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February 7, 1984

Mr. John T. Greeves  
Acting Branch Chief, Engineering Branch  
Division of Waste Management  
Nuclear Regulatory Commission  
Washington, D.C. 20555

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WM Project 10,11,16  
Docket No. \_\_\_\_\_

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Dear Mr. Greeves:

In accordance with NRC/BOM Interagency Agreement No. NRC-02-08-075, "Technical Assistance for Assessment of Repository Siting and Design," we are forwarding a review conducted for NRC by BOM's Methane Control specialists at the Pittsburgh Research Center. The documents reviewed were:

- 1) Report entitled, "Methane Gas Production Testing in the Vicinity of the Candidate Repository Site."
- 2) "Report Covering the Possibility of a Methane Accumulation Under the Reference Repository Location Hanford Site."
- 3) Consultant report from Roger L. King, BOM.

Sincerely,

*Harry R. Nicholls*

Harry R. Nicholls  
Assistant Director, Mining Research

Enclosures

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January 31, 1984

Memorandum

To: Chief, Division of Health and Safety Technology *DAF 4/6*  
Through: Research Director, PRC *gmm*  
From: Research Supervisor, GMC  
Subject: Review of BWIP documents, NRC/BOM Interagency Agreement  
No. NRC-02-80-075

Per your request I have had a technical review made of the following documents:

- 1) Report entitled, "Methane Gas Production Testing in the Vicinity of the Candidate Repository Site."
- 2) "Report Covering the Possibility of a Methane Accumulation Under the Reference Repository Location Hanford Site."
- 3) Consultant report from Roger L. King, BOM.

All of the documents address methods to assess the potential methane reservoir in the vicinity of the Reference Repository Location. The documents are all straightforward, in that the theories postulated for the genesis of the methane are standard. The recommended tests (isotopic characterization of various gases,  $\Delta C$  geochemical soil survey, etc.) are all standard practice for the oil and natural gas industry. The suite of tests and analysis recommended by the three documents are all valid and, depending upon the resources, available should all be pursued in attempting to characterize the potential methane reservoir.

I have also enclosed a recent paper on genetic characterization of gas for forwarding to the NRC.

*Roger L. King*  
Roger L. King

cc: J. N. Murphy  
R. L. King  
A. T. Iannacchione  
D. M. Hyman

GMC:RLKing:a11:FTS 723-6550

# Genetic Characterization of Natural Gases<sup>1</sup>

MARTIN SCHOELL<sup>2</sup>

## ABSTRACT

Natural gases can be characterized genetically using four properties:  $C_{2+}$  concentration, carbon and hydrogen isotope variations in methane, and carbon isotope variation in ethane. Three diagrams for genetic characterization of gases have been designed in which the carbon isotopic composition of methane is correlated with the other parameters. In these diagrams, compositional fields have been defined for primary gases (biogenic, thermogenic associated, and thermogenic nonassociated) and for gases which result from mixing of these gases. These fields are strictly empirical and comprise compositional variations found in about 500 natural gases. The isotopic and compositional variations in natural gases can be described in terms of (1) processes during formation of the gases such as bacterial fermentation or maturation of organic matter, and (2) processes during secondary migration. Mixing of primary gases is an important and common process. Migration of gases predominantly affects the  $C_{2+}$  concentration, whereas the isotopic properties of gaseous hydrocarbons primarily remain unchanged, allowing an assessment of the origin of migrated gases and properties of their source rocks. The formation of gas from humic organic matter and coals is not yet clear from published data.

The diagrams use data from various basins and areas. Interstitial gases from the Gulf of California are entirely of bacterial origin; traces of thermogenic gases are formed only in the vicinity of dolerite sills; gases in the south German Molasse basin and in the Vienna basin are of bacterial, mixed, and thermogenic origins. Data from the north Italian Po basin provide examples for genetic characterization of migrated gases.

## INTRODUCTION

Natural gases occur in a variety of environments. Bacterial processes form gases in continental swamps or marine sediments. Natural gases of bacterial origin are found in

basins where the sediments are immature; such gases are rich in methane and are not associated with oils. In deeper strata, natural gases are formed and are often associated with petroleum. These deep gases result from processes of thermal alteration of petroleum and/or organic matter in source rocks. In more mature areas, dry gas may form from decomposition of oil and/or organic matter source rocks.

Once gases have formed in a specific environment, they migrate to a reservoir. The new environment may represent a different maturation regime than that of the source. Gases of different origins may thereby become mixed during migration. Therefore, primary processes of gas generation and the subsequent changes (which could be referred to as secondary processes) account for the variety of natural gases found.

Many attempts have been made in natural gas geochemistry to deduce the origin and in many cases complex history of gases from their compositional variations. In particular, the carbon isotopic composition of methane and, more recently, its hydrogen isotopic composition have been found useful for recognition of the origin of a gas. Bacterial gases are devoid of most  $C_{2+}$  hydrocarbons, and the methane in them is depleted in  $^{13}C$  (Nakai, 1960; Colombo et al, 1969; Claypool and Kaplan, 1974; Coleman, 1978; Schoell, 1980). Some coal gases are enriched in  $^{13}C$  in their methane compared to gases from type II organic matter (Stahl, 1977). Also  $^{13}C$  in methane increases with maturity (Galimov, 1968). Similar effects have been found for the hydrogen isotopic composition in methane (Schoell, 1980).

No consistent description currently exists of all types of natural gases in terms of these genetically controlled properties. It is the objective of this paper to establish a generally applicable genetic characterization of natural gases. This in turn will allow recognition of complex origins of natural gases. It must be emphasized that this approach has the principal limitation of a restricted data base. Approximately 500 natural gas analyses have been used to establish variability boundaries of some genetically relevant properties. In natural gases, however, absolute boundaries do not exist for these properties. Also, it is likely that exceptions will be found to the generalization presented. Application of the presented model is to be seen as a guide to the genetic interpretation of properties in natural gases. A first detailed example of the application of this concept is given in a companion paper by Mattavelli et al (1983) in this issue.

## PREVIOUS GENETIC MODELS FOR NATURAL GASES

Past genetic models tried to explain the origin of natural gases in terms of variation of their  $^{13}C$  concentration of the

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This paper could only be written by using many samples made available by various oil companies. I am particularly grateful to AGIP San Donato, Brigitta Elwerath Betriebsführungsgesellschaft, Deminex, Deutsche Schachtbau und Tiefbohrergesellschaft, Preussag AG, Deutsche Texaco, Österreichische Mineralölverwaltung Wien, Rohöl Aufsuchungsgesellschaft Wien, Tenneco Oil Co., and Wintershall AG Kassel.

The paper benefitted from many comments by M. Whiticar, G. E. Claypool, S. Silverman, and D. D. Rice, which are gratefully acknowledged.

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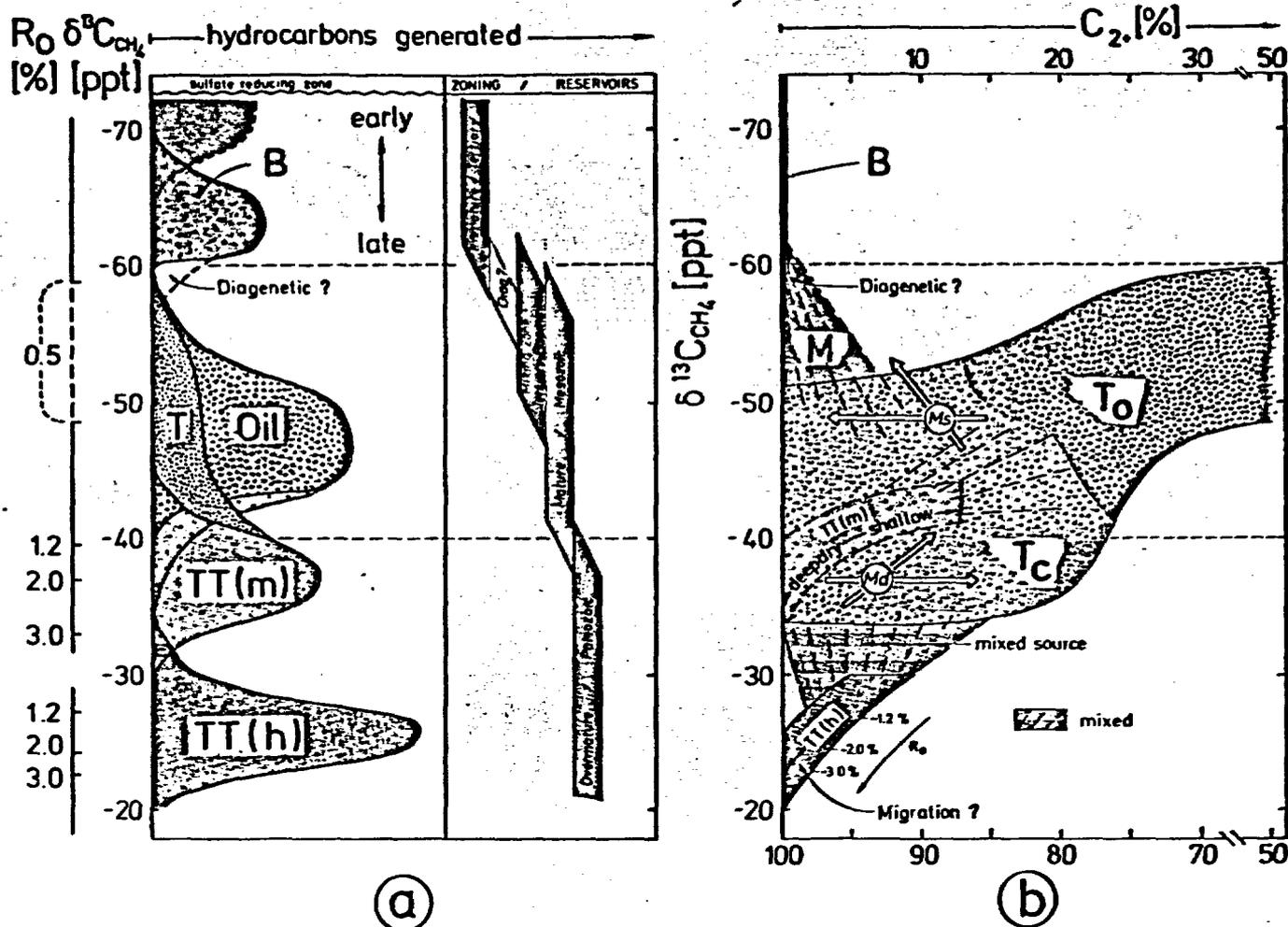


FIG. 1—Genetic characterization of natural gases by compositional and isotopic variations. Genetic fields for various types of gases are defined in diagrams, allowing recognition of origin of a gas.

(a) Schematic illustration of formation of natural gas and petroleum in relation to maturity of organic matter.

(b) Relative concentration of C<sub>2+</sub> hydrocarbons in gases in relation to <sup>13</sup>C concentration in methane. Arrows Ms and Md indicate compositional changes owing to shallow and deep migration, respectively (see text). Mixing of gases results in linear trends of compositional changes (see Figure 2).

(c) Variation of deuterium and <sup>13</sup>C in methane of natural gases. Mixing in diagram results in linear changes between compositions of respective end members.

(d) Carbon isotope variations in ethane related to carbon isotope variations in methane. Compositional changes because of mixing of gases depend on methane and ethane concentrations. Bent mixing pathways are given schematically to indicate isotopic changes due to deep migration. Arrow Md would result if pure isotopically positive CH<sub>4</sub> were to mix with a gas. Admixture of biogenic methane results in change of δ<sup>13</sup>C of methane only (arrow Ms).

methane in relation to the concentration of hydrocarbons in the gas. Based on carbon isotope variations in methanes, Kartsev et al (1971), Alekseyev et al (1972), and Alekseyev (1977) proposed a general zoning of gas formation by defining a biochemical, a transition, and a thermochemical zone, respectively. Stahl (1974) presented a concept in which immature, mature, and overmature gases were characterized by continuously increasing <sup>13</sup>C concentrations in their methanes, and the C<sub>2+</sub> concentrations were inferred to change in a continuous fashion: low C<sub>2+</sub> content in immature, high C<sub>2+</sub> content in mature, and decreasing amounts of higher hydrocarbons in overmature gases. Also, gases from terrestrial and marine source rocks were differentiated. His model, though very useful

as a first attempt, did not incorporate associated gases and did not consider secondary processes.

Bernard et al (1977) proposed a genetic diagram similar to Stahl's (1974) by correlating C<sub>1</sub>/(C<sub>2</sub> + C<sub>3</sub>) ratios with the <sup>13</sup>C concentration of the methane. In this genetic diagram, compositional fields were defined for thermogenic or bacterial gases, and mixing of both types of gases was considered. However, this model did not incorporate gases of specific origins (terrestrial or marine source), nor did it give credit to the maturity concept.

In this paper, an entirely empirical approach is suggested for the genetic characterization of natural gases. An attempt is made to explain all compositional variations in gases in terms of (1) processes during their formation, and

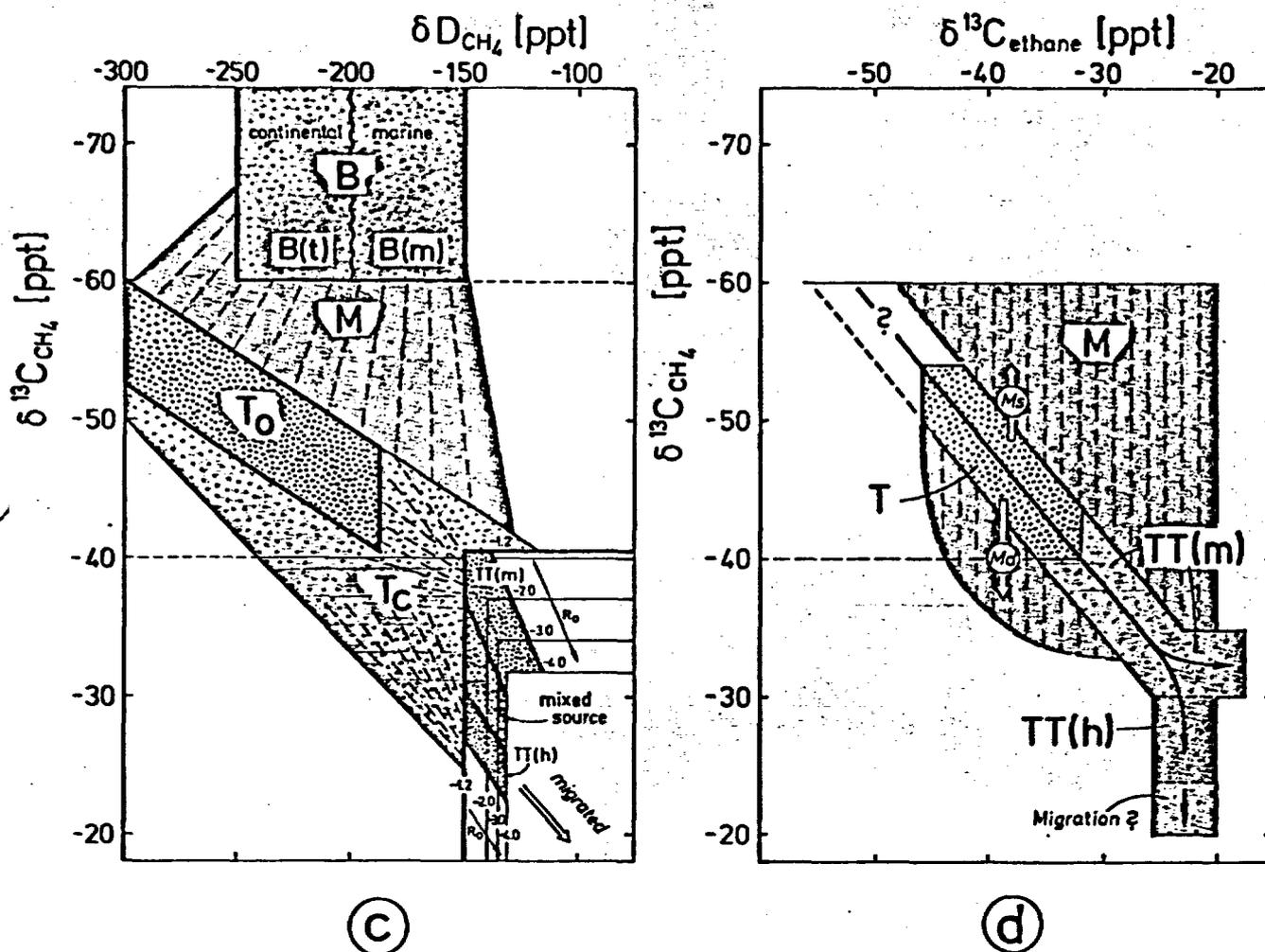


FIG. 1 Continued

(2) compositional changes after their formation.

#### PREREQUISITES AND DEFINITIONS

##### Primary Gases

This paper follows the classification of types of natural gases used by Schoell (1980) (Fig. 1a). Primary gases originate from the two principal processes of gas formation—bacterial respiration (biogenic) and thermal alteration of liquid or solid organic precursors (thermogenic).

Biogenic gases (B)<sup>3</sup> originate in immature regimes from bacterially mediated anaerobic mineralization of organic matter in sediments. There is convincing evidence that the same bacterial processes observed in recent sediments account for gas accumulations in young sedimentary basins (Schoell, 1977; Claypool, 1979; Rice and Claypool, 1981; Mattavelli et al, 1983).

<sup>3</sup>The following abbreviations are used in this paper.

B = Biogenic gas; B(m) and B(t) denote marine and terrestrial (or continental) environments, respectively; T = associated gases; T<sub>o</sub>/T<sub>c</sub> = gases associated with petroleum and condensates respectively; TT(m) = nonassociated dry gases from sapropelic liptinitic organic matter; TT(h) = nonassociated gases from humic organic matter; M = mixed gas.

Two stages of thermogenic gas formation may be differentiated: (1) during or immediately following oil formation, which results in gases associated with crude oils (T), and (2) following the principal stage of oil formation, which results in dry or deep dry gases (TT).

The use of terms "associated" and "nonassociated" in this paper is different from the standard petroleum geologic usage, which has no genetic connotation. Levorsen and Berry (1967) defined associated gases as those produced when oil exists as a separate phase in the reservoir; if only gas is present, it is termed nonassociated. If these definitions are to be used when discussing the origin of gases, the usage becomes slightly different. If, for example, a gas from a gas cap migrates off its primary reservoir it may become a nonassociated gas in standard usage but it still has the isotopic composition of an associated gas. Subsequently, it may become a nonassociated, extremely dry gas in a shallow reservoir, yet it still would be recognized isotopically as a formerly associated gas. In genetic terms, this gas is a migrated associated gas. Examples are given below.

The problem of the precursor of associated and nonassociated thermogenic gases has not yet been addressed in the literature, particularly to what extent cracking of either oil or kerogen contributes to the formation of gas. The sim-

plest assumption is that associated gas originates predominantly from cracking of petroleum, and deep dry gas originates from cracking reactions in kerogens. However, if petroleum becomes deeply buried, thermal alteration in overmature environments would also lead eventually to the formation of dry gases, and both kerogen and petroleum may form gas.

Dry gases and associated gases may be differentiated by their  $C_{2+}$  compositions. In this context, it should be emphasized that the  $C_{2+}$  content of a gas is sensitive to many secondary processes. Primarily, it is controlled by the present-day temperature and pressure conditions in the reservoir as well as the composition of the reservoir system. The use of  $C_{2+}$  concentration as a genetically controlled property is based primarily on the fact that  $C_{2+}$  concentration in gases is high at peak oil generation levels and it decreases with increasing maturity (Evans et al, 1971). A value (level of organic matter maturity)  $> 1.2\%$  on the vitrinite reflectance scale is commonly agreed to be the deadline for oil occurrence and the onset of dry gas formation (Teichmüller, 1971; Dow, 1977; Robert, 1980).

#### The Co-Source Concept

Constituents of a primary gas may be called "cogenetic" when its compounds result from the same bacterial or thermochemical process at the same level of thermal alteration of organic matter. This is to be differentiated from compounds in a gas which originate from different processes as a result of mixing of two gases of different origins. For example, bacterial methane and thermogenic ethane are noncogenetic compounds in a gas. Stated as a general rule: noncogenetic compounds in a gas indicate different sources, and vice versa.

#### Isotope Effects During Maturation

Isotopic composition of methane in natural gases is dependent on type and maturity of the source; this has been established from natural samples and from laboratory pyrolysis experiments (Galimov, 1968; Stahl, 1977, 1979; Chung and Sackett, 1979). The concept has been developed in mature to overmature areas with marine source rocks (Stahl and Carey, 1975) and coal source rocks (Stahl et al, 1977). From published data, an estimate reveals the following relation between the  $^{13}C$  concentration in methane and the vitrinite reflectance:

$$\text{coal gases: } \delta^{13}C \approx 14 \log R_o - 28$$

gases from sapropelic source materials (Type II/I kerogens):  $\delta^{13}C \approx 17 \log R_o - 42$ .

The relationship for coal gases has been developed in the Emsland area in northwest Germany. There are no published data from other areas to which this relationship applies. In particular, coal gas data from North America fit better to a relationship  $\delta^{13}C \approx 15 \log R_o - 35$  (G. E. Claypool, personal communication); i.e., there is a 7 ppt difference between coal gases of different areas. Rice (1983) reported gases from coals in the San Juan basin with  $\delta^{13}C$  values for methane about  $-42$  ppt. The above

equation for coal gases predicts a  $\delta^{13}C$  value about  $-29$  ppt at the maturity level given, a difference of 13 ppt.

Relationships between the maturity of a fixed phase (vitrinite) and a mobile phase (gas or oil) can be obscured for many reasons, including gases being derived from mixed organic matter, or gases of different origins becoming mixed. Also kinetic isotope effects in associated gases seem to be independent of the maturity of the source. This concept has been extended to maturities in the range of 0.3% vitrinite (Stahl, 1979). This reflectance, however, is generally assumed to be the immature stage of organic matter, and mixing with biogenic gas is likely in these maturity regimes. Also, associated gases from mature regimes have been reported as low in  $\delta^{13}C$  as  $-60$  ppt for which mixing with bacterial gas can be excluded (A. N. Fuex, personal communication). This indicates that effects other than those controlled by maturity may play a role in determining the  $^{13}C$  concentration in thermogenic methane and, in particular, in methanes from associated gases. Because of this, the maturity concept cannot be applied straightforwardly by use of the above equations.

#### Migration and/or Mixing of Gases

Migration of gases is the process of physical movement of gas from its source to a reservoir. A gas from a gas cap, although exceptions are conceivable, is an example of a natural gas which probably has not migrated. A criterion to determine which gases did not migrate (indigenous) may be the correlation of internal maturity parameters with the maturity of their environment (Schoell, 1983). An indigenous gas, therefore, may be defined as a gas for which the "isotopic maturity" estimated from the  $\delta^{13}C$  of the methane is identical with the maturity of the environment where it is encountered.

In this paper, it is assumed that migration of gases in most situations does not change appreciably the isotopic composition of the hydrocarbons (discussion in Fuex, 1980; Schoell, 1983; James, 1983). This assumption is the ultimate prerequisite for genetic characterization of natural gases because it assumes that isotopic and compositional variations predominantly reflect processes that occur during formation of gases. It must be emphasized that this concept applies to most natural gas accumulations that have been investigated by the writer. Specific areas with porous sandstones exist (such as the Cambrian of the Russian platform or the Rotliegende of the North Sea and Germany) where isotope effects between 3 and 15 ppt are attributed to migration (Galimov, 1967; May et al, 1968; Stahl et al, 1977). These case histories are regarded as exceptional and not typical for most natural gases.

The mixing of a gas is defined as a simple physical process of mixing of gases of various origins.

#### Diagenetic Gas Formation

The occurrence of ethane and propane in immature sedimentary environments has been observed by recent investigators (Claypool, 1974; Claypool and Kaplan, 1974; Claypool, 1979; Schoell, 1980; Rice and Claypool, 1981). The formation of  $C_{2+}$  hydrocarbons in this early maturation stage has been attributed to initial diagenetic reactions

in the sediments prior to thermal rearrangements of kerogens (Claypool, 1974, 1979). Such diagenetic reactions may parallel or immediately follow biogenic methane formation. This results in an almost continuous change of the gas composition which prevents a clear differentiation of bacterial and "diagenetic" gas. In this paper the terms "early" and "late" bacterial gas as proposed by Bernard (1978) are used to indicate an increase of diagenetic compounds in the gases.

## MODEL AND DIAGRAMMATIC REPRESENTATION

### Parameters and Data Base

Four values are found useful in describing variability in natural gases and deducing their origin and processes involved with their origin: the concentration of  $C_2$  to  $C_3$  hydrocarbons ( $C_{2+}$ ) relative to  $C_1$ , the carbon and hydrogen isotopic composition of methane, and the carbon isotopic composition of ethane. These properties are defined as follows:

$$C_{2+} = \left(1 - \frac{C_1}{\Sigma C_n}\right) \times 100 \quad (\text{pph})$$

where  $C_n$  is the sum of all hydrocarbons  $C_1$  through  $C_n$ , and  $C_1$  denotes relative methane content. The carbon and hydrogen isotope concentrations of methane and ethane are expressed in the usual  $\delta$ -notation,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000 \quad (\text{ppt})$$

where  $R$  is the isotope ratio of deuterium versus hydrogen and  $^{13}\text{C}$  versus  $^{12}\text{C}$ , respectively. The analytical procedures have been described by Schoell (1980).

Three diagrams have been developed in which the  $C_{2+}$  concentration, the hydrogen isotopic composition of methane, and the carbon isotopic composition of ethane are each correlated with the carbon isotopic composition of methane. Figure 1 displays genetic diagrams with schematic representation of the main stages of gas and oil formation (Fig. 1a). Processes which predominantly bring about compositional changes in natural gases are shown schematically in Figure 2.

The diagrams and their compositional fields have been designed on the basis of published data by Schiegl and Vogel (1970), Nakai (1974), Lyon (1974), Stahl (1971), Boigk et al (1976), Baker et al (1977), Stahl et al (1977), Schoell (1977, 1980, 1982), Schoell (in press), and Mattavelli et al (1983) which comprise more than 500 analyses from the following areas: northwest Germany and south Germany, North Sea, Vienna basin (Austria), Italy, Texas, Illinois, the Near East, Japan, and several offshore sites from the Deep Sea Drilling Project (DSDP), as well as some unpublished data from Trinidad, Peru, southeast Asia, and Taiwan.

### $^{13}\text{C}$ in Methane and $C_{2+}$ Concentrations

Figure 1b is a plot of  $C_{2+}$  versus  $\delta^{13}\text{C}$ , which essentially makes use of the same parameters as Stahl (1974), but no

continuous change of isotopic and  $C_{2+}$  composition is inferred as was done in the earlier model. Only fields for the various genetic types of natural gases are given. Moreover, only three processes which may change the  $^{13}\text{C}$  and/or the  $C_{2+}$  concentration are considered (see also Figure 2). These processes are maturation (both parameters), mixing (both parameters), and migration ( $C_{2+}$  concentration).

The stages of maturity—immature (bacterial/diagenetic), mature, and overmature—are defined according to Teichmüller (1971) and Dow (1977) by the maturity of organic matter in terms of vitrinite reflectance ( $R_o$ ). Based on the relation between maturity and the  $^{13}\text{C}$  concentration in the methane,  $\delta^{13}\text{C}$  is used as a qualitative maturity parameter despite the constraints discussed above. Therefore, both parameters  $R_o$  and  $\delta^{13}\text{C}$  are presented in Figure 1a. The maturity values are not to scale below maturity levels of 0.5% vitrinite reflectance. The mature stage (or oil window) has been assumed to cover maturities from 0.5 to 1.2% vitrinite reflectances (Dow, 1977; Robert, 1980).

### Carbon and Hydrogen Isotopic Composition of Methane

The plot of the carbon and hydrogen isotopic composition of methane makes use of genetically relevant properties which are independent of the compositional changes in a gas. The diagram in Figure 1c is an improved version of an earlier plot of the carbon versus hydrogen isotopic composition of methanes (Schoell 1980, 1981). Again, fields are defined for the three primary genetic types of gases—biogenic, associated, and nonassociated.

### $^{13}\text{C}$ in Methane and Ethane

This combination of parameters is useful to define cogenetic pairs on the basis of their  $^{13}\text{C}$  isotopic composition. Silverman (1971) has shown that methane and ethane in an associated gas generally follow the relation  $\delta^{13}\text{C}_2 \approx \delta^{13}\text{C}_1 + 8$ , i.e., ethane primarily is 5 to 10 ppt enriched in  $^{13}\text{C}$  as compared to methane. This relation defines the genetic field of associated gases.

With increasing positive  $\delta^{13}\text{C}$  values of the methane, the correlated  $\delta^{13}\text{C}_1/\delta^{13}\text{C}_2$  relation changes (TT(m) in Figure 1d). Also coal gases from northwest Germany exhibit a different  $\delta^{13}\text{C}_1/\delta^{13}\text{C}_2$  relation (TT(h) in Figure 1d). Again, primary gases occupy the indicated fields, and the mixing of different gases results in a  $\delta^{13}\text{C}_1/\delta^{13}\text{C}_2$  relation different from that of the genetic fields as indicated in Figures 1d and 2.

James (1983) has calculated quasi-equilibrium isotope fractionations between methane and ethane in natural gases, resulting in decreasing isotopic differences between methane and ethane with increasing maturity. Using the theoretical  $\delta^{13}\text{C}_1/\delta^{13}\text{C}_2$  relations of James, a slightly different genetic field would result in Figure 1d. However, the empirical compilation of data (Schoell, in press) reveals genetic fields as indicated in Figure 1d.

### COMPOSITIONAL VARIATIONS IN PRIMARY GASES

The diagrams and their genetic fields have been developed from variations found in the specific types of gases

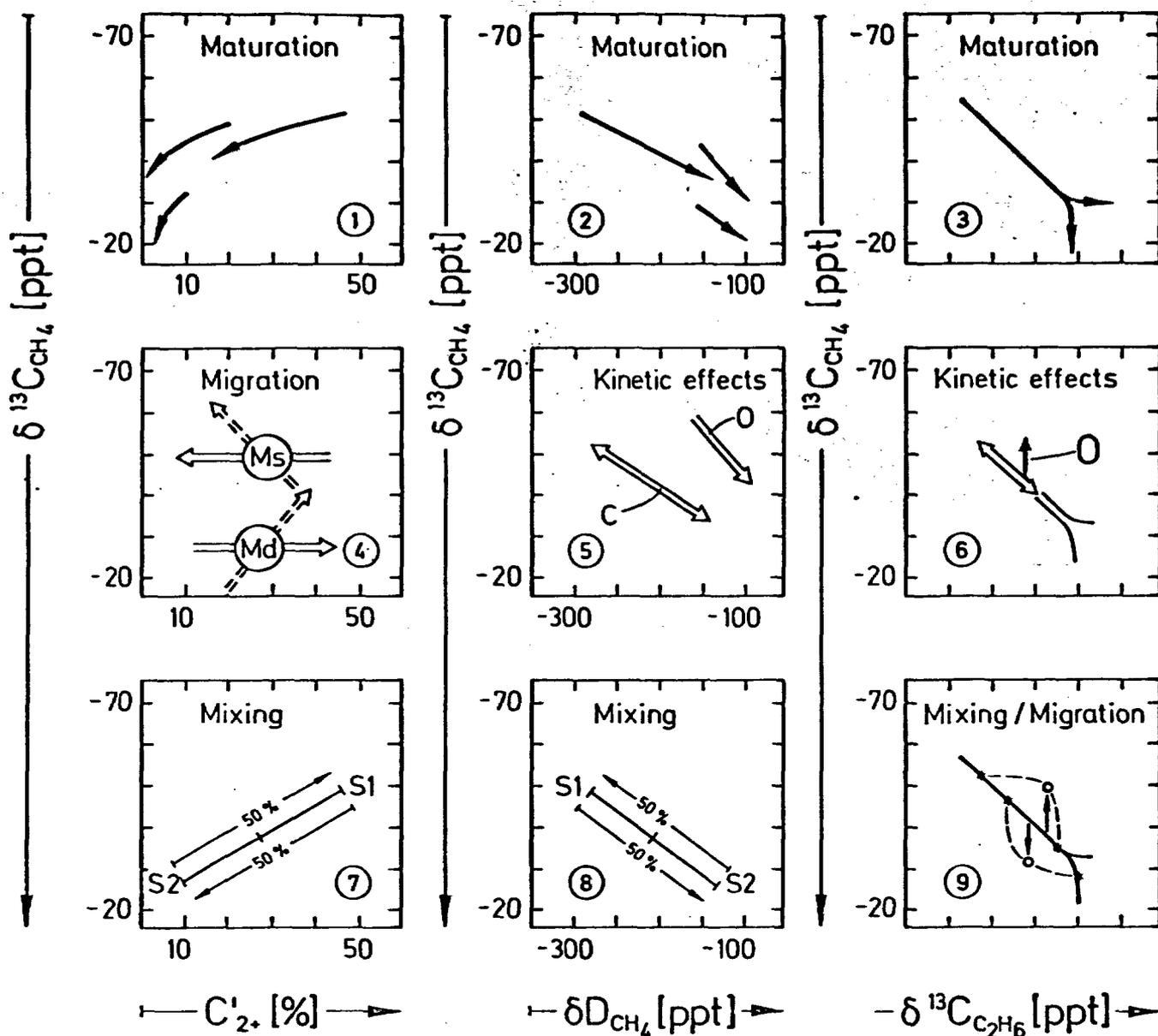


FIG. 2—Various processes and resulting compositional variations in natural gases. C = chromatographic effect; O = oxidation; S1/S2 = end members of mixed gases. Note various possibilities owing to migration. Dashed arrows indicate mixing owing to migration. Horizontal arrows result from a change of the  $C_{2+}$  concentrations only. Mixing in  $\delta^{13}\text{C}$ -methane/ $\delta^{13}\text{C}$ -ethane diagrams may result in bent mixing pathways if gases with different  $C_1$  and  $C_{2+}$  concentrations are mixed.

analyzed, so there is no inference to the fields. The design and statistical reliability of such diagrams will improve with an increasing number of analyses. The fields may change slightly with inclusion of new analytical data. Justification of the fields shown is discussed briefly below.

#### Biogenic Gases (B)

Biogenic gases, denoted as B(m) in Figure 1, are derived from Holocene to sub-Holocene marine sediments from DSDP drilling sites at the Cape Verde Rise (Baker et al, 1977), the Cariaco Trench (Lyon, 1974), and the Gulf of California (Schoell, 1982). The isotope compositions in interstitial gases from localities worldwide are surprisingly uniform; they range between  $-60$  and  $-75$  ppt and  $-170$

and  $-190$  ppt in  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values, respectively. Interstitial gases are isotopically similar to methanes from gases of Tertiary basins (Schoell, 1977; Mattavelli et al, 1983), which suggests that essentially similar processes are operative in marine sediments and Tertiary basins (Schoell, 1982).

The second group of biogenic gases, B(t), are derived from continental environments. Examples include various swamp gases and gases from glacial deposits in Illinois (glacial drift gases) described by Coleman (1976). The different deuterium concentrations in continental methane compared to marine methane results from the different deuterium concentrations in the respective environmental waters (Schoell, 1980). Recent findings by Woltemate et al (in press) indicate that active freshwater environments

produce yet another methane which possibly is derived from fermentation processes and not from reduction of  $\text{CO}_2$ . This methane is depleted in deuterium; its  $\delta\text{D}$  ranges from  $-250$  ppt to  $-400$  ppt.

The limit of the bacterial field with respect to the carbon isotopic composition of methane at  $\delta^{13}\text{C}$  values of  $-60$  ppt is justified by the fact that bacterial gases with  $\text{C}_{2+}$  contents below  $0.2\%$  have more negative  $\delta^{13}\text{C}$  values than  $-60$  ppt in most situations. Exceptions are bacterially formed methanes from fermenters and freshwater environments in which  $\delta^{13}\text{C}$  values between  $-60$  and  $-40$  ppt have been observed (Coleman, 1976). These gases, however, have not been observed as natural gases of commercial quantities. Also, specific environmental conditions could lead to a  $^{13}\text{C}$  enrichment in bacteriogenic methane (e.g., if the interstitial  $\text{CO}_2$  in sediments, from which methane is formed, has already been enriched in  $^{13}\text{C}$ ) (Nissenbaum et al, 1972). These particular conditions, however, do not exist in most environments in which bacterial gases of commercial quantities are formed. Claypool (1974, 1979) observed increasing  $\text{C}_2/\text{C}_1$  ratios in bacterial gases with increasing depth, and he interpreted ethane to be a product of early thermochemical processes. Similar changes are also noted in natural gases from Tertiary basins where a slight increase in  $\delta^{13}\text{C}$  in the methane with increasing depth is also observed (Schoell, 1977; Claypool, 1979; Mattavelli et al, 1983). The terms "early" and "late" biogenic gas are adopted from Bernard (1978) to indicate these changes. Ethane concentrations from diagenetic processes rarely exceed  $0.2\%$  by volume, and such gases are more negative than  $-60$  ppt in almost all examples.

Mixing with thermogenic gas also increases the  $\text{C}_{2+}$  content. In mixed gases,  $\text{C}_{2+}$  generally exceeds  $0.2\%$  by volume, and with the increase of  $\text{C}_{2+}$  an increase in  $^{13}\text{C}$  in methane occurs (Fuex, 1977; Schoell, 1977; Rice and Claypool, 1981; Mattavelli et al, 1983).

#### Thermogenic Gases ( $T_o$ , $T_i$ ) Associated with Petroleum

Methanes from associated gases are depleted characteristically in deuterium, and they display a general  $\delta\text{D}/\delta^{13}\text{C}$  relationship where  $\delta\text{D}$  changes in correlation with  $\delta^{13}\text{C}$  (i.e.,  $\delta\text{D} \approx 9 \times \delta^{13}\text{C}$ ). This paper, however, does not attempt to rationalize this relationship. Some observations should be noted. Cracking reactions in octadecane and petroleum generate methane which is depleted initially  $20$  to  $30$  ppt and  $150$  to  $170$  ppt, respectively, in the heavy isotope. Also, a correlated change in the hydrogen and carbon isotopic composition of the methane is observed in pyrolysis gases (Sackett, 1978; Chung and Sackett, 1980). Oils have  $\delta^{13}\text{C}$  and  $\delta\text{D}$  compositions around  $-27 \pm 5$  ppt and  $-125 \pm 50$  ppt (Schoell and Redding, 1978; Yeh and Epstein, 1981); therefore, the first methane formed from cracking reactions in petroleum should be about  $-50$  to  $-60$  ppt and  $-245$  to  $-340$  ppt in its carbon and hydrogen isotopic composition, respectively. Some associated gases from the North Sea are close to this value (Schoell, 1980). Associated gases from a United States basin, which were rich in  $\text{C}_{2+}$ , revealed values about  $-50$  to  $-60$  ppt and  $-200$  to  $-300$  ppt for the carbon and hydrogen isotope values of their methanes, and  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values showed the same correlated change (A. N. Fuex, personal

communication). These observations indicate that early cracking products of petroleum are characterized by a depletion of heavy isotopes. This led the writer to designate field  $T_o$  as the field of primary associated gases of the early stage of gas formation.

An important fact in this paper is the better discrimination of associated and nonassociated gas because of the fractionation of hydrogen isotopes. The fields of dry gas from marine source rocks (TT(m)) and of associated gases (T) overlap with respect to the  $^{13}\text{C}$  isotope compositions. If, for example, an associated gas migrates off its gas cap and is stripped of its  $\text{C}_{2+}$  hydrocarbons (horizontal arrow Ms in Figures 1b, 2), it may enter the field of dry gases. Because the isotopic composition of methane remains unchanged generally, it would still be identified as a gas associated with oil and thus it would be indicative of pooled petroleum.

$T_c$  has been designated for gases associated with condensates. Methane  $\delta^{13}\text{C}$  values more positive than  $-40$  ppt indicate source maturities higher than  $R_o \sim 1.2\%$ , the coalification stage where thermal degradation of petroleum begins, the gas/oil ratio increases, and gases are likely to be associated with condensates. Alternatively in this field, gases would be expected which result from the mixing of deep dry gases with associated gas (mixing lines in Figures 1c).

#### Thermogenic Dry Gases

In methanes of dry nonassociated gases, deuterium increases with increasing maturity of organic matter of the source rock; however, the hydrogen isotope fractionation is the same for humic and liptinitic organic matter (Schoell, 1980). Therefore, increasing deuterium concentrations can be correlated roughly with increasing levels of maturity. A  $\delta\text{D}$  value of approximately  $-150$  ppt, correlating with the end of the oil generating zone, has been found for many gases. The maturity values ( $R_o$  in Figure 1) should be applied only for an estimate of maturity of the source. However, the tendency for increasing maturity with increasing deuterium concentration in the methane is well established. Because the  $^{13}\text{C}$  concentration fractionates differently when methane is formed from humic or liptinitic organic material, two fields (TT(h) and TT(m)) can be distinguished for the respective source rocks. The field between TT(m) and TT(h) is occupied by gases from mixed source rocks. This differentiation is important when coal contributes to gas formation in a basin.

A last group of primary gases displayed in Figure 1 are coal gases from northwest Germany (Boigk et al, 1976; Stahl et al, 1977). These gases have  $^{13}\text{C}$  concentrations in the methane which are correlated with the maturity of Upper Carboniferous strata underneath the reservoirs; in general, these gases are more enriched in  $^{13}\text{C}$  than all other natural gases (note different maturity scales for coal gases in Figure 1). Coal gases in Rotliegend reservoirs are the only known samples in which part of the  $^{13}\text{C}$  fractionation ( $\delta^{13}\text{C}$  values more positive than  $-24$  ppt) is possibly due to migration (Stahl et al, 1977).

As noted, an increase in unpublished information suggests that northwest German coal gases are not representative of gases from humic source rocks in general. This is

surprising because methane in pyrolysis gases from coals of various origins is enriched significantly in  $^{13}\text{C}$  compared with pyrolysis gases from organic materials of Type II (Chung and Sackett, 1979).

Carbon-13 isotope values around  $-45$  ppt have been reported from methane in natural gas samples from the Mahakam delta, where the source rocks only contain Type III organic matter (Durand and Oudin, 1979). However, large amounts of oil are produced in the Mahakam delta, and the gases are probably formed from oil with only subordinate contribution from kerogen. Therefore, the Mahakam delta gases probably do not contradict the observation that a  $^{13}\text{C}$  concentration in methane more positive than  $-30$  ppt is characteristic of humic source materials.

A similar example has been reported by Rigby and Smith (1981) who investigated gases from the Cooper basin (Australia) in which coals are the predominant source rocks. The  $\delta^{13}\text{C}$  values of  $\text{CH}_4$  range between  $-26$  and  $-40$  ppt, and the  $\delta\text{D}$  values range between  $-200$  and  $-275$  ppt (German coal gases range in  $\delta\text{D}$  between  $-170$  and  $-120$  ppt!). The Cooper basin, however, also produces large amounts of petroleum. It is not clear whether the gases have formed from petroleum or from coals.

Admittedly, the problem of gas formation from type III organic matter is not yet clear, and samples other than the northwest German coal gases are required to solve it. In areas of mixed source beds (i.e., humic and marine sapropelic), gases of a mixed composition should be expected (see Figure 1b, c "mixed source"); gases of such mixed origin have been reported from offshore Thailand by Stahl (1977) and from the Vienna basin (see below).

#### COMPOSITIONAL CHANGES BY SECONDARY PROCESSES

Changes in molecular as well as isotopic compositions in gases may also result from secondary processes which have been compiled schematically in Figure 2. Some of these processes, such as maturation and kinetic effects, are responsible for the isotope variations in gases during their formation. Processes such as migration, mixing, and oxidation of methane could account for changes in the gases during secondary migration.

##### Oxidation

Oxidation of methane results in an increase of  $\text{C}_{2+}$  compounds and an increase in heavy isotopes in the methane (Coleman et al, 1981). Oxidation is unlikely to play an important role in commercial gas deposits. The isotopic composition of traces of methane in marine sediments, however, can be changed significantly by oxidation (Bernard, 1979; Doose, 1980), and genetic interpretations of isotope data must be considered with caution. This particularly applies to applications of carbon isotopes in surface exploration (Stahl et al, 1981).

##### Mixing

The particular advantage of the  $\delta^{13}\text{C}/\delta\text{D}$  diagram is that mixing processes result in isotopic compositions between

the respective end members (Fig. 2). Both isotope concentrations change in strict proportion to the mixing ratios; mixing of various proportions of two gases results in a linear change in their isotopic composition. This may be used to estimate the end members if some intermediate values of different mixing proportions are known. Gases which fall into field M have been found in abundance at the base of Tertiary basins where thermogenic gases from below become mixed with indigenous bacteriogenic gases (Schoell, 1977; Mattavelli et al, 1983). Also, gases from immature marine sediments adjacent to magmatic bodies fall into this field (Baker et al, 1977; Schoell, 1982). Mixing of gases results also in a linear relationship on the  $\delta^{13}\text{C}/\text{C}_{2+}$  diagram (Fig. 2).

Mixing of two gases of different origins means that the constituents of a gas are not cogenetic. For cogenetic methane-ethane pairs in thermogenic gases, it is observed generally that ethane is enriched in  $^{13}\text{C}$  between 5 and 10 ppt compared to the methane (Silverman, 1971; Deines, 1980). This relationship can, with some exceptions, be used to differentiate gases of mixed origins. Figure 1d genetically defines natural gases by their  $^{13}\text{C}$  concentrations in methane and ethane. A good correlation is found for associated gases and for nonassociated gases. This relation changes for coal gases and for nonassociated gases from high-rank sources (fields TT(m) and TT(h) in Figure 1d). The fields of the primary gases are defined by the  $^{13}\text{C}$  variations of cogenetic methane-ethane pairs. If bacterial methane is added to a thermogenic gas, the  $\delta^{13}\text{C}$  value of the methane changes accordingly and the  $\delta^{13}\text{C}$  value of the ethane remains constant (arrow Ms in Figure 1d). Mixing a deep dry gas (i.e., predominantly methane with  $\delta^{13}\text{C}$  values of  $-30$  ppt) with an associated gas would change the  $\delta^{13}\text{C}_1/\delta^{13}\text{C}_2$  relationship accordingly (arrow Md in Figure 1d).

##### Migration

The genetically controlled isotope variations in gases indicate that the isotopic composition of methane is not significantly changed after its generation. Appreciable isotopic changes in gases during migration are to be expected when the gas becomes mixed with another gas during migration. The  $\text{C}_{2+}$  concentrations in associated gases, however, may change during migration, as has been noted. This has been demonstrated by Coleman et al (1977), who showed that migrated gases may be completely stripped of  $\text{C}_{2+}$  hydrocarbons, whereas the  $^{13}\text{C}$  concentration in the methane remained unchanged. In this situation, migration should result (Fig. 1b) as a change parallel to the  $\text{C}_{2+}$  axis or along mixing lines accordingly. Because migration can be monitored only if this results in changes of one of the investigated parameters, migrated gases can be recognized close to boundaries of maturity regimes or in very deep basins.

The writer believes that methane plays an important role in migration, as outlined by Sokolov et al (1964), Hedberg (1979, 1981), and Neglia (1980). Depending on depth, migration of methane may have two effects.

1. *Deep migration* (arrows Md in Figures 1, 2).—Deep dry methane which has been formed or is forming in over-mature zones below zones of oil formation could migrate

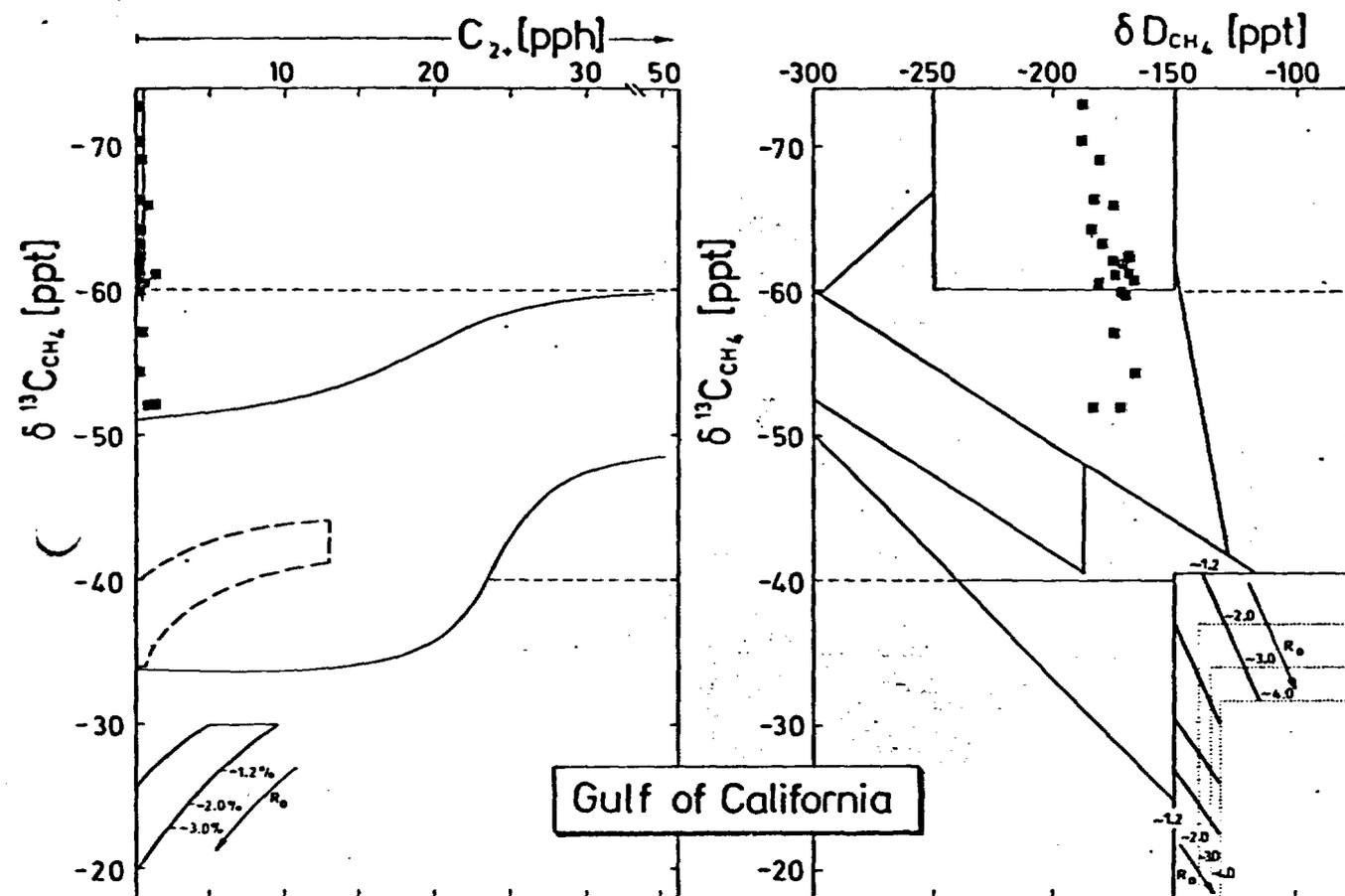


FIG. 3—Compositional variations of interstitial gases from Gulf of California. Data from Schoell (1982).

through these areas and thereby act as "carrier" for  $C_{2+}$  hydrocarbons by means of gas-liquid phase equilibria (Sokolov et al, 1964). Such gases would increase compositionally in wetness (horizontal arrow Md in Figures 1, 2). Bray and Foster (1980) have proposed  $CO_2$  as a principal extraction medium during primary migration. Methane could be an adequate carrier, probably more important during secondary migration (Sokolov et al, 1964; Hedberg, 1979, 1981). Evidence for this type migration has been found recently in the Mahakam delta (Durand and Oudin, 1979) and may be important in rapidly subsiding areas (Niger delta, Mississippi delta, etc).

2. *Shallow migration* (arrows Ms in Figures 1, 2).—Here migration results in depletion of the  $C_{2+}$  hydrocarbons because higher hydrocarbons are segregated or are stripped off during passage of the gas through less permeable, possibly unconsolidated, sediments. Part of the  $C_{2+}$  depletion may result from the process described by Silverman (1971) as "separation migration" (i.e., retrograde condensation of  $C_3$  hydrocarbons in reservoirs of lower pressure). Shallow migration may result eventually in dry gases with  $^{13}C$  isotopic compositions of methanes around  $-40$  to  $-50$  ppt, whereas deep migration may give rise to wet gases with relatively positive  $\delta^{13}C$  values in their methane ( $-40$  to  $-35$  ppt).

#### APPLICATIONS

Examples of applications of the genetic diagrams are

compiled in Figures 3 through 6 in which published data (Schoell, 1977, 1980, 1982; Schoell, in press) have been displayed.

#### Gulf of California

The first example (Fig. 3) displays values for interstitial gases from the Gulf of California. Here, the gases have been recovered from young sediments to depths of  $\approx 450$  m (1,475 ft). With few exceptions, all gases are typical bacterial gases from marine environments. The gases which were derived from locations adjacent to a dolerite sill plot in the fields for mixed gases. This area is an excellent example for the formation of mixed gases because the timing is obvious from the geology: first, bacterial gases were formed in the anoxic immature sediments and, second, the intrusion of the dolerite prompted the thermochemical formation of some methane which was mixed with the indigenous bacterial methane.

#### South German Molasse Basin

The south German Molasse basin (Fig. 4) is a typical sub-alpine basin at the northern rim of the Alps. Tertiary sediments are up to 4,000 m (13,000 ft) thick and are fairly immature ( $R_o$  at 4,000 m  $\approx 0.6\%$ ). The general geology of the basin has been described recently by Bachmann et al (1982). Gases in the Tertiary reservoirs exhibit a clear compositional grouping according to the age and/or depth of

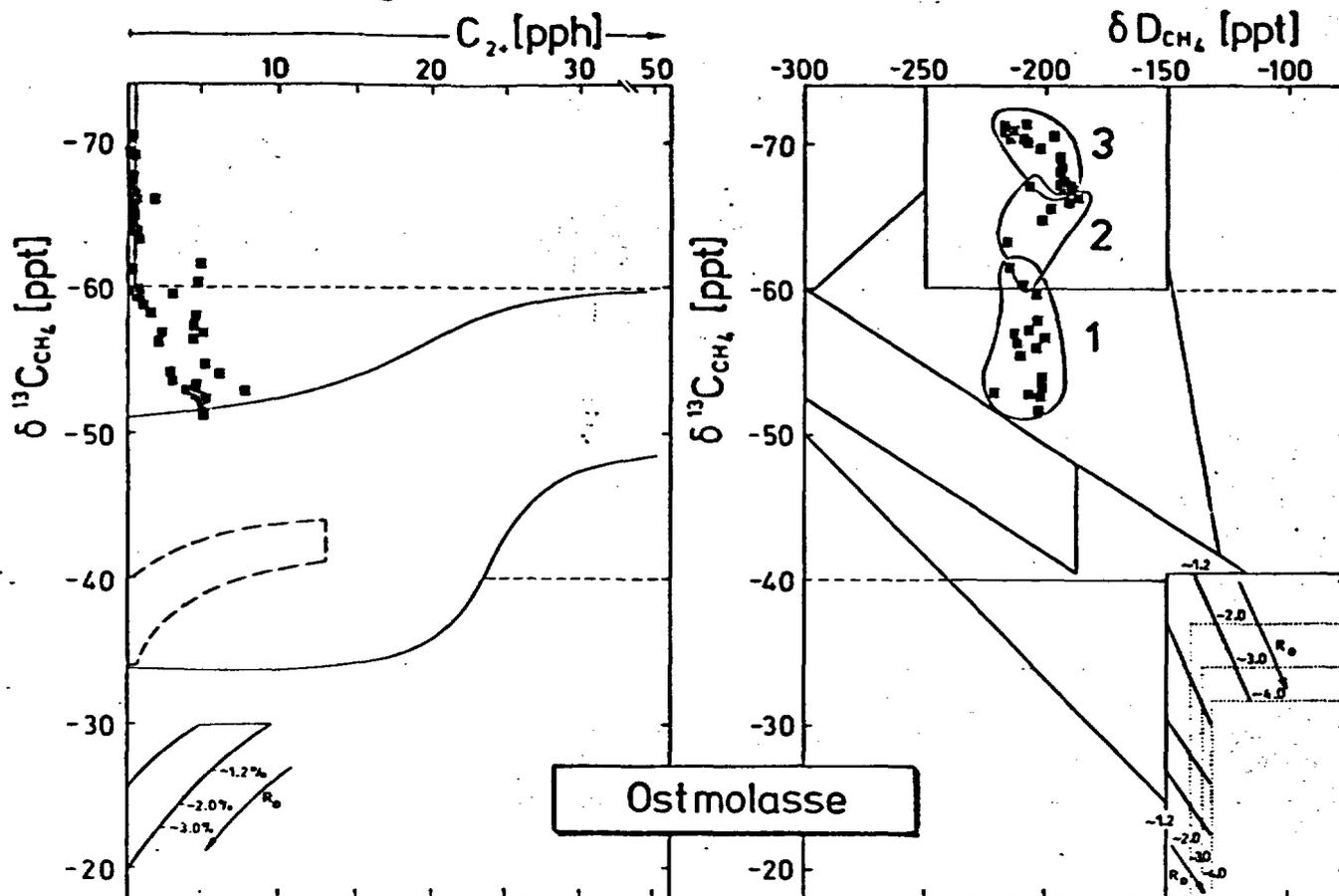


FIG. 4—Compositional variations of natural gases from south German Molasse basin. 3 = Miocene; 2 = Oligocene; and 1 = Eocene reservoirs. Data from Schoell (1977).

the reservoir. Gases from Miocene reservoirs at an approximate depth of 2,000 m (6,500 ft) are lowest in  $^{13}\text{C}$  and almost devoid of  $\text{C}_{2+}$  hydrocarbons, whereas Oligocene reservoirs at an approximate depth of 3,000 m (9,800 ft) are more enriched in  $\text{C}_{2+}$  and  $^{13}\text{C}$  in the methane. Both groups can be characterized as early and late bacterial gases, respectively. Typical mixed gases are found in the Eocene Lithothamnium limestone (depth of 3,500 to 4,000 m, 11,500 to 13,000 ft), where thermogenic gases are mixed with bacterial gases.

#### Vienna Basin

As a third example, compositional variations of gases from the Vienna basin are shown in Figure 5. The geology of the area has been described in detail by Kroell and Wesely (1973). Briefly, the Vienna basin is an intramontane basin tectonically formed within the alpine system. Below the Tertiary basin fillings are typical carbonate and dolomitic alpine rocks of Triassic age (e.g., Hauptdolomit, etc) which form the most important reservoirs in the area. Three principal types of gases can be differentiated in the basin: bacterial and associated gases in Tertiary reservoirs (1 and 4 in Figure 5), as well as deep dry gases in pre-Tertiary reservoirs (3 in Figure 5). Two gases are noteworthy. One gas, found in a Tertiary reservoir ("Migrated" in Figure 5), has an identical isotopic composition as the deep dry gases from pre-Tertiary reservoirs; this suggests that it

is a migrated thermogenic gas. Another gas, which plots in field M (2 in Figure 5) is also derived from a Tertiary reservoir. Here bacterial and deep thermogenic gases were mixed.

#### Po Basin

A last example is from a study of natural gases in the Po basin (Mattavelli et al, 1983). A compilation of these results is given in Figure 6 as an example of a basin with various origins of gases and their migration into shallow traps. Three types of gases can be differentiated in the Po basin. A quantitative assessment there revealed a predominance of biogenic gases. Gases of mixed origin could be identified by their carbon and hydrogen isotopic composition of methane and ethane (Fig. 6). Mixed gases were found predominantly in a transgressive facies that followed Miocene deposition. Thermogenic gases are subordinate in the basin. The gas of Medesano field is recognized as a migrated thermogenic associated gas, produced from a shallow reservoir of Pleistocene age at an approximate depth of 170 m (550 ft). It is dry, chemically resembling a biogenic gas, but isotopically it is recognized as an associated gas. In addition, gas from the Malossa deep gas and condensate field can be identified as a condensate associated gas. Figure 6 demonstrates the application of genetic characterization of gas types in a basin. Mattavelli et al (1983) present more details on the geology

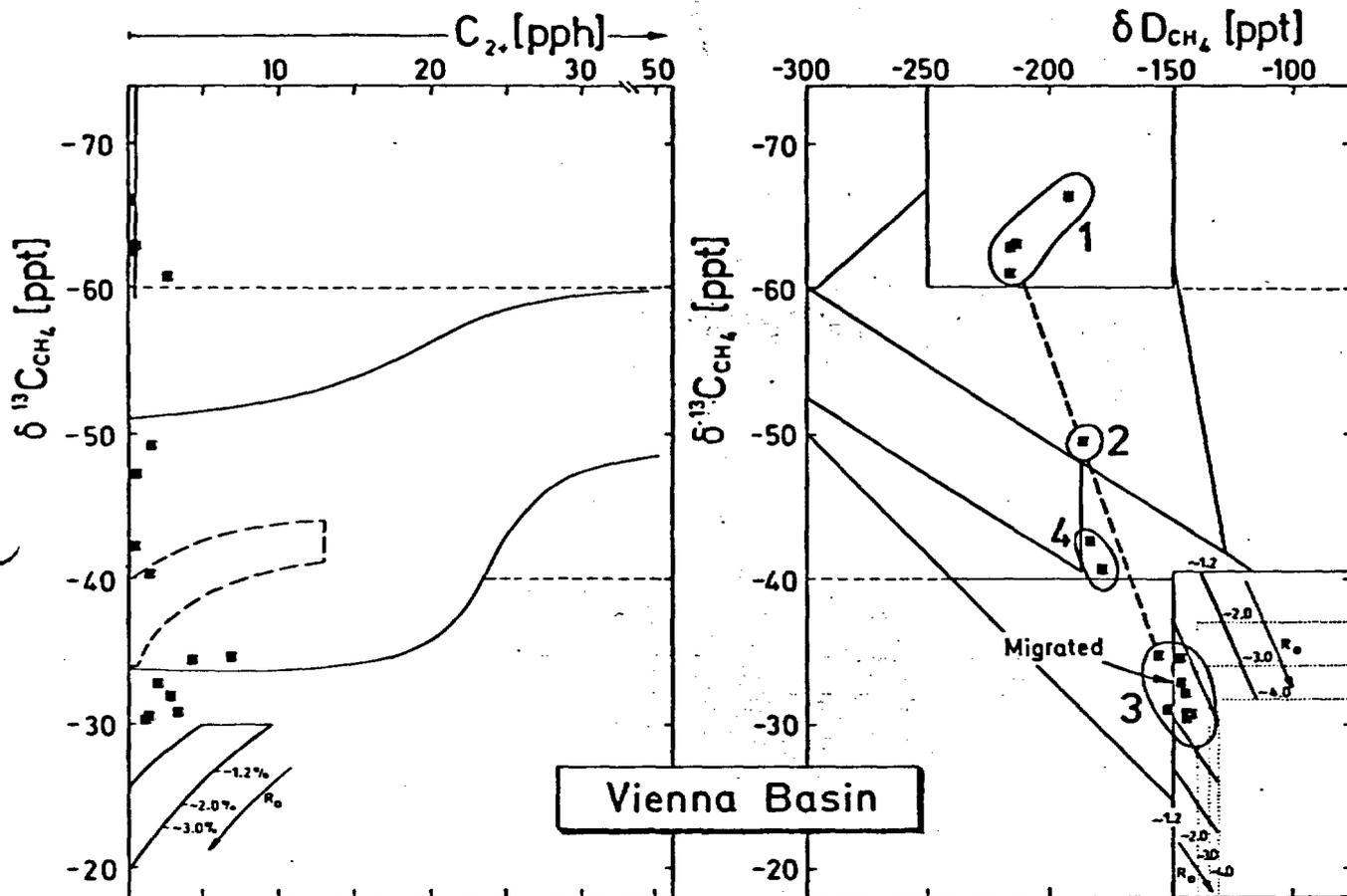


FIG. 5—Compositional variations of natural gases from Vienna basin. 1 = bacterial gases from Tertiary reservoirs; 2 = mixed deep dry and bacterial gas; 3 = deep dry gases from pre-Tertiary reservoirs; and one migrated gas (Migrated) in Tertiary reservoir; 4 = associated gases from Tertiary reservoirs. Data from Schoell (in press).

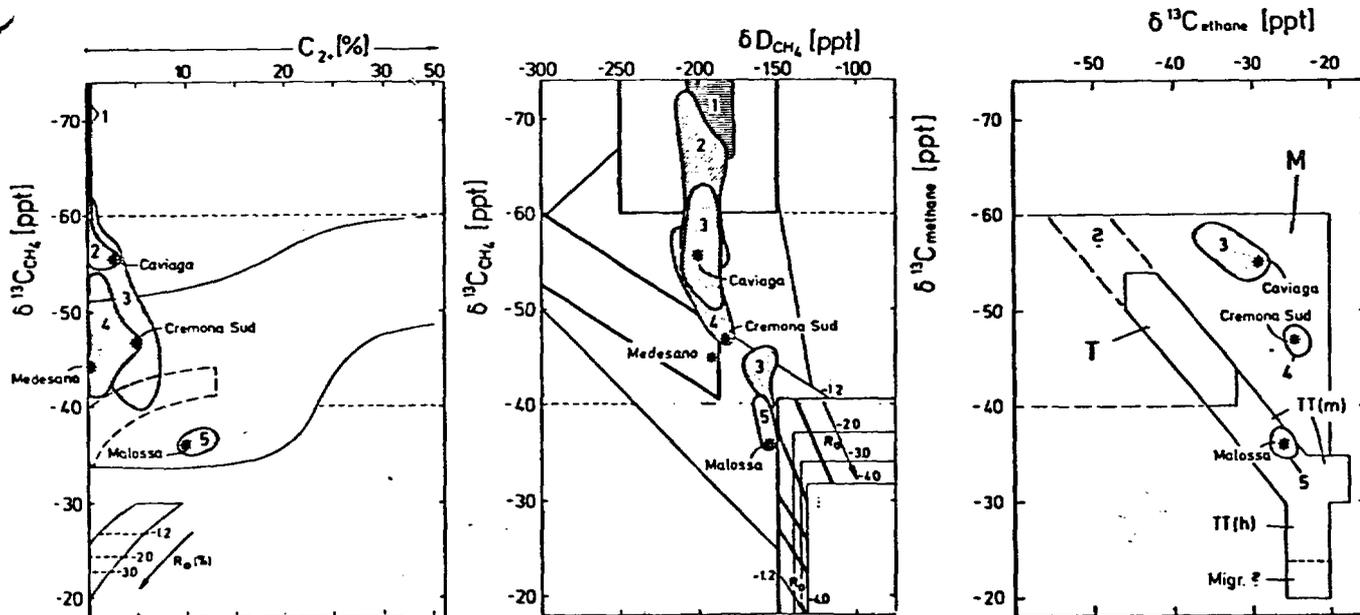


FIG. 6—Genetic characterization of natural gases in Po basin, northern Italy, as example for application of genetic diagrams. Genetic types of gases change with age and geologic condition of reservoir. Clear identification of shallow migration at Medesano; the  $\delta^{13}\text{C}/\delta\text{D}$  plot indicates this to be a gas that was associated with oil. Malossa is a deep condensate deposit, and Caviaga has a gas of mixed origin. Age of reservoirs: 1 = upper middle Pliocene; 2 = lower Pliocene; 3 = Messinian; 4 = middle Miocene; 5 = pre-Tertiary.

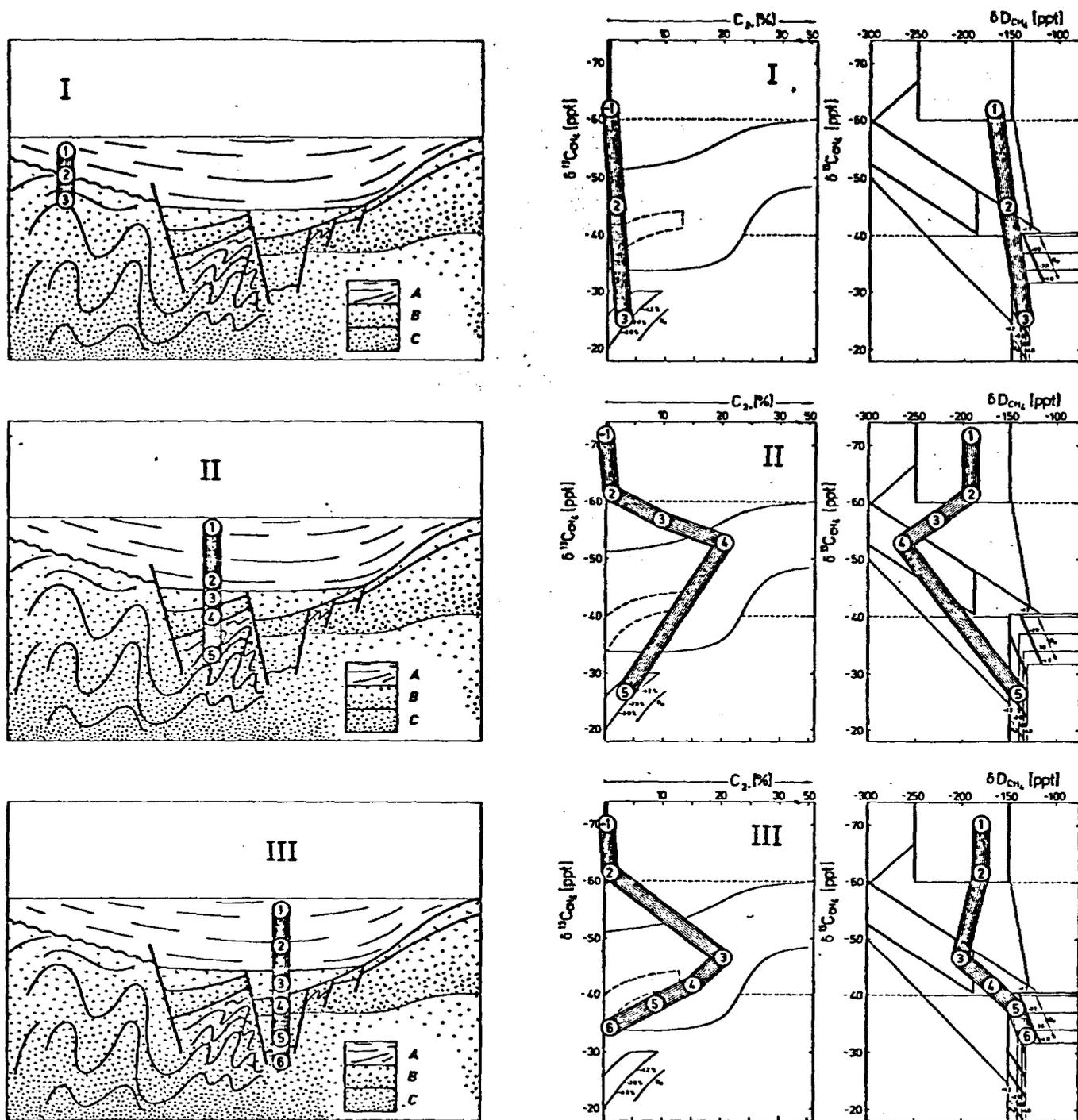


FIG. 7—Application of genetic interpretive diagrams for genetic characterization of natural gases in wells. Various well sites (I, II, III) are shown schematically as a well as inferred types of gases encountered. Regimes: A = immature; B = mature; C = overmature. For identifications of genetic fields in diagrams see Figure 1.

and other regional information.

#### Application in Exploration

Figure 7 summarizes scenarios in exploration drilling where the concept of genetic characterization of gases could be applied to test gases. Several positions within a hypothetical basin are given, and genetic types of gases likely to be encountered are portrayed.

Well site I is considered unprospective because an overmature area is covered by Tertiary strata. Positions II and III are recognized as prospective sites because the gases enter the genetic field of associated gases, indicating that the gases are formed together with petroleum. If parameters for genetic characterization of natural gases were determined in a semicontinuous fashion in wells (e.g., on head-space gases), the evolution pathways as indicated in Figure 7 would result. By applying genetic characteriza-

tion of gases on well sites, the principal character of an area probably could be determined at an early stage.

### Constraints

Constraints in the use of the concept are mentioned because of possible restrictions in the variety of gases examined. Specifically, solution to the problem of coal gases has to wait for more published data. Additional experimental data from pyrolysis experiments would aid the understanding of differences between associated and nonassociated gas. As noted above, the scheme should be used as a guide to interpretation rather than as a strict scheme. Finally, geochemistry is only one approach used to understand the origin and accumulation of natural gases. Proper understanding of the geologic framework is equally important.

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