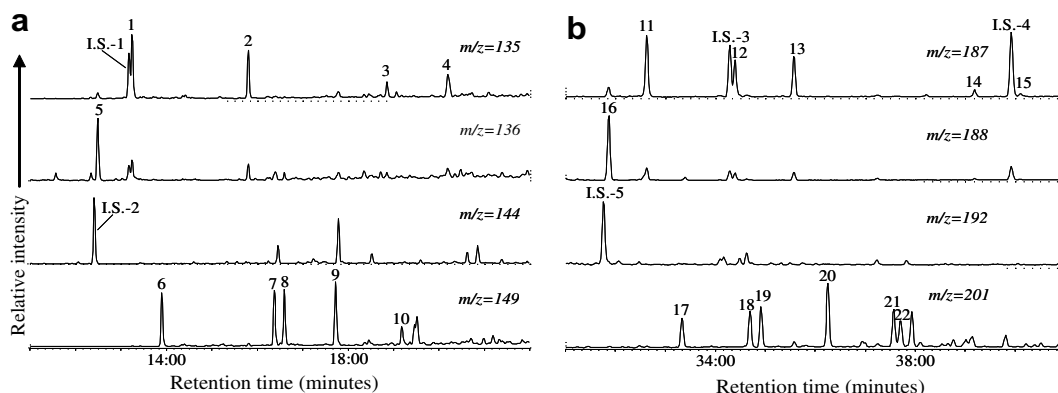


Fig. 1. Representative mass chromatograms of adamantanes (m/z 135, 136, 144, and 149) and diamantanes (m/z 187, 188, 192, and 201) generated from the catalytic pyrolysis of kerogens. 1: 1-methyladamantane; 2: 2-methyladamantane; 3: 1-ethyladamantane; 4: 2-ethyladamantane; 5: adamantane; 6: 1,3-dimethyladamantane; 7: 1,4-dimethyladamantane (*cis*); 8: 1,4-dimethyladamantane (*trans*); 9: 1,2-dimethyladamantane; 10: 2,6- + 2,4-dimethyladamantane; 11: 4-methyldiamantane; 12: 1-methyldiamantane; 13: 3-methyldiamantane; 14: 1-ethyldiamantane; 15: 2-ethyldiamantane; 16: diamantane; 17: 4,9-dimethyldiamantane; 18: 1,2- + 2,4-dimethyldiamantane; 19: 4,8-dimethyldiamantane; 20: 3,4-dimethyldiamantane; 21: dimethyldiamantane (1); 22: dimethyldiamantane (2); I.S.-1: D₃ 1-methyladamantane; I.S.-2: D₄ adamantane; I.S.-3: D₃ 1-methyldiamantane; I.S.-4: D₅ 2-ethyldiamantane; I.S.-5: D₄ diamantane.

Therefore, it is possible that the diamondoid precursor molecules or moieties might be incorporated into kerogen macromolecules during early diagenesis. Khaddor et al. (2002) reported that stanols including 5 α (H)-cholestanol and 24-ethyl-5 α (H)-cholestanol, chemically bound to the kerogen matrix with ether or ester groups, generated sterene/sterane doublets upon pyrolysis. It has also been suggested that biomarker lipids can be released from the kerogen due to the cleavage of weak carbon–heteroatom bonds, e.g., sulfide (C–S), ester, and ether, at lower temperatures (Putschew et al., 1998). Likewise, these diamondoid units might also be bound to the kerogen skeleton via polysulfide, ether, and/or ester groups similar to biomarkers and other compounds (Fig. 3). The weaker carbon–heteroatom bonds (C–S and C–O) are preferentially cleaved during the thermal evolution of kerogen. Consequently, diamondoids are released from the kerogen along with other hydrocarbons, e.g., *n*-alkanes, biomarkers, and organic sulfur compounds by thermal stress.

Under the same reaction conditions, the yield of diamondoids formed from kerogen pyrolysis seems to depend on the nature of the kerogen. It is noteworthy that the gas-prone type III kerogen produces the highest yield of diamondoids during pyrolysis (Fig. 2a). One possible explanation is that the C–C bond cleavage (cracking) of the generated hydrocarbons occurs at 340 °C since it is a mature kerogen indicated by $R_0 = 0.90\%$. Diamondoids of high sta-

bility may survive the hydrocarbon cracking process and be enriched to a degree determined by the heating temperature in the Raton kerogen pyrolysates. Type II kerogen is characterized by high abundance of heteroatomic bonds such as ester, ether and polysulfide bonds, as well as cyclic compounds (Tissot and Welte, 1984). According to the schemes shown in Fig. 3, these weak bonds, if present, would undoubtedly favor the release of diamondoid-like molecules from the Antelope kerogen skeleton upon increasing thermal stress. This is confirmed by the fact that relatively high concentrations of diamondoids, up to 4.3 ppm, were detected in the Antelope kerogen pyrolysates (Table 3). In contrast, the concentrations of diamondoids in the pyrolysates of #24 and #27 type I kerogens are relatively low but very similar because the number of heteroatomic cross-linkages is less (Fig. 2a). Only very low quantities of diamondoids were produced from the two Monterey type II-S kerogens (Fig. 2a). The formation of diamondoids might be complicated by the presence of sulfur species derived from the decomposition of sulfur-rich type II-S kerogen. Free radical reactions triggered by sulfur species might be unfavorable for the formation of diamondoids.

Also, note that anhydrous pyrolysis of kerogen gives larger yields of diamondoids compared with hydrous pyrolysis of kerogen (Fig. 2a). Lewan (1997) suggested that at 330–350 °C the presence of liquid water in the pyrolysis system significantly reduces the rate of thermal decomposition of pro-

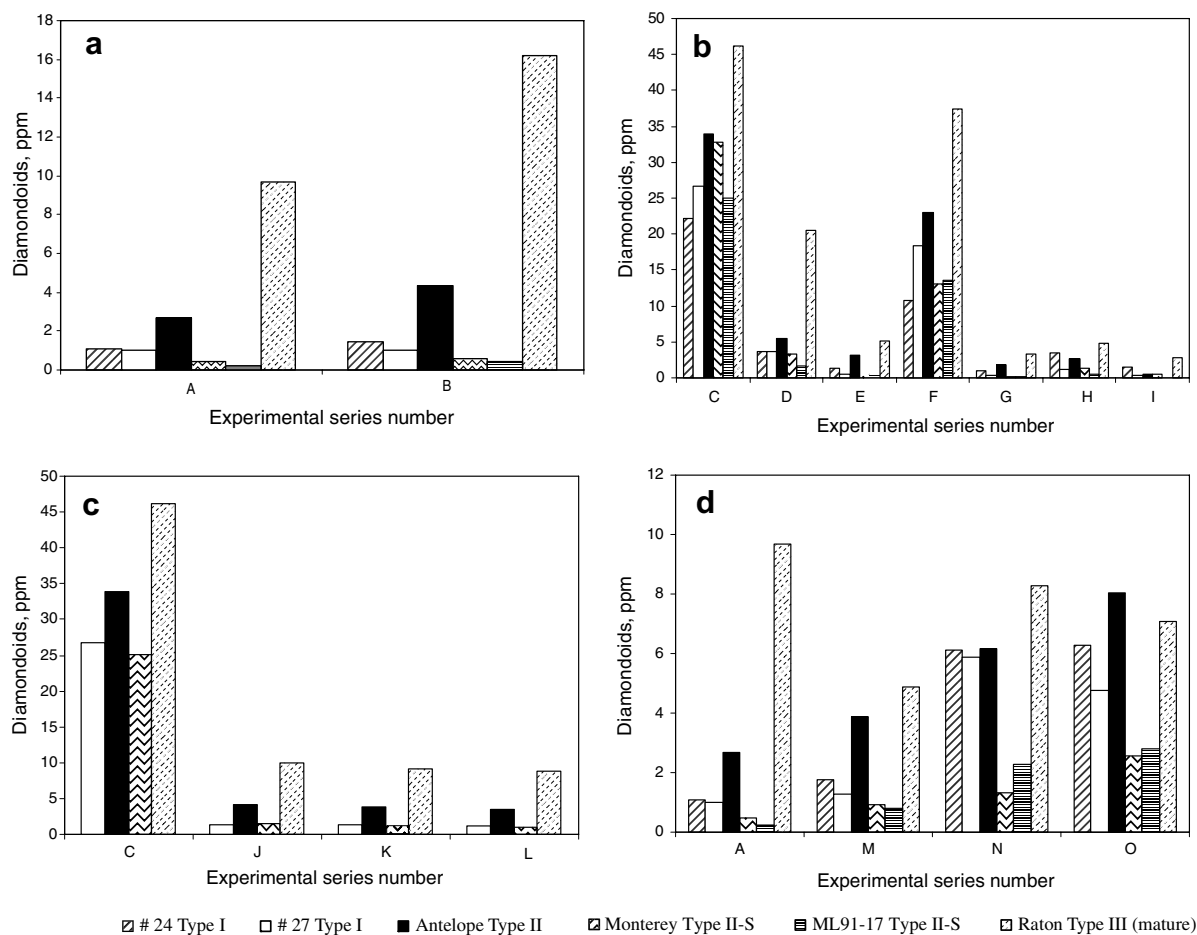


Fig. 2. The concentrations of diamondoids in the pyrolysates from different pyrolysis experiments in the presence and absence of various minerals and their mixtures. For hydrous pyrolysis experiments, a kerogen/water ratio of 1:20 was used. (a) The concentrations of diamondoids in the pyrolysates from anhydrous (B) and hydrous pyrolysis (A) of kerogen at 340 °C for 72 hr. (b) The concentrations of diamondoids in the hydrous pyrolysates from kerogen with individual minerals at 340 °C for 72 h. C: kerogen + montmorillonite K10 (1:20); D: kerogen + kaolinite (1:20); E: kerogen + illite (1:20); F: kerogen + acidic aluminosilicate (1:20); G: kerogen + CaCO₃ (1:20); H: kerogen + CaSO₄ (1:20); I: kerogen + sulfur (1:2). (c) The concentrations of diamondoids in hydrous pyrolysates from kerogen/montmorillonite K10 and CaCO₃ with different mixing ratios of kerogen:montmorillonite K10:CaCO₃, 1:20:2 (J), 1:20:10 (K), and 1:20:20 (L). (d) The concentrations of diamondoids in the hydrous pyrolysates from kerogen with mixtures of different minerals. M: kerogen + montmorillonite K10 + sulfur (1:20:2); N: kerogen + CaCO₃ + sulfur (1:20:2); O: kerogen + CaCO₃ + montmorillonite K10 + sulfur (1:20:2:2). The quantitation of diamondoids (3- and 4-methyldiamantanes) is based on ion *m/z* 187 response for methyldiamantanes compared to isotopically labeled deuterated 1-methyldiamantane and quoted as ppm of hydrous pyrolysates.

duced bitumen, and thus suppresses C–C bond cross linking that is the formation pathway for pyrobitumen. The main reason is that water provides the hydrogen source required for the formation of hydrocarbons. It is assumed that some of the hydrogen transfer reactions that favor the formation of petroleum hydrocarbons are blocked under dry pyrolysis conditions resulting in the occurrence of large amounts of olefinic hydrocarbons (Hoering, 1977, 1984). In addition, the water is acting as a diluent retarding the secondary C–C bond formation reactions required for diamondoid formation.

Besides the direct breakdown of diamondoid units from the kerogen skeleton, the isomerization and cyclization of these olefinic hydrocarbons may also contribute to the relatively high concentrations of diamondoids in the pyrolysates of kerogen under dry conditions. Carbonium ions may react with molecular hydrogen and higher pressure favors more rapid hydride in transfer. Thus, hydrogen partial pressures may exert a controlling influence on diamondoid formation, i.e., low hydrogen partial pressures would enhance their formation, whereas high pressures would diminish their formation.

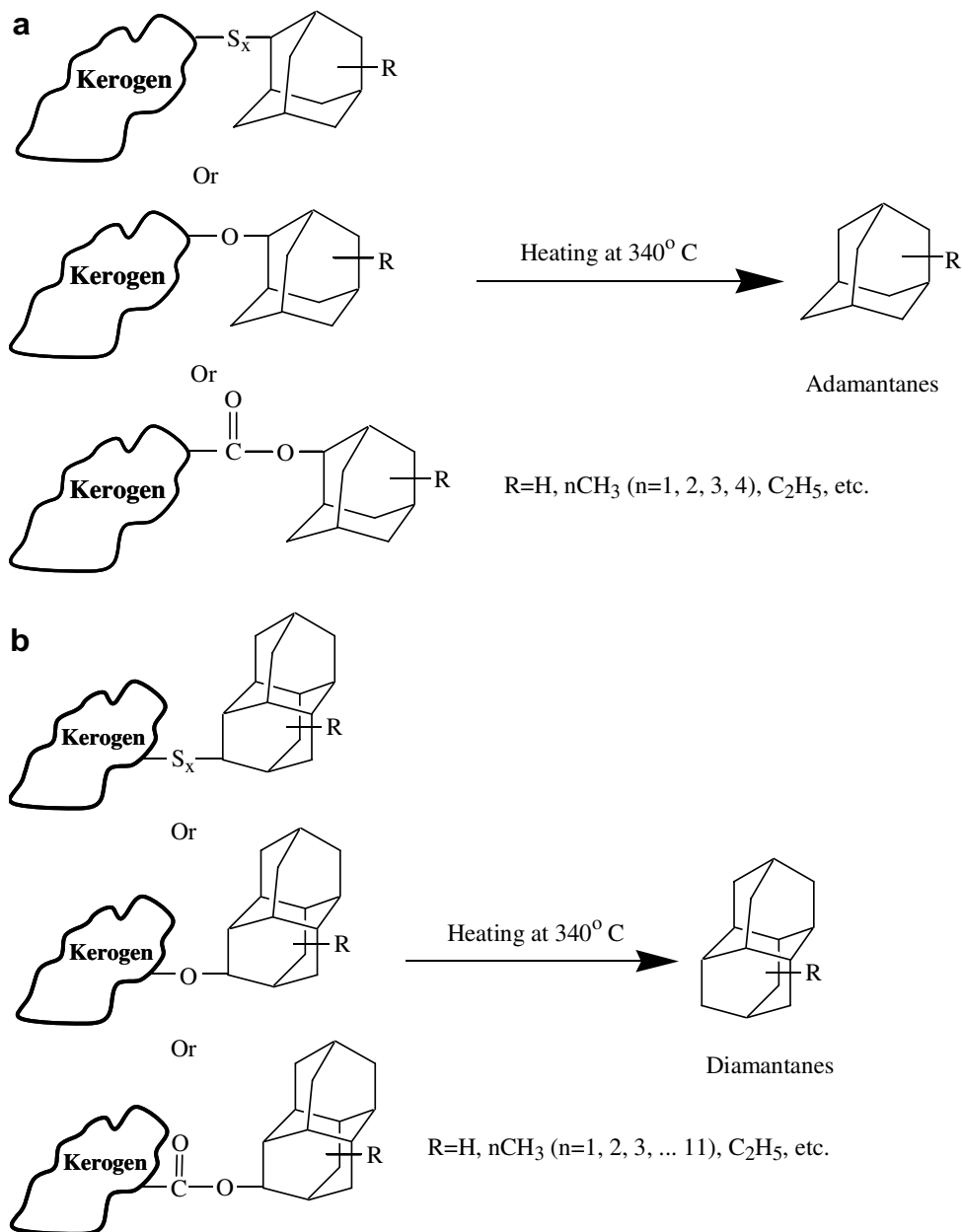


Fig. 3. Possible schemes for the generation of diamondoids from kerogen pyrolysis without catalysts. (a) Adamantanes bound to the kerogen skeleton with polysulfide, ether or ester groups. (b) Diamantanes bound to the kerogen skeleton with polysulfide, ether or ester groups. Note: $x \geq 1$.

3.2. The catalytic effects of individual minerals on the formation of diamondoids from kerogen

Hydrous pyrolysis of kerogen with different minerals including clays, $CaCO_3$, inorganic sulfate, and S^0 produces various amounts of diamondoids (Fig. 2b). From the experiments in this study, the catalytic activity decreases in the following order: montmoril-

lonite K10 > MS-25 > kaolinite > $CaSO_4$ > illite > $CaCO_3$ > S^0 . As expected, montmorillonite K10 and MS-25 with strong-acid sites are the most catalytically active in converting the hydrocarbons generated from kerogen to diamondoids. For example, the concentration of diamondoids reaches 46.15 ppm in the hydrous pyrolysates of Raton type III kerogen (Table 3). These clay catalysts have been

Table 3

The concentrations of diamondoids (3- + 4-methyldiamantanes) in pyrolysates from various catalytic pyrolysis experiments at 340 °C for 72 h

Experimental series number	Experimental description	Sample ID					
		#24 type I kerogen	#27 type I kerogen	Antelope type II kerogen	Monterey type II-S kerogen	ML91-17 type II-S kerogen	Raton type III kerogen
A	Kerogen:H ₂ O	1.09	0.99	2.68	0.46	0.23	9.68
B ^a	Kerogen alone	1.47	1.01	4.32	0.59	0.43	16.23
C	Kerogen:montmorillonite = 1:20	22.14	26.70	33.92	32.72	25.04	46.15
D	Kerogen:kaolinite = 1:20	3.72	3.57	5.47	3.26	1.65	20.57
E	Kerogen:illite = 1:20	1.33	0.58	3.11	0.43	0.53	5.05
F	Kerogen:acidic aluminosilicate = 1:20	10.81	18.36	23.07	13.09	13.53	37.49
G	Kerogen:CaCO ₃ = 1:20	1.04	0.41	1.81	0.23	0.14	3.28
H	Kerogen:CaSO ₄ = 1:20	3.50	1.23	2.62	1.33	0.43	4.82
I	Kerogen:S ⁰ = 1:20	1.51	0.32	0.44	0.56	0.04	2.74
J	Kerogen:montmorillonite:CaCO ₃ = 1:20:2		1.37	4.15		1.49	10.04
K	Kerogen:montmorillonite:CaCO ₃ = 1:20:10		1.29	3.74		1.13	9.09
L	Kerogen:montmorillonite:CaCO ₃ = 1:20:20		1.10	3.47		0.92	8.77
M	Kerogen:montmorillonite:S ⁰ = 1:20:2	1.75	1.28	3.86	0.94	0.80	4.88
N	Kerogen:CaCO ₃ :S ⁰ = 1:20:2	6.13	5.89	6.15	1.30	2.29	8.29
O	Kerogen:montmorillonite:CaCO ₃ :S ⁰ = 1:2:20:2	6.30	4.77	8.02	2.57	2.80	7.08
	Kerogen:montmorillonite:CaCO ₃ = 1:2:20		0.50	1.95		0.19	3.56
	Kerogen:montmorillonite:CaCO ₃ = 1:10:20		0.98	3.27		0.65	6.37
	Kerogen:montmorillonite = 1:2		2.06	5.20		1.38	22.16
	Kerogen:montmorillonite = 1:5		12.05	19.48		2.55	31.11
	Kerogen:montmorillonite = 1:10		23.79	28.35		13.32	38.15
	Kerogen:montmorillonite = 1:15		26.40	31.84		19.96	45.84

^a The only anhydrous pyrolysis experiment.

reported to adsorb a substantial amount of hydrocarbons and catalyze a variety of organic reactions during pyrolysis of kerogen, oil shale and sediments (Sieskind et al., 1979; Johns, 1979; Goldstein, 1983; Alexander et al., 1984; Tannenbaum et al., 1986; Huizinga et al., 1987; Li et al., 1998). In particular, montmorillonite can adsorb large amounts of hydrocarbons due to its large surface area (Espitalié et al., 1984). During pyrolysis, possible organic precursors released from the kerogen are adsorbed by montmorillonite K10 and MS-25. Subsequently, the Lewis acid sites mainly associated with octahedral Al³⁺ in both catalysts become available at an increasing rate as temperature rises, due to the dehydration at the edges of crystallites (Solomon et al., 1971; Kumar et al., 1995; Brown and Rhodes, 1997; Rhodes and Brown, 1997; Raimondo et al., 1998). The protons from both montmorillonite K10 and MS-25 are then transferred to various unsaturated organic compounds to produce carbonium ions, followed by the rearrangements of these carbonium ions. The transfer of the catalytic protons from the rearranged carbonium ion intermediates yields strained isomeric forms of these organic molecules. The subsequent cyclization, fragmentation and alkylation of these

isomerized compounds at Lewis acid sites result in the observed high yields of diamondoids. Our results also show that the presence of montmorillonite K10 yields more diamondoids than MS-25 (Fig. 2b), although the surface area of MS-25 is larger (408 m²/g) than that of montmorillonite K10 (220–270 m²/g). However, the adsorption of organic compounds is controlled by several factors such as CEC, the amount and type of clay, and pH, as demonstrated by Balakrishnan et al. (2004). The activity of clay catalysts is mainly determined by the number of acid sites as well as the acid strength (Tamele, 1950; Rupert et al., 1987). The increasing CEC of clay minerals may also be responsible for the enhancement of the strength of Lewis acid sites. Montmorillonite K10 may be endowed with the highest catalytic activity in the generation of diamondoids during kerogen pyrolysis because it has the highest CEC (about 80–120 meq/100 g) among the clay minerals.

Due to lower surface area (10.05 ± 0.02 m²/g) and lower CEC (2.0 meq/100 g), kaolinite has relatively less Lewis acid sites at 340 °C than montmorillonite K10, and thus is a less active catalyst. The presence of kaolinite promotes poorer genera-

tion of diamondoids than the presence of montmorillonite K10 and MS-25 during hydrous pyrolysis of these kerogens. Despite the strong adsorption capacity of illite (Huizinga et al., 1987), no catalytic effect was observed on the production of diamondoids, presumably because the surface area and CEC of illite are much lower compared with other clay minerals such as montmorillonite K10 and MS-25. The IMt-1 illite has slightly higher CEC (17 meq/100 g), but lower surface area (11 m²/g) than kaolinite. As a result, the acidity of illite is much weaker than that of kaolinite. The amount of diamondoids obtained from kerogen pyrolysis with illite is approximately equivalent to that from anhydrous or hydrous pyrolysis of kerogen alone with the exception of the type III kerogen (Fig. 2b). Thus, illite does not appear to catalyze diamondoid formation.

Moreover, Fig. 2b shows that the yield of diamondoids is reduced by the addition of CaCO₃ to the kerogen pyrolysis system compared to that of anhydrous or hydrous pyrolysis of kerogen alone. This is because CaCO₃ neutralizes the acidity under hydrous conditions and thereby also inhibits protonation reactions and carbonium ion rearrangements. Thus, CaCO₃ exhibits an inhibitive effect on the formation of diamondoids. For instance, the concentration of diamondoids was reduced from 0.99 ppm in hydrous pyrolysates of #27 type I kerogen to 0.41 ppm when CaCO₃ was included. Similarly, reduced yields were observed for other kerogens when CaCO₃ was present. Nevertheless, CaCO₃ has been observed to increase the yield of oil and to change the molecular distribution of kerogen pyrolysates (Horsfield and Douglas, 1980; Rose et al., 1992). The negligible adsorption capacity of CaCO₃ leads to the dominance of heavy hydrocarbons in their pyrolysis products (Tannenbaum et al., 1986). The catalytic activity of CaCO₃ is much weaker than that of clay minerals regarding the yield of hydrocarbons generated (Taulbee and Seibert, 1987), particularly with increasing temperature (Li et al., 1998). Although CaCO₃ catalyzes oil generation, with an altered composition, it probably produces intermediates that do not favor production of diamondoid structures. Therefore, CaCO₃ appears to have the inhibition effect on the occurrence of diamondoids.

The CaSO₄ is considered to be a weak Brønsted acid. Fig. 2b shows that it increases the concentration of diamondoids by 2–3 times in the pyrolysates

of type I and II-S kerogens in comparison to those in hydrous pyrolysate of kerogen alone. In contrast, type II and III kerogen pyrolysates contain slightly reduced concentrations of diamondoids (Fig. 2b). Goldhaber and Orr (1995) suggested that TSR alteration of toluene occurred with variable pressure of hydrogen sulfide at measurable rates at 250 °C on a laboratory time scale. Therefore, it is possible that in the presence of CaSO₄, the hydrocarbons generated from kerogen alteration might undergo thermochemical sulfate reduction (TSR) at 340 °C. This may accelerate the destruction of relatively unstable compounds. Diamondoids released from kerogen matrices, however, might be relatively resistant to TSR alteration because of their unique chemical structures, and are thus enriched in the remaining pyrolysates, leading to a slight increase in the yield of diamondoids.

Sulfur plays an important role in the genesis of petroleum (Lewan, 1998), and is known to be a free radical initiator. Sulfur radicals derived from the thermal degradation of kerogen initiate the cleavage of C–C bonds during hydrocarbon generation (Lewan, 1998). Fig. 2b illustrates that the yield of diamondoids was greatly reduced when a small quantity of sulfur was added to each of the kerogens, suggesting that sulfur alone does not promote reactions leading to diamondoid formation. On the contrary, more diamondoid precursors may be destroyed by sulfur, releasing abundant hydrogen sulfide and various organic sulfur species. There are also lines of evidence from the GC and SIR-GCMS chromatograms showing that biomarkers and organic precursors of diamondoids are cracked and converted into more stable compounds or organic sulfur compounds during these sulfur and kerogen reactions. For example, Fig. 4a shows that the chemical composition of the hydrous pyrolysates of Monterey type II-S kerogen and sulfur mix is dominated by the low molecular weight (LMW) *n*-alkanes (C₁₅⁻). The high molecular weight (HMW) *n*-alkanes (C₁₅⁺) are almost absent because of catalytic degradation to smaller molecules. As shown in Fig. 4b, most triterpanes have also experienced cracking, and only 0.831 ppm of C₃₀17 α ,21 β (H)-hopane is generated during hydrous pyrolysis. Similarly, trace amounts of steranes are observed in the sulfur-catalyzed kerogen pyrolysates (Fig. 4c), among which C₂₉5 α ,14 α ,17 α -stigmasterane 20R is as low as 0.18 ppm in the pyrolysates. For the Antelope type II kerogen, the GC traces of the hydrous pyrolysates of its mix with sulfur also show

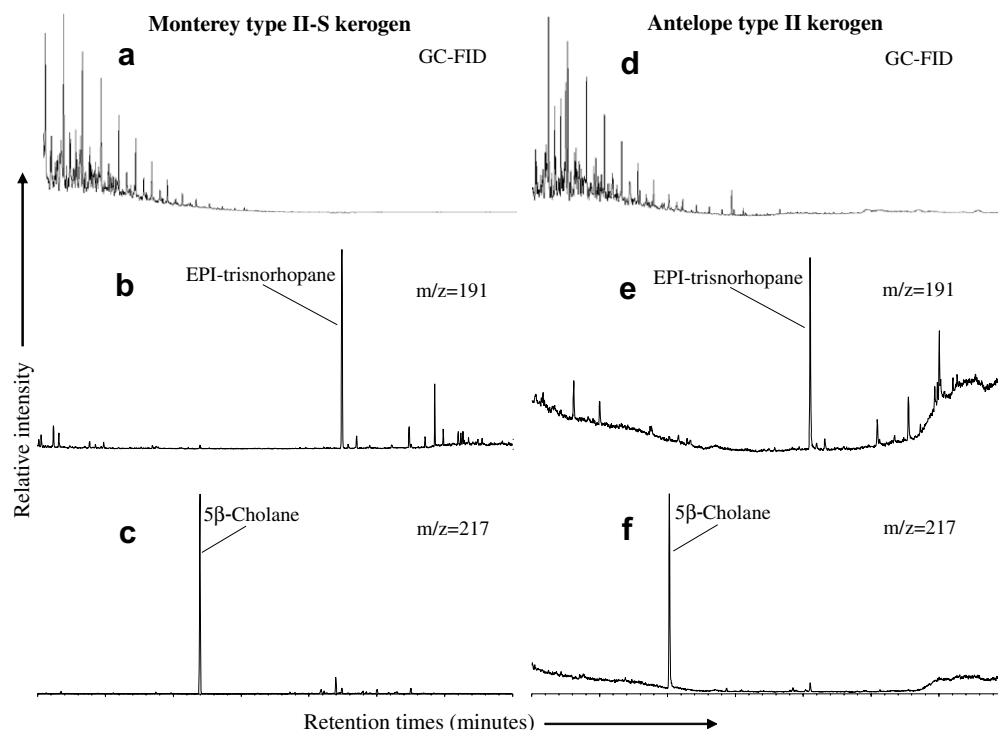


Fig. 4. (a) GC-FID of saturate hydrocarbons separated from hydrous pyrolysates of Monterey type II-S kerogen and elemental sulfur mix. (b) Mass chromatogram of terpenoids (m/z 191) in the corresponding saturate fraction. (c) Mass chromatogram of steranes (m/z 217) in the relative saturate fraction. (d) GC-FID of saturate hydrocarbons separated from hydrous pyrolysates of Antelope type II-S kerogen and elemental sulfur mix. (e) Mass chromatogram of terpenoids (m/z 191) in the corresponding saturate fraction. (f) Mass chromatogram of steranes (m/z 217) in the relative saturate fraction. Note: 5 β -cholane and EPI-trisnorhopane are internal standards used in the quantitation of biomarkers that are generated from hydrous pyrolysis.

a depletion of HMW n -alkanes, but a predominance of LMW n -alkanes (Fig. 4d). Similarly, most of the biomarkers including triterpanes and steranes are also destroyed during the hydrous pyrolysis of Antelope type II kerogen and sulfur mix, as illustrated in Fig. 4e and f.

3.3. The neutralizing effects of CaCO_3 on the catalytic activity of montmorillonite K10

Increasing portions of CaCO_3 were added to the kerogen/montmorillonite K10 mixture (1:20) to investigate the effect of CaCO_3 on the catalytic activity of montmorillonite K10 during kerogen pyrolysis. Fig. 2c illustrates that the presence of a small amount of CaCO_3 in the kerogen/montmorillonite K10 mixture significantly inhibits the catalytic activity of the mix towards diamondoid formation. For example, hydrous pyrolysis of the Antelope type II kerogen gives about 33.9 ppm of diamondoids in the pyrolysates of 20:1 montmoril-

lonite to kerogen. With the smallest proportion of CaCO_3 (kerogen/ CaCO_3 = 1:2) added to the kerogen/montmorillonite K10 mixture, the concentration of diamondoids in the pyrolysates was only 4.15 ppm (Table 3). The yields of diamondoids showed only slight decreases with increasing amounts of CaCO_3 in the kerogen/montmorillonite K10 mixture (Fig. 2c). Similar results were obtained for #27 type I, ML91-17 type II-S, and Raton type III kerogens. Although the inhibition effect of CaCO_3 is significant on the formation of diamondoids, the yield of diamondoids is still three times higher in the presence of montmorillonite K10 compared to that in experiment G (Fig. 2b and c).

It is assumed that CaCO_3 acts to block strong-acid sites on montmorillonite. While the acidic clay catalysts such as montmorillonite K10 promote the yield of diamondoid formation via carbonium ion mechanisms, the presence of CaCO_3 seems to readily neutralize this catalytic activity.

3.4. The effects of montmorillonite K10:kerogen ratio on the formation of diamondoids

Two series of experiments were designed to examine if the amount of montmorillonite K10 in the isolated kerogen could influence the generation of diamondoids. The first series of experiments are characterized by the addition of increasing quantities of montmorillonite K10 to the kerogen/ CaCO_3 mixture (1:20). Fig. 5a illustrates that the yield of diamondoids is only slightly increased in the presence of more montmorillonite K10 during kerogen pyrolysis. The catalytic activity of montmorillonite K10 is inhibited by the buffering effect of CaCO_3 . Hence, the formation of diamondoids is not very sensitive to the amount of montmorillonite if CaCO_3 is present in the pyrolysis system.

In the other experiment series, hydrous pyrolysis was conducted on the montmorillonite K10/kerogen mixtures of varying ratios at 340 °C for 72 h. It is obvious that the diamondoid yields are very sensitive to the amount of montmorillonite K10 mixed with the kerogen (Fig. 5b). Increasing amounts of montmorillonite K10 result in the availability of more Lewis acid sites at the surface of montmorillonite K10, as well as the adsorption of more organic compounds. During kerogen pyrolysis, octahedrally coordinated Al^{3+} ions exposed at the edges of montmorillonite particles can serve as electron acceptors, which catalyze carbonium ion formation (Johns, 1979; Rupert et al., 1987). Evidence is shown in Fig. 5b that the catalytic effect of montmorillonite K10 on the formation of diamondoids becomes surprisingly more intense with increasing montmorillonite K10/kerogen ratios until 15:1, where the effect of further increasing montmorillonite K10 on the synthesis of diamondoids tends to be negligible. In particular, striking increases in the concentrations of diamondoids in the produced pyrolysates were observed at the montmorillonite K10/kerogen ratio of 10:1 (23.8 ppm for type I kerogen, 28.4 ppm for type II kerogen, 13.3 ppm for type II-S kerogen, and 38.2 ppm for type III kerogen), which is in agreement with the results from the former series of experiments. Each kerogen appeared to reach its maximum generation capacity of diamondoids, except for the type II-S kerogen ML 91-17 when the montmorillonite K10/kerogen ratio of 15:1 was used. After that, no discernible change was observed regarding the yield of diamondoids with

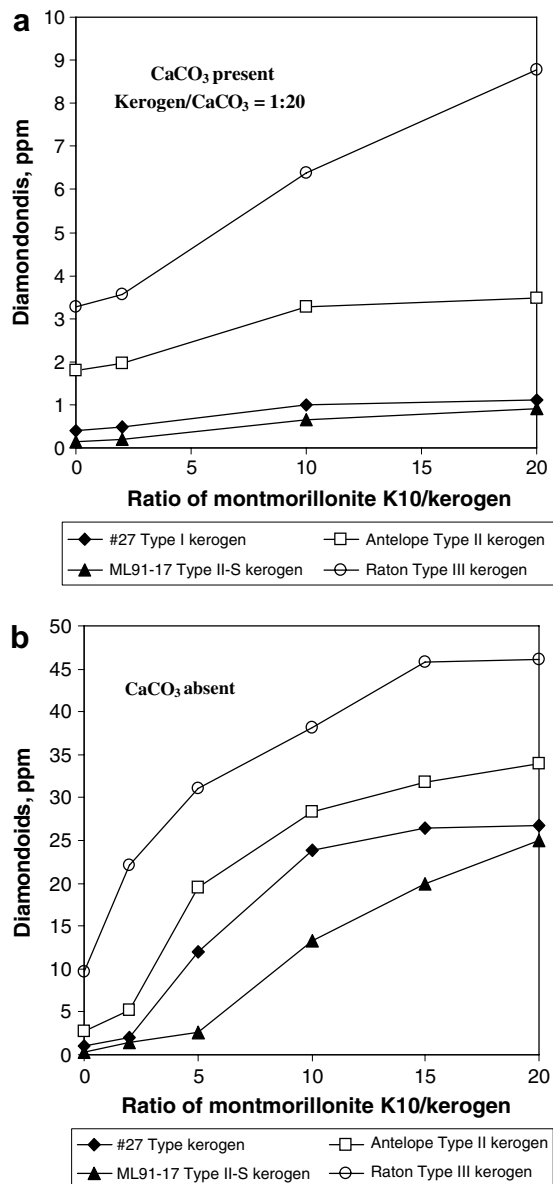


Fig. 5. (a) The concentrations of diamondoids in the pyrolysates from catalytic hydrous pyrolysis of kerogen with different quantities of montmorillonite and a fixed amount of CaCO_3 (kerogen: CaCO_3 = 1:20). (b) The concentration of diamondoids in the pyrolysates from hydrous pyrolysis of kerogen/montmorillonite K10 mixtures of different ratios. A kerogen/water ratio of 1:20 was used in each experiment.

increasing amount of montmorillonite K10. It is likely that the organic precursors of diamondoids from the decomposition of kerogen were fully coordinated with the accessible Lewis acid sites at the montmorillonite K10/kerogen ratio of 15:1. With respect to the type II-S kerogen (ML91-17), more

hydrocarbons in general may be generated from this type of kerogen, as indicated by the high S_2 value (67.82 mg HC/g TOC, Table 1), potentially leading to overloading of the active catalytic sites of montmorillonite K10 in the 15:1 mix. It is possible that the diamondoid precursors from this kerogen become fully coordinated only at a higher montmorillonite K10/kerogen ratio.

3.5. The effects of sulfur on the inhibitory/catalytic activity of $CaCO_3$ and montmorillonite K10

In nature, a sedimentary rock may contain a variety of minerals, e.g., clays, calcite, dolomite, sulfur, and pyrite. A better understanding of diamondoid formation in sedimentary rocks can be achieved through experiments mixing a variety of minerals with kerogen. The strong catalytic activity of montmorillonite K10 clay in the generation of diamondoids was largely inhibited by a small amount of sulfur added to a kerogen-montmorillonite K10 mixture (1:20) (Fig. 2b (I), cf. Fig. 2a (A)). In general, many catalysts can be poisoned by sulfur species in catalytic reactions, e.g., Pd/HY- Al_2O_3 by sulfur, Ni/clinoptilolite by thiophene, Y zeolites by thiophene, and platinum/alumina by sulfur (e.g., Kochubei et al., 1982; Guenin et al., 1987; Arcoya et al., 1997; Gravit and Toulhoat, 1999; Hu et al., 2001). Kochubei et al. (1982) suggested that, in the presence of sulfur species, dense S-containing polymers may be formed on the catalyst surface, which block the catalytically active center (Lewis acid sites). Consequently, this lowers the activity of catalysts because of S poisoning. Similarly, our experiments indicated that montmorillonite K10 was poisoned by sulfur, because the concentrations of diamondoids in the pyrolysates of kerogen/montmorillonite/sulfur mixture were only slightly higher than in the hydrous pyrolysates of kerogen alone, with the exception of type III kerogen (Fig. 2d).

Our experiments suggest that neither sulfur nor $CaCO_3$ catalyze the formation of diamondoids during kerogen pyrolysis. However, the combination of $CaCO_3$ with sulfur does seem to have a catalytic effect on diamondoid formation. For instance, pyrolyzing the kerogen/ $CaCO_3$ mixture (1:20) with sulfur elevated the yield of diamondoids by 4–11 times compared with hydrous pyrolysis of kerogen alone (experiments A, N, Fig. 2d) for all but the type III kerogen. The reason for this is unclear, but may relate to the maturity of the latter kerogen. Therefore, although $CaCO_3$ demonstrated the abil-

ity to inhibit the formation of diamondoids, the combined effects of sulfur and $CaCO_3$ appear to exhibit a net catalysis, probably because the oxidation of hydrocarbons by sulfur may be lowered by competition with the formation of other mineral species from $CaCO_3$ and sulfur during pyrolysis. A possible explanation is that a newly-formed mineral might be $CaSO_4$, which is a weak Brønsted acid and has some catalytic effects on the formation of diamondoids, as previously mentioned. This could explain why diamondoids are also abundant in oils generated from marine carbonate source rocks deposited in an anoxic marine environment in which sulfur is also present. Furthermore, even when a small portion of montmorillonite K10 was added to a kerogen/ $CaCO_3$ mixture (1:20) in the presence of sulfur (e.g., experiment O), it made little difference to the abundance of diamondoids in pyrolysis products of kerogen compared with that in experiment N (Fig. 2d). This suggests that sulfur has a pronounced suppression effect on the catalytic activity of montmorillonite K10.

4. Conclusions

Pyrolyses of kerogen with the addition of minerals were conducted, allowing the catalytic effects of the minerals on the formation of diamondoids to be investigated. Montmorillonite K10 and acidic aluminosilicate are largely shown to largely promote the formation of diamondoids during pyrolysis, probably because of their strong Lewis acidity. However, kaolinite shows less activity, attributable to lower surface area and lower cation exchange capacity. Illite shows little or no catalytic activity during the formation of diamondoids. The occurrence of diamondoids in the kerogen pyrolysates results from the thermal degradation of kerogens of different types regardless of the availability of water. The presence of montmorillonite K10 and acidic aluminosilicate favors diamondoid formation, but $CaCO_3$ inhibits it. The formation of diamondoids, thus, appears to follow a carbonium ion mechanism rather than an electron transfer mechanism. The presence of $CaSO_4$ can improve the yield of diamondoids by 2–3 times for type I and II-S kerogens, but how such catalysis arises is not well understood at present.

$CaCO_3$ tends to neutralize the catalytic activity of montmorillonite K10 even though only a small amount of $CaCO_3$ is present in the pyrolysis system. In general, the more Lewis acid sites, e.g., montmoril-

lonite K10, present, the more diamondoids are generated, although the catalytic effect diminishes at a montmorillonite K10/kerogen ratio $\geq 15:1$. In addition, the catalytic activity of montmorillonite is apparently poisoned by the presence of S^0 . Although $CaCO_3$ on its own inhibits the formation of diamondoids, in the presence of elemental sulfur, it can increase the yield of diamondoids during pyrolysis.

Acknowledgements

We are grateful to Larry McDorman for providing the MS-25 catalyst. We acknowledge the great efforts made by Ken Peters, Paul Lillis, and Les Magoon in searching for type II-S kerogen, and for providing the Antelope shale sample containing type II kerogen. Mike Lewan is thanked for providing a sulfur-rich Monterey shale from his rock collection for isolation of type II-S kerogen and for his helpful discussions regarding hydrous pyrolysis and the possible sources of diamondoids. Critical comments given by Albert Holba, Michael Siskin, Clifford Walters, and Lloyd R. Snowdon greatly improved this manuscript. We also appreciate the financial support from Molecular Organic Geochemistry Industry Affiliates and McGee funds at Stanford University.

Associate Editor—Clifford C. Walters

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