

EasyDelta: A spreadsheet for kinetic modeling of the stable carbon isotope composition of natural gases[☆]

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Abstract

A new kinetic model and an Excel[®] spreadsheet program for modeling the stable carbon isotope composition of natural gases is provided in this paper. The model and spreadsheet could be used to describe and predict the variances in stable carbon isotope of natural gases under both experimental and geological conditions with heating temperature or geological time. It is a user-friendly convenient tool for the modeling of isotope variation with time under experimental and geological conditions. The spreadsheet, based on experimental data, requires the input of the kinetic parameters of gaseous hydrocarbons generation. Some assumptions are made in this model:

- (1) the conventional (non-isotope species) kinetic parameters represent the light isotope species;
- (2) the initial isotopic value is the same for all parallel chemical reaction of gaseous hydrocarbons generation for simplicity,
- (3) the re-exponential factor ratio, $^{13}A/^{12}A$, is a constant, and
- (4) both heavy and light isotope species have similar activation energy distribution.

These assumptions are common in modeling of isotope ratios. The spreadsheet is used for searching the best kinetic parameters of the heavy isotope species to reach the minimum errors compared with experimental data, and then extrapolating isotopic changes to the thermal history of sedimentary basins. A short calculation example on the variation in $\delta^{13}C$ values of methane is provided in this paper to show application to geological conditions.

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1. Introduction

The stable carbon isotope ratios of individual light hydrocarbon components are the most important parameters to classify natural gases with respect to its generation process and its post-genetic history (Cramer et al., 2001). Because natural gas is dominated by a few

[☆] Code available from server at <http://www.iamg.org/CGEditor/index.htm>

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simple, low-molecular weight hydrocarbons, important genetic information is commonly obtained from stable carbon and hydrogen isotope ratios. Stable isotope measurements on natural gases provide a kind of “fingerprint” used to assess the nature and thermal maturity of potential source rock, the pathway of gases migration, the presence of mixed-sources gases and, more controversially, reservoir accumulation/loss histories (Tang et al., 2000).

Stable carbon isotopic values and chemical compositions of natural gases have been used to identify both the type of organic matter (Schoell, 1980, 1983; Mattavelli et al., 1983; Faber and Stahl, 1984), and the maturity of source rocks (Stahl and Carey, 1975; Stahl, 1977; Schoell, 1983; Clayton, 1991). Some empirical relationships have been established between carbon isotope of natural gases and the maturity of related source rocks (Stahl and Carey, 1975; Stahl, 1977; Faber and Stahl, 1984; Shen et al., 1988; Dai and Qi, 1989). However, the relationship cannot be applied to other basins due to differences in organic matter type, thermal history, and the accumulation history of natural gases, etc. Therefore, it is necessary to develop mathematical models to describe and predict the variation in $\delta^{13}\text{C}$ values of gaseous hydrocarbons, specifically, $\text{C}_1\text{--C}_3$ hydrocarbons, during natural gas generation. Some kinetic models have been proposed in the last ten years, such as the models by Galimov (1988), Berner et al. (1992), Tang et al. (2000), Cramer et al. (1998, 2001) and Xiong et al. (2004).

Variations in $\delta^{13}\text{C}$ values of natural gases with geological time, maturation or pyrolysis temperature have been observed and measured; the variations show a complex sigmoid shape as described by Rohrbach et al. (1984), Cramer et al. (1998) and Gaschnitz et al. (2001). During both the early stage and late stages of maturation, the carbon isotope compositions become lighter and lighter, and only in the intermediate stage do the $\delta^{13}\text{C}$ values get gradually heavier. In the proposed models, those based on isotope distillation (Berner et al., 1992; Rooney et al., 1995) can only simulate the process of carbon isotope compositions becoming heavier at the middle stage, while the models based on the difference of activation energy distribution between ^{12}C - and ^{13}C -bearing hydrocarbon generation, such as the Model 2 by Cramer et al. (1998), can model the variation in $\delta^{13}\text{C}$ values of natural gases at the early and middle stages. The Model 3 by Cramer et al. (2001) can be used to model the change of $\delta^{13}\text{C}$ values at each stage during organic-matter maturation. However, as suggested by Tang et al. (2000), complicated mathematics hinders model application.

Spreadsheet programs have been employed to simulate hydrocarbon generation, optimize kinetic parameters (Jain et al., 2000), organic-matter maturation (Sweeney and Burnham, 1990) and methane carbon

isotope modeling (Xiong et al., 2004). The aim of this paper is to provide a simple, effective model and spreadsheet tool for modeling the variation in $\delta^{13}\text{C}$ values of natural gas under experimental and geological conditions.

2. Theory and model

2.1. Kinetic equations

Natural gas generation, like the formation of petroleum from kerogen (Ungerer and Pelet, 1987; Schaefer et al., 1990; Schaefer et al., 1999), can be adequately described by a set of n parallel, first-order reactions with a distribution of activation energies (E_i), with a common pre-exponential factor (A). Below, we provide an example of methane generation to describe the kinetic equation, which is the same with any species in natural gas.

The reaction rate constants (k_i) of methane generation from organic-matter or kerogen can be described by the Arrhenius equation

$$k_i = A \exp(-E_i/RT) \quad (i = 1, \dots, n), \quad (1)$$

where T is the absolute temperature (K), R the universal gas constant (kcal/mol/K), A the pre-exponential (or probability factor), and k_i denotes the reaction rate constant (s^{-1}) of methane generation associated with the i th chemical reaction. At time t (in seconds), the unconverted amount of methane precursor associated to the i th reaction (x_i) is expressed by the equation

$$x_i(t) = \exp\left[-\int_0^t k(t) dt\right]. \quad (2)$$

For a constant heating rate (i.e. $dT/dt = H_t$), the unconverted fraction x_i of the i th precursor at time t is given by

$$x_i(t) = \exp[-\Sigma_t \Delta U_i(t)], \quad (3)$$

where

$$\Delta U_i(t) = [U_i(t) - U_i(t-1)]/H_t, \quad (4)$$

and

$$U_i(t) = T(t)A \exp(-E_i/RT(t)) \times \left\{ 1 - \frac{[E_i/RT(t)]^2 + a_1[E_i/RT(t)] + a_2}{[E_i/RT(t)]^2 + b_1[E_i/RT(t)] + b_2} \right\}, \quad (5)$$

where $a_1 = 2.334733$, $a_2 = 0.250621$, $b_1 = 3.330657$, and $b_2 = 1.681534$. Thus, Eq. (2) can be accurately calculated by the Eqs. (3)–(5) (Sweeney, 1990; Sweeney and Burnham, 1990; Burnham and Braun, 1999). The converted fraction (F_i) of a precursor for i th reaction

at time t can be calculated by

$$F_i(t) = f_{0i}[1 - x_i(t)]. \quad (6)$$

The reaction rate (r_i) for i th reaction at time t is expressed as

$$r_i(t) = k_i(t)[f_{0i} - F_i(t)]. \quad (7)$$

For n parallel reactions at time t ,

$$F(t) = 1 - \sum\{f_{0i} \exp[-\sum_i \Delta U_i(t)]\} \quad (i = 1, \dots, n), \quad (8)$$

and

$$r(t) = \sum k_i(t)(1 - F_i(t)) \quad (i = 1, \dots, n), \quad (9)$$

where, f_{0i} is a stoichiometric or weighting factor for the generation potential of reaction i and the sum of the f_{0i} is equal to 1.

Both ^{12}C - and ^{13}C -hydrocarbon generation can be described by the above expressions.

2.2. Isotope kinetic model

Isotope ratios are frequently reported as δ -values, which are defined as

$$\delta^{13}\text{C} = (R/R_{\text{std}} - 1)1000 \text{ (‰)}, \quad (10)$$

where R denotes the $^{13}\text{C}/^{12}\text{C}$ ratio of product and R_{std} the isotope ratio of the standard. Carbon isotope values are frequently given with reference to the PDB standard using Eq. (10). Based on the Eq. (10), the initial $^{13}\text{C}/^{12}\text{C}$ ratio (R_0) can be derived and calculated by

$$R_0 = (\delta^{13}\text{C}_0/1000 + 1)R_{\text{std}}. \quad (11)$$

Here, $\delta^{13}\text{C}_0$ is a given initial carbon isotope value.

As well known, the total generated methane composes both ^{12}C - and ^{13}C -methane, but ^{12}C -bearing methane is predominant, close to 99% in the total methane. Tang et al. (2000) and Xiong et al. (2004) take the total methane measured as ^{12}C -bearing methane during modeling. Therefore, in our model, the following assumptions are made:

- (1) The kinetic parameters of ^{12}C -bearing methane formation can be replaced by those of the whole methane generation.
- (2) The activation energy distribution of ^{13}C -bearing methane generation is similar to ^{12}C -bearing methane, e.g. Gaussian distribution—one of the earliest distributions to receive wide usage (Braun and Burnham, 1998), but the stoichiometric fractions ($^{13}f_{0i}$) of ^{13}C -bearing methane precursors are different from those of ^{12}C -bearing methane precursors ($^{12}f_{0i}$).
- (3) The pre-exponential factor ratio of ^{13}C -methane and ^{12}C -methane generation, i.e. $^{13}A/^{12}A$, is a constant ranging from 1.00 to 1.04 (Cramer et al., 1998; Tang et al., 2000). The $^{13}A/^{12}A$ ratio is taken as 1.02 for simplicity in this paper.

- (4) The initial isotopic value ($\delta^{13}\text{C}_0$) of methane is a constant for n parallel chemical reactions of methane generation, depending on kerogen type. It is close to the cumulative isotopic value of the methane to which all precursors are completely converted.

According to assumption (1), the kinetic parameters of ^{12}C -methane generation can be obtained by fitting two curves of methane generation at different heating rates. Here, the KINETICS2000TM software, a user-friendly kinetics analysis package developed by Braun and Burnham (1998), is applied to fit the ^{12}C -methane kinetic parameters. It can fit rate parameters to chemical reaction data (rate or cumulative reacted) measured at a series of constant temperatures, constant heating rates, or arbitrary thermal histories. The calculation of the Gaussian distribution was done with KINETICS2000. The discretized Gaussian distribution was employed in our spreadsheet.

When the kinetic parameters of ^{13}C -methane generation are given, the following expressions are used to calculate the $\delta^{13}\text{C}$ values from the equations

$$\delta^{13}\text{C}_{\text{cum}}(t) = [R_0 F^*(t)/F(t)/R_{\text{std}} - 1]1000 \quad (12)$$

or

$$\delta^{13}\text{C}_{\text{cum}}(t) = \delta^{13}\text{C}_0 F^*(t)/F(t) + [F^*(t)/F(t) - 1]1000, \quad (13)$$

$$\delta^{13}\text{C}_{\text{inst}}(t) = \{R_0 \sum k_i^*(t)/\sum k_i(t) \times [1 - F^*(t)]/[1 - F(t)]/R_{\text{std}} - 1\}1000. \quad (14)$$

The $\delta^{13}\text{C}$ values of methane cumulating from time $t-1$ to t is given by

$$\delta^{13}\text{C}_{\text{step}}(t) = \delta^{13}\text{C}_{\text{inst}}(t-1) \times \{[F^*(t) - F^*(t-1)]/[F(t) - F(t-1)]\} + \{[F^*(t) - F^*(t-1)]/[F(t) - F(t-1)] - 1\}1000. \quad (15)$$

Here, $\delta^{13}\text{C}_{\text{cum}}(t)$, $\delta^{13}\text{C}_{\text{inst}}(t)$ and $\delta^{13}\text{C}_{\text{step}}(t)$ stand for cumulative, instantaneous and stepwise isotope composition at time t , respectively, and star (*) denotes the ^{13}C -methane. Xiong et al. (2004) also gave the calculation method for cumulative isotope composition of methane.

The spreadsheet is applied to search the kinetic parameters of ^{13}C -methane generation in order to minimize the errors between experimental and calculated data.

3. Spreadsheet structure and notes

This spreadsheet, called EasyDelta, consists of three modules (Input, Modeling and Output—see Table 1)

Table 1
List of modules and sheets of EasyDelta spreadsheet program together with their functions

Name of modules	Sheets	Name of sheets	Functions
Input	1	Input	This sheet is an interface for users keyboarding the essential data to model carbon isotope evolution with heating temperature and time. The kinetic parameters of ^{12}C -methane generation, experimental data and geological conditions are input here
Modeling	2	Modeling	This sheet is an interactive interface and work area. The user can interact with the EasyDelta by setting and adjusting parameters for modeling
	3	Exp 1	These sheets are designed for computing and displaying results and graphs under experimental and geological conditions. The three sheets are hidden to protect them from accidental changes
	4	Exp 2	
5	Application		
Output	6	Report	This sheet contains three tables, which summarize all the details and parameters of the EasyDelta modeling. This sheet provides an opportunity for user to generate graphs
	7	Graph	Several Excel TM charts that are identical to the “Modeling” module are given here. Having completed the modeling, the users can copy or past them into another document or spreadsheet

with a total of seven sheets, for modeling two sets of experimental data at different heating rates, and an application extrapolating to geological conditions.

The input module is a user interface, placed on the first sheet, enabling the kinetic parameters of ^{12}C -methane generation obtained from the KINETICS2000TM software, experimental data at different heating rates (including pyrolysis temperature, heating time and measured carbon isotope composition), and the thermal history of the sedimentary basin. These data are essential for isotope kinetics modeling. The kinetic parameters (i.e. Gaussian distribution) from KINETICS2000TM are keyboarded on “Kinetics Parameters” section of “Input” sheet. The Gaussian distribution will be automatically discretized to 45 activation energies and transferred to the modeling module. The experimental data (heating duration, heating temperature and carbon isotope composition) and geological data (geological time and temperature) are input on the bottom section of the “Input” sheet. The maximum of laboratory data points and geological time steps is allowed up to 15.

The modeling module is composed of four sheets, i.e. “Modeling”, “Exp 1”, “Exp 2” and “Application” sheets, which are used for searching the best-fit parameters, modeling carbon isotope composition at experimental conditions and extrapolating, if required, to sedimentary basin conditions. The parameters modifiable within this module are: mean activation energy, variance (Sigma) and stoichiometric fractions related to ^{13}C -methane generation. A fourth modifiable value is the initial carbon isotope composition ($\delta^{13}\text{C}_0$), which is

adjusted according to the $\delta^{13}\text{C}$ value when the methane generation reaction completed. Other data are transferred from the input module and cannot be modified. Once the four parameters are given, the calculated results and graphs are displayed in the “Modeling”, “Report” and “Graph” sheets, respectively. The four parameters (mean activation energy, variance (Sigma), stoichiometric fractions and the initial carbon isotope composition ($\delta^{13}\text{C}_0$)) can be adjusted or optimized by the nonlinear programming solver built in ExcelTM until an acceptable result is achieved. This sheet is the work area where the user can interact with EasyDelta by setting and adjusting the parameters of modeling.

The output module is made up of two sheets, “Report” and “Graph” sheet. Modeling results, calculated errors, as well as instantaneous, cumulative and stepwise isotope composition under geological conditions are summarized on the “Report” sheet. This sheet contains all the details and parameters of the EasyDelta modeling to display the details on one page. This sheet also provides an opportunity for the user to choose the graphical output. Graphs, including a histogram of the activation energy distribution and variations of carbon isotope composition with geological time, are together displayed on the “Graph” sheet. These graphs, identical to the graphs in the “Modeling” module, can be copied and pasted into other documents or spreadsheets. The E-mail address of the correspondence author and faculty website are also given on the top of every page for correspondence and future reference.

When modeling methane isotope fractionation the Gaussian energy distribution is automatically discretized

in EasyDelta. Generally, the spacing of activation energies should be less than 1 kcal/mol or 5 KJ/mol; the trend of isotope compositions, especially instantaneous isotope composition, may be unsmoothed or even oscillatory when discrete distributions with irregular activation energy intervals are employed (Tang et al., 2000; Cramer et al., 2001). Therefore, discrete distributions of activation energy are little used in isotope modeling but if necessary, acceptable results can be achieved by using the discrete activation distribution with no greater than 1.0 kcal/mol spacing between energies.

Both the mean activation energy and the variance of ^{13}C -methane generation can be optimized with the nonlinear programming solver, a tool built in ExcelTM. The two initial values are based on those of ^{12}C -methane kinetics. Usually, the isotopically heavy species shows slightly higher mean activation energy and a slightly greater variance than that of the isotopically light one. In the calculated example (see Section 5), the mean activation energy and the variance (Sigma) of ^{13}C -methane generation are 0.2% and 0.5% greater than those of ^{12}C -methane generation, respectively, suggesting that the activation energy distribution of ^{13}C -methane is a little wider than that of ^{12}C -methane and a little higher mean activation energy.

Generally, initial carbon isotope values are lighter than those of bulk organic-matter. Therefore, the initial carbon isotope composition, depending on the organic-matter type, is given by a smaller value than bulk organic-matter. Realistic results were not reached when applying the measured carbon isotope ratios of total organic carbon (Cramer et al., 1998). Here, the methane $\delta^{13}\text{C}$ near the end of conversion is used as the initial carbon isotope value for modeling.

Every given initial parameter, such as $^{13}\text{A}/^{12}\text{A}$ ratio, can be optimized with the solver built in Microsoft[®] ExcelTM. This spreadsheet can be also used for modeling the isotope fractionation of ethane and propane. If improved a little, the spreadsheet can be applied to another types of isotope models with different activation energy distributions, such as a Weibull distribution, or other types of kinetic models. It has the potential to be further developed for related use.

4. How the spreadsheet works

The schematic presentation of the EasyDelta spreadsheet is given in Fig. 1. The spreadsheet carries out the modeling and generates the results in three steps:

1. Input of the essential data and kinetic parameters.
The kinetic parameters (i.e. mean activation energy and its variance) of ^{12}C -methane generation and

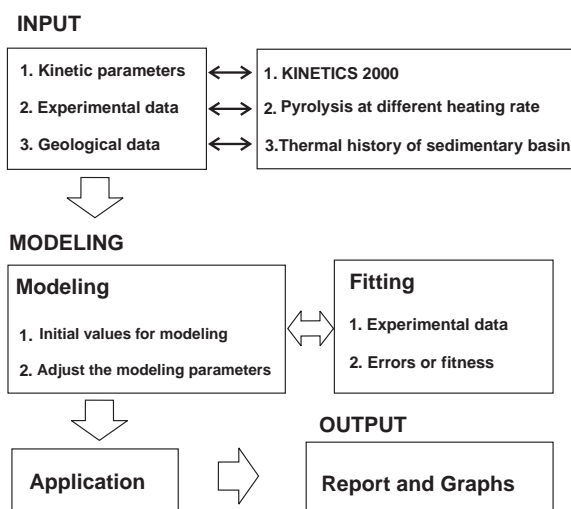


Fig. 1. Schematic flowchart of EasyDelta modeling.

measured isotope values are the essential data for modeling. They are input via the “input” sheet. The kinetic parameters are typed in the top box on this sheet. The experimental data and geological times/temperatures are input in the following three boxes, respectively. When inputting the essential data and kinetic parameters, the module calculates the essential data necessary for modeling, such as heating rate, and then transfers them into the corresponding sheets needed for the “modeling” module computation after checking effective range of each input entry. The software KINETICS2000TM is necessary for the user to obtain kinetic parameters from pyrolysis experiments.

2. Search of the mean activation energy and the variance of ^{13}C -methane generation.
After the calculation of essential data, the “modeling” module starts to compute the converted fraction of heavy species of methane, carbon isotope values and total error between measured and calculated isotope values according to the given initial parameters of the activation energy distribution of ^{13}C -methane generation (i.e. mean activation energy and its variance). The mean activation energy and its variance of ^{12}C -methane generation can be taken as the initial values of ^{13}C -methane generation kinetics. These two parameters have to be adjusted manually or by using the built-in nonlinear programming solver within Microsoft[®] ExcelTM. Once any one of the two parameters is changed, every sheet of the “modeling” module will be updated, and will illustrate the error between measured and computed values. Usually, the initial result is not good enough as the total error is too great to be accepted. However, the initial result restricts the activation energies distribution of ^{13}C -methane to a certain

range. It is well known that the initial parameters are very important for most programming solutions. Therefore, this step is necessary for searching for the best-fitting parameters.

3. Optimization of the stoichiometric fractions of ^{13}C -methane generation.

When the mean activation energy and variance of ^{13}C -methane generation have been estimated or optimized, the calculated isotope values will be roughly close to the measured. Generally, the total error is too great to apply to geological conditions or to explain the experimental data. The most important step is that the stoichiometric fractions of ^{13}C -methane generation kinetics, named “variant” column on “modeling” sheet, are optimized with the nonlinear programming solver built in EXCEL™. The sum of numbers on the “variant” column will be normalized to 1.0 as the stoichiometric fractions of ^{13}C -methane generation. For most cases, acceptable results and total error will be achieved by above steps and techniques except the initial isotope value ($\delta^{13}\text{C}_0$) is improper.

The results of this calculation are presented in table form on the “Report” sheet and in chart form on the “Graph” sheet of output module. After reaching an acceptable error, the results can be employed to extrapolate them sedimentary basins. The “Graph” sheet provides several charts usually employed according to modeling results. All the details of the modeling calculation and the interesting figures are provided on the “Report” sheet to meet on users’ needs.

The next section presents the use of the EasyDelta spreadsheet and its capabilities with an example calculation based on the closed pyrolysis experiment of coal and geological setting.

5. Example calculations

Well Kela 2 is the biggest gas field in Tarim Basin, Northwestern China. It is commonly accepted that the source bed is Jurassic coal. However, the reservoir accumulation history is not understood clearly. The stable carbon isotope modeling of methane is helpful to understand the gas accumulation history of this gas field. The calculation process is here provided as an example; complete information will be published elsewhere. The EasyDelta spreadsheet has been used in this paper for modeling the variation of carbon isotope ratios with geological time and thermal history.

5.1. Pyrolysis experiments

A coal source rock sample from the basin was ground into powder to 80–100 mesh after cleanout. The

powdered samples were processed with HCl, HF and distilled water to isolate the kerogen. Kerogen powder (10–30 mg), depending on heating temperature, was put into gold tubes and welded under an argon atmosphere. Then, the welded tubes were heated in a confined system at heating rates of 2 and 20 °C/h, respectively. Details of the system have been described by Behar and et al. (1992).

The products were analyzed by GC with FID and GC-IR-MS. GC analysis can provide the information on variance in individual gas components with heating temperature and time at different heating rates. By using the KINETICS2000 software, the kinetic parameters of the total methane generation can be obtained. Here, a Gaussian distribution is assumed to achieve a smooth isotope trend. The kinetic parameters are, respectively, the pre-exponential factor ($A = 5.5096E+08 \text{ s}^{-1}$), mean activation energy ($E1 = 46.74 \text{ kcal/mol}$) and its variance ($S1 = 9.571\%$, $E1$). They were used as the kinetic parameters for ^{12}C -methane formation.

GC-IR-MS analysis provides the data on carbon isotope change with heating temperature/time, and yields the constraints and calibrations on ^{13}C -methane generation kinetics. For simplification, the pre-exponential factor ratio is assumed to be a constant ($^{13}A/^{12}A = 1.02$). Now, the methane isotope ratio modeling is reduced to the activation distribution of ^{13}C -methane generation.

5.2. Methane carbon isotope modeling

The mean activation energy (46.74 kcal/mol) and its variance (4.47 kcal/mol, i.e. 46.74*9.571%) of ^{12}C -methane are first given as initial values of the activation distribution of ^{13}C -methane generation. This results in a big total error and a bad fit between measured and calculated cumulative isotope ratios, which indicates the initial values are not good parameters and have to be adjusted. The nonlinear programming solver built-in Excel™ is then used as a convenient method to search for the best solutions for both mean activation energy and the corresponding sigma (i.e. variance) to minimize the total error in the cell D18 of the “Modeling” sheet. The default settings of the solver are then employed in the EasyDelta spreadsheet program. When searching for the best solutions of mean activation energy and the corresponding sigma, the total error (D18) was chosen as the target cell, the target value of the total error was set zero, the cells D15:D16 were used as the variant cells with a restrain value ($> = 0$). The resulting solution is 46.81 and 4.49, respectively. Yet the fit is still not acceptable, but the activation energies distribution range for modeling ^{13}C -methane generation is restricted by this initial solution (i.e. mean activation energy and the corresponding sigma). Based on the above solution, a fast and effective way to modeling ^{13}C -methane

generation and isotope composition is to search the best stoichiometric fractions of ^{13}C -methane generation by using the nonlinear programming solver. Usually, the final solution will be achieved by searching the stoichiometric fractions of ^{13}C -methane. In this case, as stated above, the total error (D18) was chosen as the target cell with the target value equal to zero and the column “Variant” on the “Modeling” sheet as the variant cells with a restrain value (≥ 0). The best fit between measured and calculated isotope values and the best stoichiometric fractions of ^{13}C -methane generation corresponding to activation distribution are obtained and illustrated in Fig. 2. Total error is 2.99, which is low enough to be accepted.

In this case, the total error is a sum of square of the differences between measured cumulative carbon iso-

tope composition and calculated values. As the confined system pyrolysis used here yields only cumulative data with a sufficiently low error to suggest that the calibrated parameters can be extrapolated to geological conditions to model natural gas isotope variance, and its accumulation/loss history in sedimentary basins.

5.3. Application

The calibrated parameters of ^{13}C -methane kinetics are coupled with those of ^{12}C -methane to address actual reservoir accumulation/loss history. Kela 2, located at Kuqa depression, is the biggest natural gas field in the Tarim Basin. The gases are derived from gas-mature Lower Jurassic coals ($>2.4\%$ Ro) at the center of Kuqa depression. The mudstones overlying the coal beds are

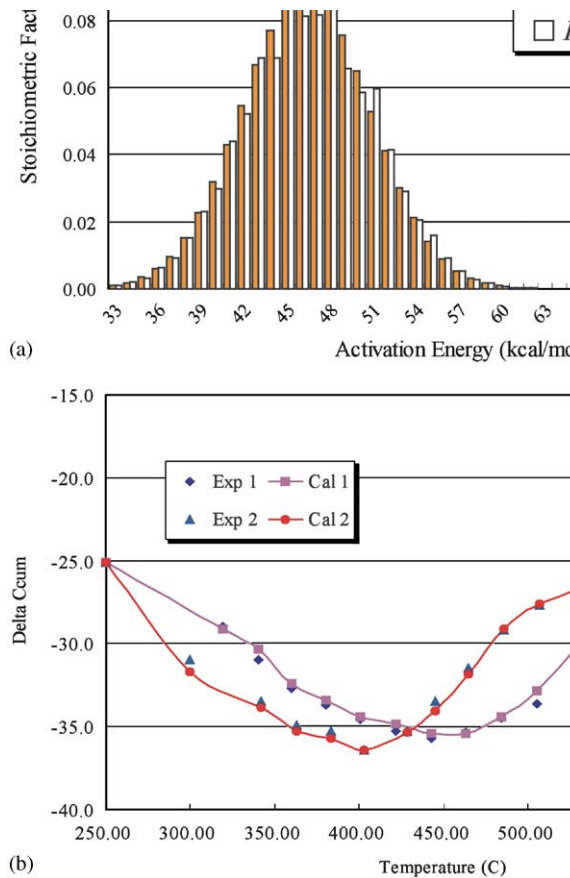


Fig. 2. Screen shot showing (a) activation energy distributions of ^{12}C - and ^{13}C -methane generation and (b) fitness between measured and calculated $\delta^{13}\text{C}$ values.

the local seal. While Cretaceous and low Tertiary sandstones are the main reservoir rocks, Tertiary gypsum-bearing mudstone, up to 1000 m, are the regional seal rocks. At the beginning of Jurassic, the depression began to continuously sink except for a mild uplift at the end of Cretaceous. From 5.3 to 2.0 Ma, however, the compressive stress increased. At about 2.0 Ma before present, some thrust faults cut the bottom of the seals (Liu et al., 2001) and overpressure occurred in this field (Pi et al., 2002; Song et al., 2002).

The methane in the reservoir has a $\delta^{13}\text{C}$ value of -27 to -28 (‰, PDB). When the variation in $\delta^{13}\text{C}$ value of methane with geological time/temperature is coupled with geological structure evolution, both match satisfactorily (Fig. 3). The arrow and line at 16.9 Ma indicate the

variation in methane carbon isotope values if the natural gases start accumulation at 16.9 Ma. The filled box is the range of measured methane carbon isotope values of Kela 2 field. The cross point of the box and the lines of $\delta^{13}\text{C}$ variation with geological time indicate the end of gas accumulation. If the natural gas accumulated from 16.9 Ma, this field would have had too short a time to accumulate natural gas generated under geological conditions, and a little gas would have been trapped in this field. Therefore, gas accumulation must have started before 16.9 Ma. The isotopic composition suggests that the natural gas in Kela 2 gas field was accumulated from Early Cretaceous to 2.0 Ma. However, from 2.0 Ma to present, this gas pool was no longer filled because of faulting and overpressure. If the pool started accumulation too late, there would not be enough gas sources to form such a big field.

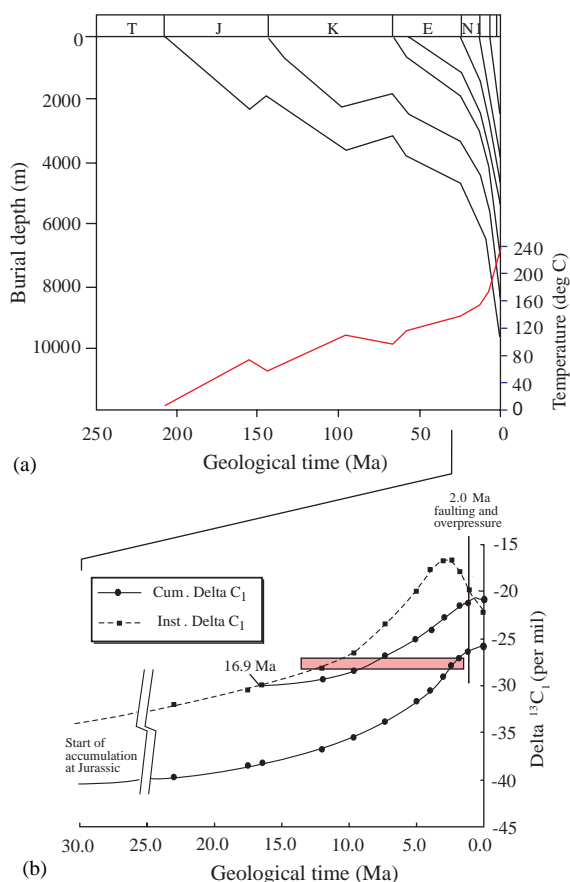


Fig. 3. Burial history and thermal history of natural gas kitchen (a) and $\delta^{13}\text{C}$ variation with geological time/temperature (b) marked with $\delta^{13}\text{C}$ range in Kela 2 gas field to illustrate possible accumulation/loss history. The arrow and line at 16.9 Ma indicate variation in methane carbon isotope values if natural gases start accumulation at 16.9 Ma. The filled box is range of measured methane carbon isotope values of Kela 2 field. The cross point of box and lines of $\delta^{13}\text{C}$ variation with geological time means end of gas pool charge.

6. Conclusions

EasyDelta is a spreadsheet program, which is specifically developed for the kinetics modeling of carbon isotope. It runs on Microsoft[®] Excel[™]2000 under Windows2000. With its user-friendly, interactive interface, it simplifies the modeling process and is an easy and convenient tool for fitting experimental data, gas-source correction and reconstruction of natural gas accumulation/loss history. The program also provides users with some charts and details of the modeling calculations, and allows users to readily plot interesting figures for publication.

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