

## **Organic compound-mineral interactions: using flash pyrolysis to monitor the adsorption of fatty acids on calcite**

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## **Abstract**

Fatty acids are near ubiquitous organic compounds in living organisms in the Earth's biosphere. Following death of an organism in the marine environment its fatty acids may survive descent to the sea bed where they can be juxtaposed with minerals. The aim of this study was to investigate the interaction of fatty acids with the common marine mineral calcite. Adsorption of tetradecanoic acid (C<sub>14</sub>) on calcite results in a sigmoidal or "s" isotherm. Flash pyrolysis experiments were conducted on samples of fatty acid adsorbed onto calcite and were compared with similar experiments on pure fatty acid and on salts of a fatty acid. Flash pyrolysis of pure tetradecanoic acid generated unsaturated and saturated hydrocarbons and a series of unsaturated and saturated low molecular weight fatty acids. Flash pyrolysis of free tetradecanoic acid salt produced saturated and unsaturated hydrocarbons, an aldehyde and a homologous series of saturated and unsaturated ketones, one of which was a symmetrical mid chain ketone (14-heptacosanone). Flash pyrolysis data from adsorbed tetradecanoic acid samples suggested that adsorption is analogous to the formation of the calcium salt of tetradecanoic acid. A key characteristic of the flash pyrolysis products of adsorbed fatty acids and fatty acid salts was the production of ketones with higher molecular weights than the starting fatty acids. Ketonisation was not observed from the flash pyrolysis of pure acid which implied the catalytic significance of the calcite mineral surface. The abundance of hydrocarbons relative to ketones in the pyrolysates negatively correlated with the proportion of fatty acids adsorbed to the surface of calcite. The ability to use flash pyrolysis to diagnose the nature of fatty acid interactions with mineral surfaces provides a valuable tool for monitoring the fate of these important lipids at the Earth's surface as they pass into the geosphere and are subjected to diagenetic processes.

**Keywords: Diagenesis, S-isotherm, Hydrocarbons, Carboxylate salts, Ketonisation**

## 1. Introduction

Digenesis represents a major link between Earth's surficial carbon reservoirs and their counterparts in the geosphere [1,2]. During diagenesis the juxtaposition of organic matter and minerals provides the opportunity for organic-inorganic interactions. There is a strong relationship between organic matter and clay minerals in petroleum source rocks and continental shelf sediments that has been explained on the basis of sorption of organic matter onto minerals [3,4]. The adsorption of organic molecules onto mineral surfaces has been proposed as a key mechanism for the enhancement of organic matter accumulation and preservation [5-7].

Adsorption protects organic compounds from microbial degradation in sediments [8-10] and is controlled by various mechanisms such as ligand exchange, cation bridging, van der Waals interactions and hydrophobic effects [11,12]. The nature of adsorption is inevitably related to the organic compound being adsorbed and depends on various factors such as size and functional group content [8,13,14].

Adsorption to carbonate minerals is particularly important owing to the fact that carbonate minerals preferentially attract acidic organic compounds at their surface [15,16], besides incorporating organic compounds in intra- and inter-crystalline locations [17,18]. Owing to the large surface area to volume ratio of fine grained calcium carbonate found in marine sediments, the potential for organic compound adsorption on to their surfaces is relatively high [16,19].

Previously, a few studies have investigated the adsorption of different classes of organic compounds on carbonate minerals in water and published reports included sugars [20], amino acids [20,21] and fatty acids [22-24]. Fatty acids are a particularly important class of organic compound owing to their widespread occurrence in the biosphere and their role as sedimentary organic matter precursors [25]. Although the process of fatty acid adsorption onto carbonate minerals has been studied in the laboratory, the number and scope of such studies are limited, possibly because of the relative insolubility of fatty acid compounds in water.

A common method for visualising the presence of organic compounds in the form of salts or present within mineral matrices is on-line or “flash” pyrolysis [26,27]. The rapid thermal evaporation or dissociation of organic matter effectively liberates the compounds from their associated minerals. The pyrolysis of fatty acids has been used to investigate the production of hydrocarbon fuels [28-30] but the technique has not been used previously to monitor the interactions of fatty acids and carbonate minerals. Organic compounds that are inaccessible to solvent extraction owing to their chemically-bound nature should be liberated following the rapid application of heat.

In this paper we report adsorption experiments that provide samples made up exclusively of fatty acids adsorbed on calcite. The intended outcome of this study is a method that can recognize the difference between free and calcite-adsorbed fatty acids owing to their distinct signals in response to flash pyrolysis. When free and calcite-adsorbed fatty acids are subjected to flash pyrolysis they generate distinct products that suggest a means of monitoring the passage of fatty acids into the geosphere by adsorption onto calcite mineral surfaces during diagenesis.

## **2. Experimental**

### **2.1. Preparation of calcite mineral**

Approximately 10 g of calcite (Sigma-Aldrich) was placed into 250 ml conical flask and stirred with 10% H<sub>2</sub>O<sub>2</sub> at 80 °C for 3 hours and then rinsed with deionized water (Type I, 18.2 MΩ cm<sup>-1</sup>) 7 times before drying at 110 °C. The dried calcite was powdered in a pestle and mortar. The specific surface area of calcite was determined by micromeritics-Brunauer, Emmett and Teller (BET) gas (nitrogen) adsorption method analysis.

### **2.2. Preparation of fatty acid solution**

A stock solution (219 μM) of tetradecanoic acid (Sigma-Aldrich) was prepared in an aqueous solution with 2% methanol and adjusted to be 35‰ salinity and the pH measured to be 8.0. The stock solution was heated at 27 °C for 10 minutes to aid dissolution. The NaCl (0.1 M) solution and tetradecanoic acid stock solution were then used to prepare different fatty acid concentrations (22, 44, 88, 110 and 131 μM). An internal standard solution was prepared of heptadecanoic acid (3 mM) in dichloromethane (DCM).

### **2.3. Preparation of calcium, magnesium and sodium salts of tetradecanoic acid**

Calcium salt of tetradecanoic acid was prepared by adding calcium hydroxide solution (0.2 M; 0.9g in 50 ml water) to the dissolved acid solution (0.2 M; 5g in 100 ml water) at 50 °C, while stirring. Magnesium tetradecanoate was prepared by adding sodium hydroxide solution (2.5 mM; 0.1g in 20 ml of water) to tetradecanoic acid solution (2.5 mM; 0.5 g in 50 ml of water). Subsequently, magnesium chloride solution (1.2 mM; 0.25 g in 5.0 ml water) was added to the tetradecanoic acid/sodium hydroxide solution under vigorous agitation.

Sodium tetradecanoate was prepared by first adding sodium hydroxide solution 2.5 M (5 g in 50 ml water) to 5 ml ethanol (95%) solution. Tetradecanoic acid (5 g) was then added to the sodium hydroxide/ethanol solution and then heated at 40 °C on a hot plate for about 20 minutes. During heating a small amount of the 95% ethanol/water mixture was added to stop foaming in the reaction mixture. The mixture was then quickly combined with sodium chloride solution (0.8 M; 2.5 g in 50 ml water). In all cases, the resulting insoluble precipitates were filtered, washed with water and dried in air at room temperature. The dried powders were washed 3 times in chloroform and dried again at room temperature. The purity of tetradecanoic acid and tetradecanoate salts were assessed by Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using a Nicolet™ 5700 spectrometer. Spectra were collected for 128 scans at a resolution of 4 cm<sup>-1</sup> between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>.

#### **2.4. Adsorption experiments**

The tetradecanoic acid (219 µM) and NaCl (0.1 M) stock solutions were used to prepare five different concentrations (22, 44, 88, 110 and 131 µM) of tetradecanoic acid in 10 ml borosilicate test-tubes with 50 mg of calcite. The glass test-tubes were sealed with screw caps (PTFE liner) and placed in a rotator at a constant temperature of 23 ± 2 °C. The samples were equilibrated for 24 hours, after equilibration following which the glass tubes were centrifuged 3 times for 5 minutes at 380 relative centrifugal force (RCF) and the supernatant was transferred into 20 ml glass tubes. Each glass test-tube was rinsed with 5ml of water and centrifuged again for 5 minutes at 380 RCF to remove the excess acid attached to the walls of the tubes.

The supernatants were acidified with 3 ml of 0.1 M HCl and then 300  $\mu$ l of internal standard stock solution ( $C_{17:0}$ ) (3 mM) was added to each glass tube. The unadsorbed fatty acid in the supernatant fluid after the adsorption experiment was extracted by liquid-liquid extraction with DCM in a separating funnel. The DCM extraction step was repeated 3 times for each sample and the extracts were combined in a round bottom flask and then concentrated using a rotary evaporator. Following evaporation, the extract containing unadsorbed fatty acids and internal standard was transferred into glass insert vials (300  $\mu$ l) for analysis. Five standard samples of tetradecanoic acid (22, 44, 88, 110 and 131  $\mu$ M) were also prepared in DCM as described above containing the internal standard.

All samples were quantified using a Perkin Elmer Auto System XL gas chromatograph-flame ionisation detector (GC-FID) fitted with a DB-FFAP column (30 m length  $\times$  0.25 mm internal diameter and 0.25  $\mu$ m film thickness; J & W). Hydrogen was used as the carrier gas at a column flow rate of 1.1 ml/min. Injection was splitless (0.5  $\mu$ l) and the inlet temperature was 240  $^{\circ}$ C. The oven was held at 60  $^{\circ}$ C  $\text{min}^{-1}$  followed by a temperature ramp of 10  $^{\circ}$ C  $\text{min}^{-1}$  to 240  $^{\circ}$ C, where the temperature was held for 9 min and the FID was maintained at 270  $^{\circ}$ C. The peak areas were measured for quantification using Totalchrom Navigator software and corrected for their relative response factors (RRF). The samples of calcite with adsorbed fatty acids were dried in a freeze drier for subsequent analysis by on-line pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC-MS).

## **2.5. Pyrolysis-GC-MS of tetradecanoic acid**

Pyrolysis-GC-MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a heated transfer line (320  $^{\circ}$ C) to a 7890 GC and a 5975 MS (both Agilent Technologies).

Tetradecanoic acid (0.5 mg) was placed in a quartz pyrolysis tube, with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms<sup>-1</sup> the sample was held at this temperature for 15 s in a flow of helium, upon pyrolysis the interface was heated from 40 to 350 °C at 100 °C s<sup>-1</sup> where it was held for 15 min to prevent volatilisation of the samples prior to pyrolysis. The GC injector was held at 270 °C and operated at a 50:1 split with a helium column flow rate of 1.1 mL min<sup>-1</sup>. Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness). The GC oven temperature was held for 2 min at 35 °C and subsequently ramped to 300 °C at a rate of 5 °C min<sup>-1</sup> and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) from 50 to 500 amu.

## **2.6. Pyrolysis-GC-MS of tetradecanoic acid adsorbed on calcite and salts of tetradecanoic acid**

Pyrolysis-GC-MS is a technique that accesses organic materials that cannot be mobilised by solvent extraction, such as high molecular organic networks or organic structures bound to mineral surfaces. Pyrolysis-GC-MS was performed using a 2000 Pyroprobe (CDS Analytical) fitted via a 1500 valve interface and coupled to 6890 GC and a 5973 MS (both Agilent Technologies). Dried samples of tetradecanoic acid adsorbed acid onto calcite were homogenised and approximately 20 mg were placed in quartz pyrolysis tubes, with quartz wool at each end. Similarly, dried salt samples (5 mg) were prepared in quartz pyrolysis tubes with quartz wool at each end. Following heating to 650 °C at a rate of 20 °C ms<sup>-1</sup> the sample was held at this temperature for 15 s in a flow of helium. A temperature of 650 °C was chosen because it is the temperature at which thermal dissociation of hydrocarbon-dominated structures occurs to provide information on chemical constitution. The interface was held at



200 °C until pyrolysis when it was ramped to 350 °C at 60 °C s<sup>-1</sup>. The GC injector was held at 270 °C and operated at a 10:1 split for adsorbed samples and 50:1 split for salt samples with a helium constant column flow rate of 1.1 ml min<sup>-1</sup>. All other conditions were the same as for the pyrolysis of acids as described above.

### 3. Results

#### 3.1. Adsorption isotherm

The adsorption of fatty acids on carbonate mineral surfaces (Fig 1) could be monitored by the production of isotherms. BET analysis provided the potential mineral surface area available for adsorption (Table 1) which, when combined with the measured reduction in concentration of fatty acids free in solution, allowed calculation of the concentration of fatty acids that were adsorbed onto the mineral surface. The shape of the isotherm produced in our adsorption experiment (Fig 2, Table 2) could be described as an s-isotherm according to published classifications [31]. The s-isotherm is indicative of co-operative adsorption where both adsorbent-adsorbate and adsorbant-adsorbant interactions take place and multilayers are formed [32].

The adsorption data was further analysed by using the Freundlich equation  $q_e = K_f C_e^{1/n}$ , where  $q_e$  is the concentration of tetradecanoic acid adsorbed on calcite (μM/g),  $C_e$  is the final concentration of adsorbate in solution (μM/L),  $K_f$  and  $1/n$  are constants representing adsorption capacity and adsorption intensity, respectively. The equation can be linearized and the constants  $K_f$  and  $1/n$  are found by linear regression. The adsorption of tetradecanoic acid on calcite follows a Freundlich sorption model with  $\log K_f = 2.1622$ ,  $1/n = 1.4081$  and  $R^2 = 0.947$  (Fig 3).

### 3.2. Pyrolysis products of tetradecanoic acid

Pyrolysis of tetradecanoic acid produced tridecane, alkenes (C<sub>4</sub> to C<sub>14</sub>), a series of saturated (C<sub>8</sub> to C<sub>10</sub> & C<sub>14</sub>) and mono-unsaturated low molecular weight fatty acids (C<sub>6</sub> to C<sub>12</sub>), and toluene (Fig 4a, Table 3).

### 3.3. Pyrolysis products of calcium, magnesium and sodium salts of tetradecanoic acid

Pyrolysis of the calcium salt of tetradecanoic acid produced a series of alkanes (C<sub>8</sub> to C<sub>13</sub>), a range of alkenes (C<sub>6</sub> to C<sub>14</sub>), tetradecanoic acid, toluene, tetradecanal and a series of ketones (C<sub>15</sub> to C<sub>27</sub>). The main product was a symmetrical mid-chain ketone, 14-heptacosanone (C<sub>27</sub>) (Fig 4b, Table 3). There were only minor differences between the different salts, even between the monovalent and divalent metals (Fig 5, Table 3). Only subtle differences in molecular weight ranges for the products were evident.

### 3.4. Pyrolysis of tetradecanoic acid adsorbed on calcite

The pyrolysis products of the tetradecanoic acid adsorbed on calcite selected from the different parts of the isotherm were distinct from the free tetradecanoic acid results but similar to those from the calcium and other salts of tetradecanoic acid (Fig 6). The relative abundance of hydrocarbons and ketones in the flash pyrolysates of varying amounts of tetradecanoic acid adsorbed on calcium carbonate (Fig 7, Table 4) revealed that when the amount of tetradecanoic acid adsorbed on calcite increases the ratio of hydrocarbons/ketones in the pyrolysate decreases. Expressed statistically, there was a linear negative correlation ( $R^2 = 0.877$ ) of hydrocarbons relative to the proportion of the tetradecanoic acid adsorbed.

## 4. Discussion

### 4.1. Pyrolysis mechanisms of pure tetradecanoic acid

Within the pyrolysis products of tetradecanoic acid (Fig. 4a) the alkane, tridecane, is the straightforward decarboxylation product of tetradecanoic acid. The alkenes are the products of alkyl chain scission, where random delocalisation of the radical along the alkyl chain to eventually break the chain at different sites. The saturated and unsaturated low molecular weight fatty acids are also the products of alkyl chain scission and reveal that chain scission is preferred over decarboxylation for the free acid. The formation of a series of short chain saturated and unsaturated carboxylic acids is consistent with the results obtained in previous studies [33]. Homolysis commonly produces one saturated and one unsaturated compound and the relative lack of alkanes suggest that chain scission and intramolecular and intermolecular hydrogen transfer affecting the alkenes must involve the alkanoic moiety. Toluene is a common aromatic hydrocarbon often seen in pyrolysis products owing to the stability of the tropyllium ion which cools to produce toluene. On the whole, the formation of *n*-alkenes and *n*-alkanes suggested that the radical mechanism is the most likely mechanism explaining the thermal dissociation of pure acids.

### 4.2. Pyrolysis mechanisms of calcium, magnesium and sodium salts of tetradecanoic acid

Following flash pyrolysis of calcium, magnesium and sodium salts of tetradecanoic acid (Fig. 5), the absence of unsaturated fatty acids indicates that the transformation of fatty acid salts

proceeds readily to alternative products. The symmetrical aliphatic ketones also known as fatty ketones, i.e. 14-heptacosanone, are formed by ketonic decarboxylation [34].

From this data (Fig 5) we propose a radical mechanism for the formation of a homologous series of ketones and associated alkenes/alkanes from 14-heptacosanone. The pyrolysis of fatty acid salts show a series of saturated and unsaturated homologous ketones with a base peak  $m/z$  211  $[\text{CH}_3(\text{CH}_2)_{12}\text{CO}]^+$  in the spectra, therefore based on the assumption of Hites and Biemann [35], we speculate that this series of ketones and alkenes/alkanes are formed from the radical decomposition of the primary product, 14-heptacosanone. In contrast to Hites and Biemann [35] who only reported saturated homologous series of ketones, our pyrolysis products also showed the formation of a homologous series of unsaturated ketones which can only be produced by the radical based pyrolytic degradation of the symmetric mid chain ketone, 14-heptacosanone.

The formation of 2-pentadecanone and 1-dodecene proceeds by a  $\gamma$ -hydrogen transfer mechanism [34,36]. As it can be seen in (Fig 8) 14-heptacosanone, a symmetric mid chain ketone after  $\gamma$ -H transfer and six centre rearrangement to form dominant 1-dodecene and enol product, 2-hydroxy-1-pentadecene, which by keto-enol tautomerism, form 2-pentadecanone [34,36]. The resulting ketone, 2-pentadecanone then undergoes the same mechanism to produce 1-dodecene. The formation of dominant 1-dodecene and 2-pentadecanone show that  $\gamma$ -H transfer is the most likely mechanism for the formation of these compounds.

The aldehyde is the plausible product of homolysis and loss of an inorganic radical comprising the metal cation and an oxygen atom (e.g. CaO) to leave a tetradecanoyl radical which can receive hydrogen from another molecule to produce tetradecanal [37].

From the discussion above it seems reasonable to infer that the ketonic decarboxylation results in the production of a symmetric mid chain ketone, 14-heptacosanone which via radical mechanism forms alkenes/alkanes and a series of unsaturated/saturated ketones. 2-pentadecanone and 1-dodecene are also possibly formed from 14-heptacosanone which experiences six member ring arrangement ( $\gamma$ -H transfer mechanism). Significant to this insight is that 14-heptacosanone is a precursor for the formation of alkenes/alkanes and saturated/unsaturated ketones which suggests that the fatty acids are degraded to its subsequent pyrolysis products via ketone formation.

#### **4.3. Adsorption and relative abundance of flash pyrolysate hydrocarbons and ketones**

Formation of the s-isotherm in this experiment is indicative of an adsorption mechanism [38], which reflects the formation a monolayer of adsorbent followed by the formation of multilayers [39]. As the adsorption of tetradecanoic acid on calcite mineral increases, the overall yield of hydrocarbons and ketones increases, however the abundance of hydrocarbons decreases relative to ketones (Fig 6 and 7, Table 4). Apparently, the increase in ketones can be attributed to the high yield of the primary product 14-heptacosanone from which other homologous ketones are formed (Fig 6). One another possibility for the high yield of ketones is a possible reaction between the fatty acid and short chain carboxylate salts [34]. The minor acid peaks at adsorption maximum, (Fig 6d and e) indicate the excess layers of acids that can react with the carboxylate salt to form ketones.

We have demonstrated that flash pyrolysis of tetradecanoic acid produces hydrocarbons and a series of low molecular weight fatty acids while flash pyrolysis of tetradecanoic acid salt produces hydrocarbons and a series of ketones. The exclusive appearances of ketones from fatty acids that are bound to cations suggest that calcite adsorbed fatty acids can be identified

by the production of these compounds. The reduction in the ratio of hydrocarbons/ketones in the pyrolysis products following an increase in the amount of fatty acid adsorbed onto calcite (Fig 7, Table 4) provides an opportunity to monitor the progress of fatty acid adsorption in natural settings.

#### **4.4. Implications for monitoring fatty acid diagenesis**

When organic matter reaches the base of the water column in marine environments it is juxtaposed to minerals. The nature of the interaction between the organic compound and the mineral surface has a significant control on the fate of the organic matter. There are a number of theories that rely on the adsorption of certain organic structures to mineral surfaces. The ability to monitor the interaction of quantitatively important and relatively universal organic compounds such as fatty acids with mineral surfaces provides a means to obtain insights into the early diagenetic process. Our study has revealed that distinct flash pyrolysis responses occur for those acids which are free and those which are adsorbed onto calcite mineral surfaces. The newly recognised diagnostic information offers the use of flash pyrolysis to reflect the state of fatty acids in the presence of minerals as they pass into the geosphere. The unadsorbed acid recently released from its role in biological organisms is indicated by the presence of alkenes and a characteristic series of unsaturated and saturated low molecular weight fatty acids. Once the fatty acid is adsorbed onto the surface of carbonate minerals its flash pyrolysis products become saturated hydrocarbons, unsaturated hydrocarbons and a characteristic homologous series of relatively high molecular weight saturated and unsaturated ketones. Inevitably, because the results of flash pyrolysis reflect the surface binding characteristics of the fatty acids the products reflect the relative abundance of fatty

acids and the available surface area of the mineral. The flash pyrolysis data can, therefore, track fatty acid-mineral interactions during diagenesis in calcite rich environments.

Our experimental conditions were highly constrained to understand the adsorption characteristics of fatty acids on calcite mineral surfaces. Natural conditions are inevitably more complicated by the presence of mineral mixtures and multiple organic compound classes. Yet this study provides a valuable indication of how flash pyrolysis methods can be used to deconvolve the complex chemistry occurring between organic compounds and minerals and it is expected that further similar studies will provide a more comprehensive understanding of organic compound-mineral interactions during early diagenesis.

## **5. Conclusions**

On-line “flash” pyrolysates of both tetradecanoic acid adsorbed on calcite and tetradecanoic acid salts contain saturated hydrocarbons, unsaturated hydrocarbons, and a homologous series of saturated and unsaturated ketones. On-line pyrolysates of pure tetradecanoic acid include alkenes, an alkane and a series of unsaturated and saturated low molecular weight fatty acids. Our data indicate that on-line pyrolysis can be used to diagnose interactions between fatty acids and calcite mineral surfaces. Progressive adsorption can be recognised by the increase in ketones relative to hydrocarbons in the pyrolysates. On-line pyrolysis, therefore, is an effective method for monitoring the fate of these near ubiquitous lipids as they undergo diagenesis. In particular, theories that invoke the adsorption of organic compounds such as fatty acids to mineral surfaces can be tested in the natural environment.

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Figure captions:

**Fig. 1.** ATR-FTIR spectra of tetradecanoic acid (black line), calcium tetradecanoate (red line), magnesium tetradecanoate (green line), and sodium tetradecanoate (blue line). C=O stretching absorption of  $1700\text{ cm}^{-1}$  moves to the lower wave number for salts.

**Fig. 2.** Adsorption isotherm for tetradecanoic acid adsorbed on calcite,  $q_e$  ( $\mu\text{M/g}$ ) plotted against final tetradecanoic concentration,  $C_e$  ( $\mu\text{M/L}$ ) in 35‰ NaCl saline solution.

**Fig. 3.** Freundlich isotherm of adsorption data plotted logarithmically. The y-intercept is equivalent to  $\log K_f$  and the slope is equal to  $1/n$ .  $\log K_f = 2.1622$ ,  $1/n = 1.4081$  and  $R^2 = 0.947$ .

**Fig. 4.** Total ion chromatograms showing products from flash pyrolysis at  $650\text{ }^\circ\text{C}$ . (a) tetradecanoic acid, retention time between 1.606 to 60.00 min. (b) calcium tetradecanoate, retention time between 0.450 to 60.00 min.  $C_{12:1}$  indicates the dominant peak dodocene, K refers to the main ketones with carbon numbers indicated by the subscripts. See Table 3 for a full list of compounds identified.

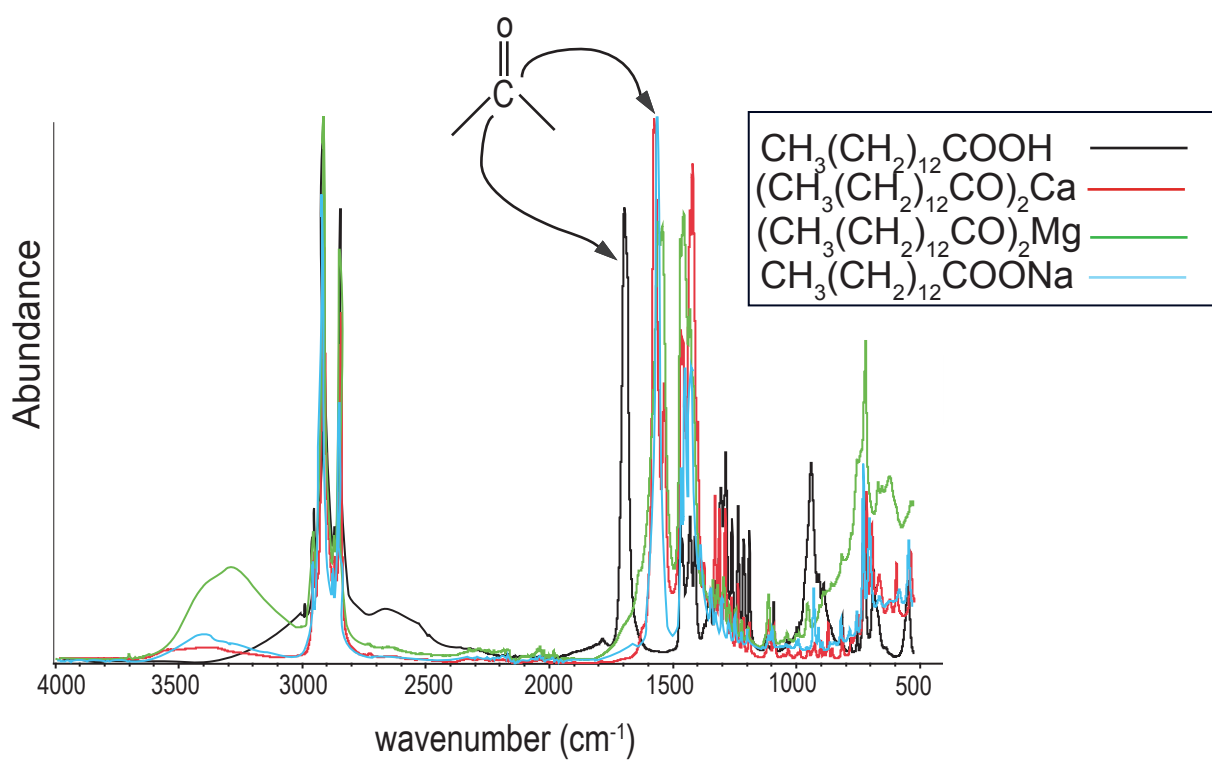
**Fig. 5.** Total ion chromatograms showing products from flash pyrolysis at  $650\text{ }^\circ\text{C}$ . (a) sodium tetradecanoate (b) magnesium tetradecanoate (c) calcium tetradecanoate.  $C_{12:1}$  shows the dominant peak, dodocene, K refers to the main ketones with carbon numbers indicated by the subscripts. See Table 3 for a full list of compounds identified.

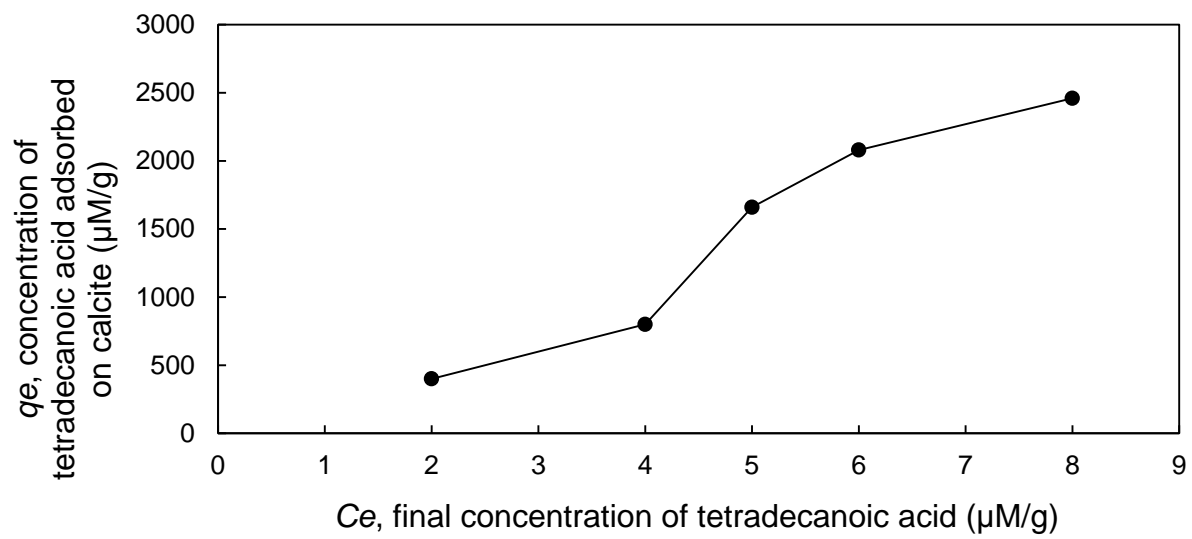
**Fig. 6.** Total ion chromatograms showing products from flash pyrolysis at  $650\text{ }^\circ\text{C}$  of tetradecanoic acid adsorbed on calcite.  $C_{12:1}$  indicates the dominant peak of dodocene, K

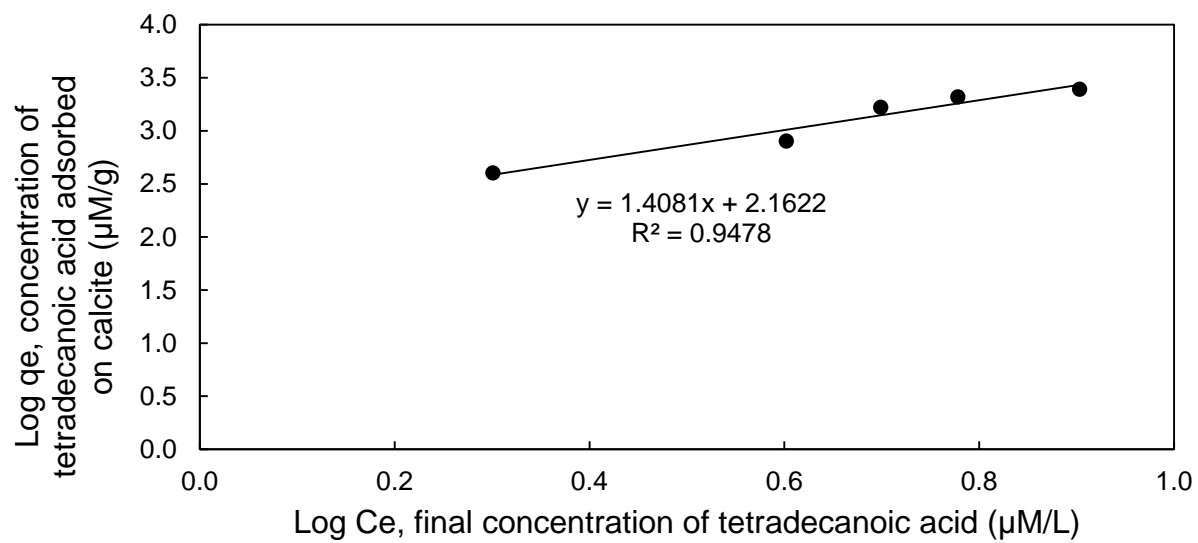
refers to main ketones with carbon numbers indicated by the subscripts. See Table 3 for full list of compounds identified.

**Fig. 7.** Peak areas obtained after manual integration of total ion chromatograms from flash pyrolysis at 650 °C of calcite samples with adsorbed tetradecanoic acid plotted against the amount of tetradecanoic acid adsorbed on calcite ( $\mu\text{M/g}$ ).

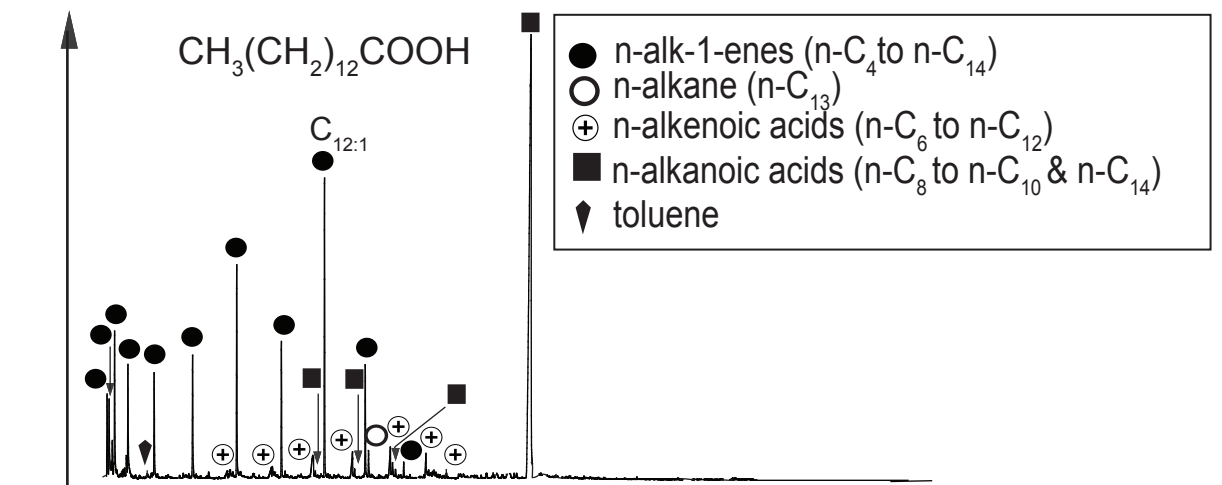
**Fig. 8.** Proposed reaction mechanism for ketonic decarboxylation and rearrangement of two tetradecanoic acid molecule in the presence of calcite to form long chain ketones (fatty ketones) and alkenes.



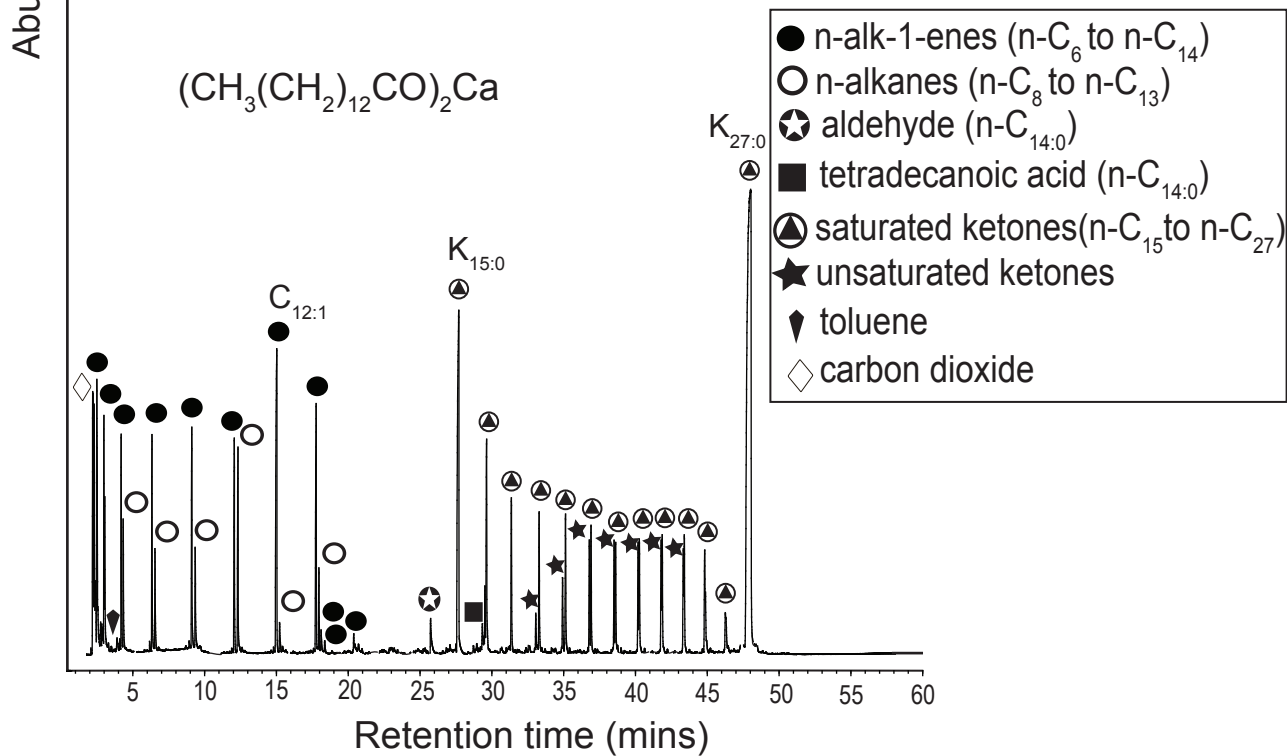




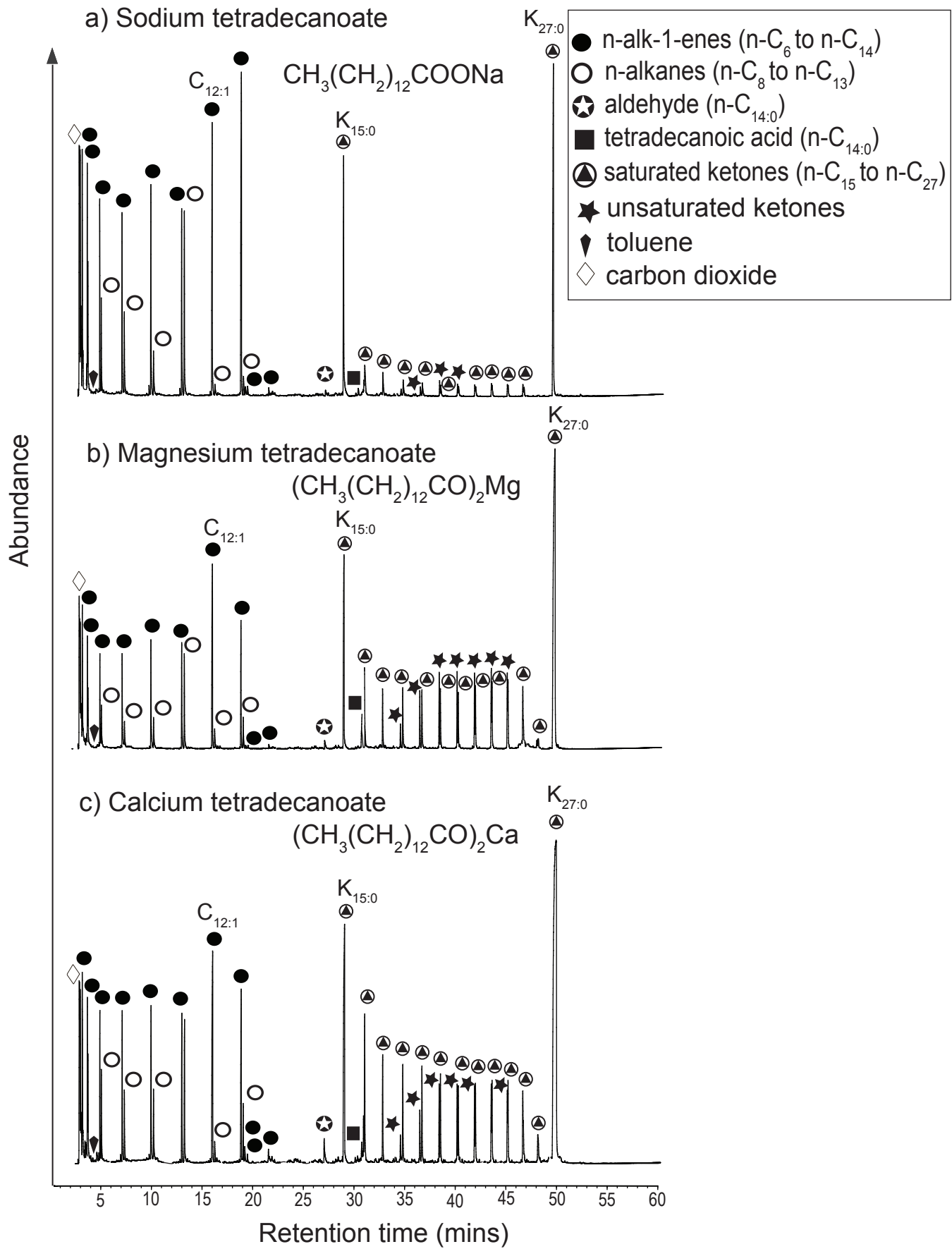
a) Flash pyrolysis of tetradecanoic acid at 650 °C

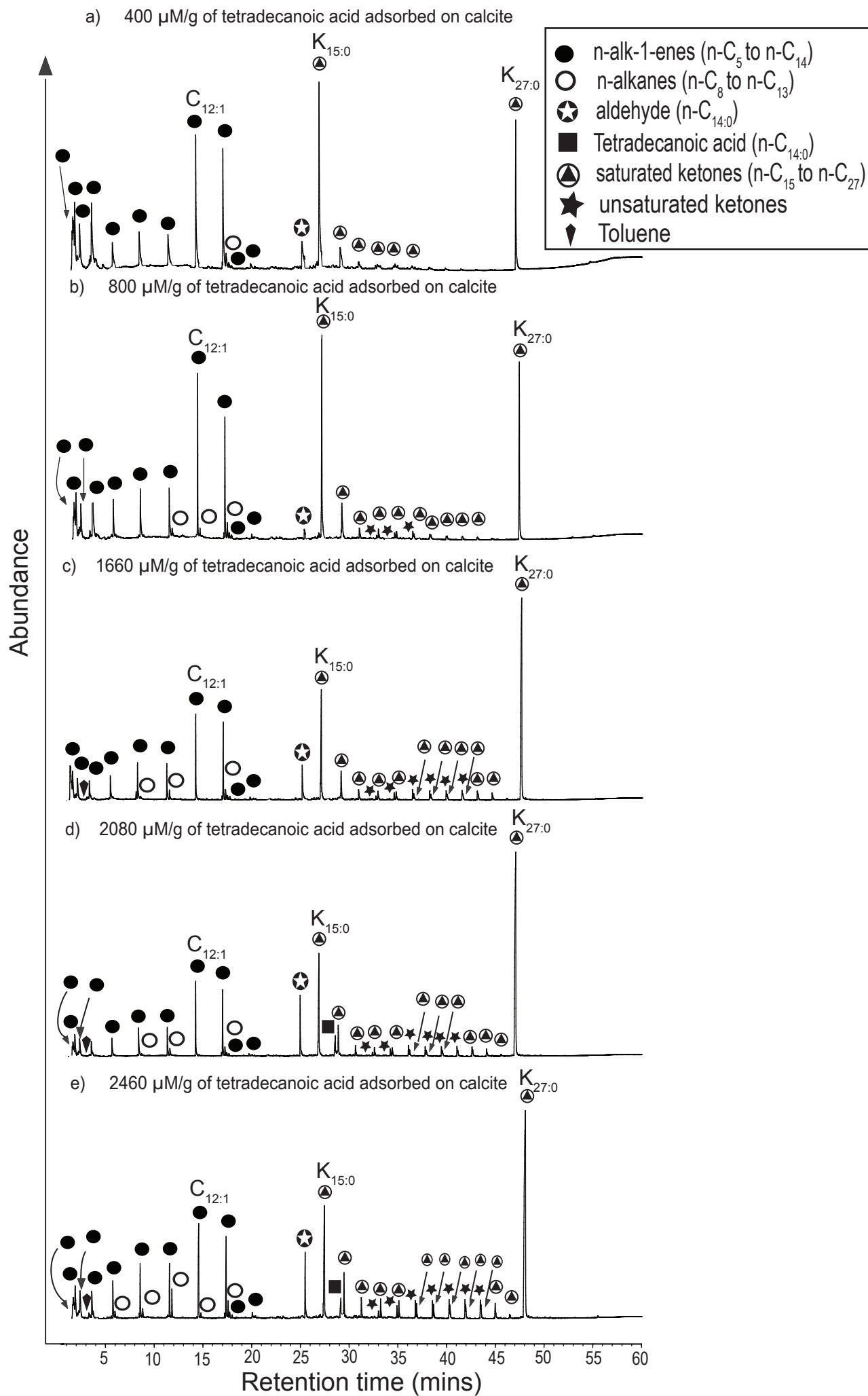


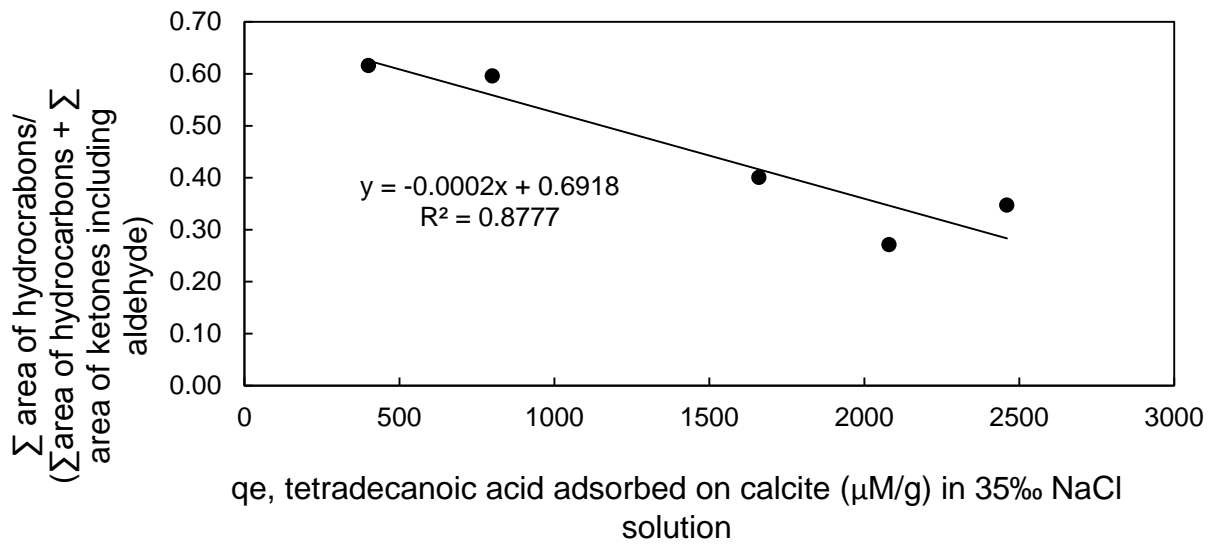
b) Flash pyrolysis of calcium tetradecanoate at 650 °C

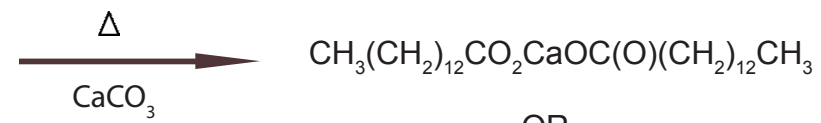
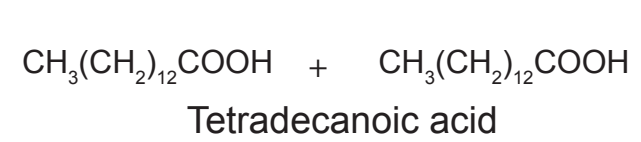




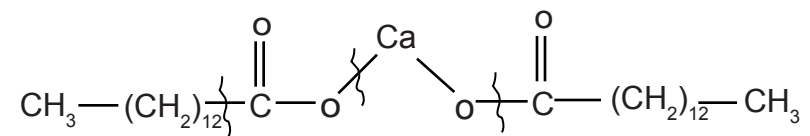






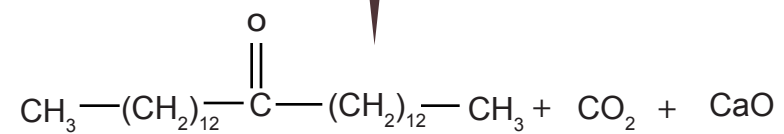


OR



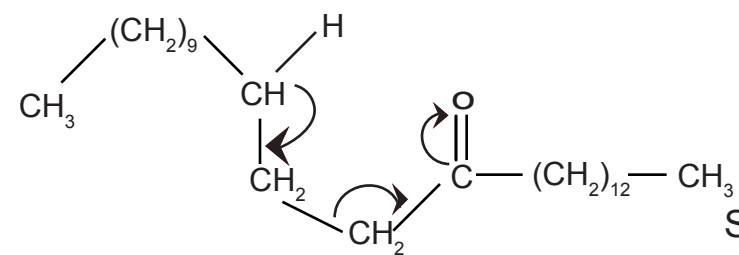
Calcium tetradecanoate

Ketonic decarboxylation

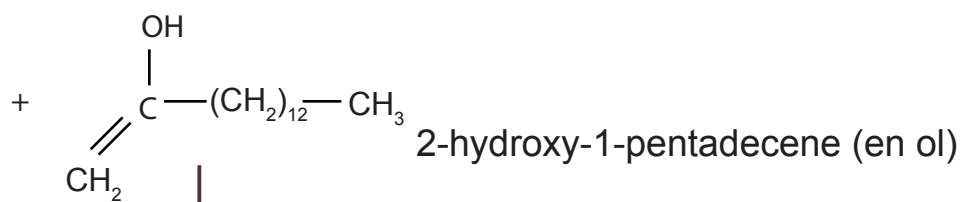
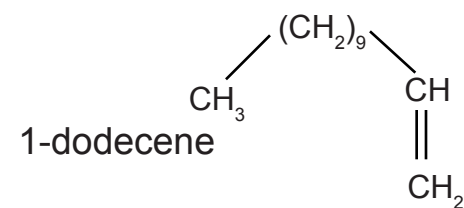
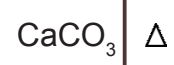


14-heptacosanone (n-C<sub>27</sub>)

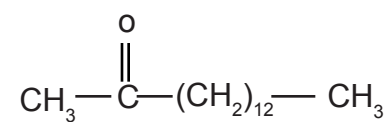
γ - H transfer



Six centre rearrangement



tautomerization



2-pentadecanone

Table 1. Micromeritics Tristar-BET surface area for the calcite adsorbent.

Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	pore size (nm)
0.219	10.74
0.201	11.25
0.206	11.26

Table 2. Adsorption data for tetradecanoic acid on calcite in 35‰ NaCl solution. Final tetradecanoic acid concentration  $C_e$  ( $\mu\text{M/L}$ ) represents the amount retained in the glass test-tubes after 24 hours equilibration at  $23 \pm 2$  °C and is calculated from relative response factors. Adsorbed tetradecanoic acid concentration  $q_e$  ( $\mu\text{M/g}$ ) is obtained after subtracting the final acid concentration from initial acid concentration and then normalized to per gram of calcite.

Calcite (g)	Tetradecanoic acid initial concentration ( $\mu\text{M/L}$ )	$C_e$ , final concentration of tetradecanoic acid ( $\mu\text{M/L}$ )	$q_e$ , concentration of tetradecanoic acid adsorbed ( $\mu\text{M/g}$ )
0.05	22	2	400
0.05	44	4	800
0.05	88	5	1660
0.05	110	6	2080
0.05	131	8	2460

Table 3. Classes of compounds identified in the flash pyrolysates of tetradecanoic acid, adsorbed tetradecanoic acid on calcite and salts of tetradecanoic acid (calcium, magnesium, sodium).

Classes of compounds identified from pyrolysis	Tetradecanoic acid	Tetradecanoic acid adsorbed on calcite	Calcium-tetradecanoate	Magnesium-tetradecanoate	Sodium-tetradecanoate
<b>Alkenes</b>					
	1-Butene	1-Pentene	1-Hexene	1-Hexene	1-Hexene
	1-Pentene	1-Hexene	1-Heptene	1-Heptene	1-Heptene
	1-Hexene	1-Heptene	1-Octene	1-Octene	1-Octene
	1-Heptene	1-Octene	1-Nonene	1-Nonene	1-Nonene
	1-Octene	1-Nonene	1-Decene	1-Decene	1-Decene
	1-Nonene	1-Decene	1-Undecene	1-Undecene	1-Undecene
	1-Decene	1-Undecene	1-Dodecene	1-Dodecene	1-Dodecene
	1-Undecene	1-Dodecene	1-Tridecene	1-Tridecene	1-Tridecene
	1-Dodecene	1-Tridecene	2-Tridecene	2-Tridecene	2-Tridecene
	1-Tridecene	2-Tridecene	3-Tridecene	3-Tridecene	3-Tridecene
	1-Tetradecene	3-Tridecene 1-Tetradecene	1-Tetradecene	1-Tetradecene	1-Tetradecene
<b>Alkanes</b>					
	Tridecane	Octane Nonane Decane Undecane Dodecane Tridecane	Octane Nonane Decane Undecane Dodecane Tridecane	Octane Nonane Decane Undecane Dodecane Tridecane	Octane Nonane Decane Undecane Dodecane Tridecane
<b>Aldehyde</b>					
		Tetradecanal	Tetradecanal	Tetradecanal	Tetradecanal
<b>Ketones</b>					
<b>Methyl ketone</b>					
Symmetric mid-chain ketone		2-Pentadecanone 14-Heptacosanone	2-Pentadecanone 14-Heptacosanone	2-Pentadecanone 14-Heptacosanone	2-Pentadecanone 14-Heptacosanone
Homologous series of saturated and unsaturated ketones		Hexadecanone to Hexacosanone	Hexadecanone to Hexacosanone	Hexadecanone to Hexacosanone	Hexadecanone to Hexacosanone
<b>Unsaturated Carboxylic acid</b>					
	5-Hexenoic acid 6-Heptenoic acid 7-Octenoic acid 8-Nonenoic acid 9-Decenoic acid Undecylenic acid				
<b>Saturated Carboxylic acid</b>					
	Octanoic acid Nonanoic acid Decanoic acid Dodecanoic acid Tetradecanoic acid	Tetradecanoic acid	Tetradecanoic acid	Tetradecanoic acid	Tetradecanoic acid
<b>Aromatics</b>					
	Toluene	Toluene	Toluene	Toluene	Toluene
<b>Gases</b>					
			Carbon dioxide	Carbon dioxide	Carbon dioxide

Table 4. Peak areas obtained after manual integration of total ion chromatograms of flash pyrolysis at 650 °C.  $\sum$ area of hydrocarbons / ( $\sum$ area of hydrocarbons +  $\sum$ area of ketones including aldehydes) shows the ratio of hydrocarbons to ketones including aldehyde.  $q_e$ , tetradecanoic acid adsorbed on calcite ( $\mu\text{M/g}$ ) in 35 % NaCl solution).

$q_e$ , tetradecanoic acid adsorbed on calcite ( $\mu\text{M/g}$ ) in 35 % NaCl solution)	$\sum$ Area (hydrocarbons)	$\sum$ Area (ketones including aldehydes)	$\sum$ area of hydrocarbons / ( $\sum$ area of hydrocarbons + $\sum$ area of ketones including aldehydes)
400	$8.13 \times 10^8$	$5.07 \times 10^8$	0.62
800	$1.69 \times 10^9$	$1.15 \times 10^9$	0.60
1660	$2.51 \times 10^9$	$3.76 \times 10^9$	0.40
2080	$1.55 \times 10^9$	$4.06 \times 10^9$	0.28
2460	$3.16 \times 10^9$	$5.94 \times 10^9$	0.35