

# Hydrothermal hydrocarbon gases:

## 1, Genesis and geothermometry

W. G. DARLING

British Geological Survey, Wallingford, Oxfordshire OX10 8BB, UK

**Abstract**—Various sources for hydrothermal methane have been proposed over the years. While carbon isotope studies have narrowed the possibilities, enough higher hydrocarbon gas data now exist both to supplement the isotopic data and to permit additional deductions regarding origins. Comparison of typical C<sub>1</sub>-C<sub>6</sub> data for gases of various origins (from sedimentary and crystalline rocks, and hydrothermal systems) reveals certain characteristics. Apart from isotopic differences, hydrothermal hydrocarbons differ from sedimentary hydrocarbons mainly in possessing tendencies towards a relative excess of methane, higher normal/iso ratios for butane and pentane, and relatively high amounts of C<sub>6</sub> gases.

Despite these differences, consideration of the evidence indicates that hydrothermal hydrocarbon gases in most cases originate like sedimentary basin gases by thermal degradation of organic matter in the relatively shallow subsurface. The principal characteristic of these hydrothermal gases, 'excess' methane, appears to have a geothermometric function. The following empirical relationship has been derived:

$$t^{\circ}\text{C} = 57.8 \log(\text{CH}_4/\text{C}_2\text{H}_6) + 96.8$$

which fits moderately well a range of geothermal fields worldwide. This gas geothermometer may be particularly applicable during geothermal exploration in areas where there is little direct knowledge of subsurface conditions.

### INTRODUCTION

The presence of methane in hydrothermal gases has been known for many years (e.g. ALLEN and DAY, 1935) and has usually been assumed to be non-biogenic (i.e. non-bacterial) in origin. Possible sources of non-biogenic CH<sub>4</sub> in general have been debated in numerous publications, with various authors advocating a juvenile source (e.g. MCDERMOTT, 1940; GOLD and SOTER, 1982), a nearer-surface inorganic synthetic source (e.g. ROBINSON, 1963; SZATMARI, 1989) and, by a vast majority, an organic source of some kind (e.g. LEVORSEN and BERRY, 1967; TISSOT and WELTE, 1984). In an attempt to discover to what extent these sources are represented in hydrothermal systems, this paper examines available data on hydrocarbon concentrations in hydrothermal systems worldwide by comparing and contrasting them with hydrocarbon gases from sedimentary and miscellaneous sources. Following on from this, the effect of hydrothermal system temperatures on hydrocarbon gas concentrations is considered.

## GENESIS OF HYDROTHERMAL HYDROCARBON GASES

The hydrothermal systems under consideration here are nearly all of high enthalpy type, that is systems with temperatures high enough to generate a significant steam phase on reduction of pressure. The systems are found in a variety of geological situations, generally but not exclusively related to zones of extension or subduction. They may be marine or terrestrial, though for obvious reasons there are more data on the latter type.

### Alkane Content, and Carbon Isotope Ratios in Methane

Detailed conclusions about the origin of hydrothermal CH<sub>4</sub> require information about higher hydrocarbon gases ('C<sub>2+</sub>') and <sup>13</sup>C contents. The applied nature of much geothermal exploration work has meant that this kind of information is relatively rare, but enough data now exist for an attempt at comparison with non-hydrothermal systems to be made. Comparisons will be restricted to alkane (paraffin) homologues plus benzene, and δ<sup>13</sup>C-CH<sub>4</sub>; there are still too few data to consider broadening the approach to include δ<sup>2</sup>H-CH<sub>4</sub> and alkene compounds.

Fig 1 shows a small but representative selection of the vast amount of data from thermogenic 'natural' gases in sediment-hosted gas fields, plotted in the form of the ratio of methane to ethane, propane, butane, pentane and undifferentiated C<sub>6</sub> respectively. Methane/ethane (C<sub>1</sub>/C<sub>2</sub>) ratios within the range 10-100 are followed in a fairly linear way through C<sub>1</sub>/C<sub>3</sub> and C<sub>1</sub>/C<sub>4</sub> to C<sub>1</sub>/C<sub>5</sub>, which lies between 10<sup>2</sup> and 10<sup>3</sup>. C<sub>6</sub> data where available mostly indicate a slight rise in concentration relative to C<sub>5</sub>. The average δ<sup>13</sup>C values of CH<sub>4</sub> in these gas fields range from -38.3 to -52.4‰, with a mean value of -44.0‰ PDB (data from references quoted in the title of Fig 1).

Published data on compositions of hydrocarbon fractions in gases not apparently from basinal or hydrothermal sources are depicted in Fig 2. The relationship of C<sub>1</sub>/C<sub>2</sub>-C<sub>1</sub>/C<sub>3</sub>-C<sub>1</sub>/C<sub>4</sub>-C<sub>1</sub>/C<sub>5</sub> ('C<sub>1</sub>/C<sub>2</sub> to C<sub>1</sub>/C<sub>5</sub>') in these 'crystalline' gases is seen to be similar to but steeper than that of the gas fields in Fig 1, resulting in some overlap between the gas types for C<sub>1</sub>/C<sub>2</sub> but virtually none for C<sub>1</sub>/C<sub>3</sub> and C<sub>1</sub>/C<sub>4</sub>. The compositional range therefore occupies an area of the plot almost entirely separate from the sedimentary natural gases. There are few C<sub>5</sub> data for these gases and only one C<sub>6</sub> value, so it is not possible to draw conclusions regarding relative amounts of C<sub>5</sub> and C<sub>6</sub> compounds. These crystalline gases come from a variety of sources - diatremes, ophiolites and ancient shield rocks - and their averaged δ<sup>13</sup>C-CH<sub>4</sub> values reflect this by falling within a large range from -7.1 to -48.3‰ (data from references quoted in the title of Fig 2). This suggests that at least in some instances the hydrocarbon gases could be of abiogenic

origin. However, detailed consideration of these cases is beyond the scope of the present paper.

Most hydrothermal gases which have been analysed for hydrocarbon contents have been obtained from geothermal energy exploration of, or production from, systems related to subduction zones. Published data are plotted in Fig 3, which shows that on average there is a relationship between  $C_1/C_2$  to  $C_1/C_5$  broadly resembling the sedimentary and crystalline gases already considered, although the slopes are more similar to sedimentary than crystalline hydrocarbons. In terms of  $C_1/C_2$  to  $C_1/C_5$ , subduction-related hydrothermal gases occupy roughly the same zone as the crystalline gases. For  $C_1/C_6$ , however, there is a considerable difference in relative terms between the hydrothermal and other gases, with values often near those of the  $C_1/C_3$  ratio (though this refers to undifferentiated  $C_6$ , and different  $C_6$  compounds may be involved). Averaged  $\delta^{13}C\text{-CH}_4$  data occupy the narrow range of  $-25.7$  to  $-33.7\%$ , though data are relatively sparse (extracted from references quoted in the title of Fig 3).

The composition of other hydrothermal gases, mainly from oceanic spreading centres but also from continental rift and hotspot sources, is shown in Fig 4. Because of their diverse origins in a range of environments from sediment-rich to sediment-poor, these occupy an area of the plot which covers the whole range of the gas types considered so far. They differ from subduction-related gases in that  $C_5/C_6$  appears to be on a par with sedimentary gases (except for the Azores, for reasons unknown), though there are insufficient data as yet to test this conclusively. Averaged values of  $\delta^{13}C\text{-CH}_4$  range from  $-16.3$  to  $-55.8\%$ , though most fall within the range  $-20$  to  $-40\%$  (data from the references quoted in the title of Fig 4).

### Isomers

Isomeric data for butane and pentane in the sedimentary natural gases represented in Fig 1 are plotted in histogram form in Fig 5 with the available hydrothermal data for comparison. For the natural gases the modal value lies within a normal/iso ratio of 1-2 for both butane and pentane, though the reciprocal relationship of 0.5-1 also occurs, particularly for pentane. The main differences between  $C_4$  and  $C_5$  in the natural gases considered here is that  $C_4$  is strongly represented in the normal/iso range of 2-3, where  $C_5$  is not seen at all. The hydrothermal gases have modal values in the same categories as the natural gases, but tend to be relatively better represented at normal/iso ratios above 3. To some extent (particularly for  $C_5$ ) this may be due to artefacts arising out of the difficulty in measuring the very low  $C_{2+}$  concentrations typical of hydrothermal gases, but there seems enough evidence that hydrothermal gases have a wider spread of normal/iso values in excess of unity than the natural gases. This would agree with the conclusions of ASTAFEV et al (1973) and THOMPSON (1979) that the normal/iso ratio in

butane and pentane tends to increase with rise in maximum temperature, rather than being a function of residence time.

Very few data appear to exist which differentiate between the concentrations of hexane, cyclohexane and benzene in both the natural gas and hydrothermal gas categories. As far as hydrothermal gases are concerned, consideration of data from a variety of hydrothermal systems in CAPACCIONI et al (1993) suggests that the concentration of benzene usually either equals or more commonly exceeds that of undifferentiated hexane. Fig 6(a) shows in histogram form these data plus those of OLAFSSON et al (1993) and DARLING (this issue) from a more restricted variety of sites, but there are as yet insufficient aliphatic/aromatic data to test rigorously the hypothesis that benzene most often predominates in the C<sub>6</sub> category. Nevertheless, in the literature generally more benzene than hexane results are reported. Fig 6(b) shows all relevant hydrothermal data in the form of a histogram. Although both C<sub>1</sub>/benzene and C<sub>1</sub>/hexane distributions peak in the 10<sup>3</sup>-10<sup>4</sup> range, benzene is more strongly represented in all categories, particularly at lower ratios. While this is by no means definite proof, it offers some support to the early indications that the phenomenon of relatively high C<sub>1</sub>/C<sub>6</sub> ratios in hydrothermal gases is primarily due to benzene.

## Discussion

Hydrothermal hydrocarbons differ from those in natural gases from sedimentary basins in three basic ways, though none of these is wholly diagnostic in itself. Firstly, C<sub>1</sub>/C<sub>2</sub>, C<sub>1</sub>/C<sub>3</sub>, C<sub>1</sub>/C<sub>4</sub> and C<sub>1</sub>/C<sub>5</sub> ratios are significantly higher in hydrothermal gases than in thermogenic sedimentary gases, though they may be similar to those in biogenic gases. Secondly, δ<sup>13</sup>C-CH<sub>4</sub> values are generally more positive than for thermogenic gases, and invariably significantly more positive than for biogenic gases. Thirdly, there appears to be a significantly lower C<sub>1</sub>/C<sub>6</sub> ratio in subduction-related hydrothermal gases compared to the other categories. Differences between the categories based on isomeric ratios are much less well-defined and therefore less diagnostic.

Despite the differences outlined above, several lines of evidence point to a thermogenic origin for most hydrothermal gases, rather than juvenile or synthetic sources (bacterial biogenic sources can be effectively ruled out on grounds of improbability that bacterial processes can operate on a sufficient scale at high temperatures). The similarity of C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub>/C<sub>5</sub> between hydrothermal and thermogenic natural gas hydrocarbons suggests a similar origin, and a comprehensive review of the δ<sup>13</sup>C-CH<sub>4</sub> situation by WELHAN (1988) shows this to be feasible from an isotopic viewpoint for virtually all hydrothermal gases. However, an explanation of the greater C<sub>1</sub>/C<sub>2</sub> and to a lesser extent relatively lower

$C_1/C_6$  ratios in hydrothermal gases is still required.

To deal with the latter first, it seems that the relatively low  $C_1/C_6$  ratios may often be due to the presence of benzene. It is well known that dehydrogenation of cyclohexane to benzene and hydrogen gas can take place with the aid of catalysts at high temperatures, and this process is invoked by CAPACCIONI et al (1993) to explain high  $C_6H_6$  concentrations. It would also conveniently explain the existence of free  $H_2$  in most hydrothermal systems. However, as SEEWALD (1994) has shown, hydrothermal experiments suggest that water is intimately involved in the creation of organic breakdown products as a source of  $H_2$ . In the circumstances of this water dissociation, it seems unlikely that dehydrogenation would take place; more likely the reverse. Perhaps the reason that  $C_6H_6$  is not typically hydrogenated to  $C_6H_{12}$  is because of the stability of the benzene ring structure (e.g. MORRISON and BOYD, 1966; and in a geological context DURAND-SOURON et al, 1982). This stability appears to hold up to quite high temperatures. On the other hand, competition for  $H_2$  (e.g. from sulphur) might render this explanation unnecessary. In either case, the fact that the  $C_1/C_6$  ratios in Figs 1 and 3 have the greatest overlap of any of the ratios is a possible indication that both gas types originated in the same way (i.e. the more stable  $C_1$  and  $C_6$  molecules have substantially retained their original relationship).

The simplest explanation for the greater  $C_1/C_2$  to  $C_1/C_5$  ratios is thermal breakdown: there is abundant evidence from the study of commercial natural gas fields that  $C_1/C_2$  ratios increase with reservoir temperature (e.g. TISSOT and WELTE, 1984), while the oil industry has long exploited the process of cracking long-chain hydrocarbons into shorter ones by heating, albeit catalytically mediated. Methane would be the ultimate stable hydrocarbon product of any natural cracking process operating at hydrothermal temperatures (i.e. up to 350–400°C). Direct production of  $CH_4$  from kerogen at such high temperatures could also be a potential contributor. However, elevation of  $C_1/C_2$  to  $C_1/C_5$  might also be due to mixing of hydrocarbons of thermogenic origin with 'abiogenic' methane produced in the crust by reaction between  $CO_2$  and  $H_2$ , or with the presumably relatively pure 'deep' methane from mantle sources. These possibilities are now considered.

Ideally, any discussion of thermal breakdown effects would benefit from  $\delta^{13}C$  data on the  $C_{2+}$  compounds. However, owing to the usually very low concentrations in hydrothermal gases this option is infrequently available, and consideration of general tendencies must rest on  $\delta^{13}C-CH_4$ . Fig 7 shows a plot of  $\delta^{13}C-CH_4$  versus  $C_1/C_2$  (as a good approximation for  $C_1/C_{2+C_3+C_4+C_5}$ ) for hydrothermal gases based on information compiled in Table 1. (Table 1 averages data in an attempt to give equal consideration to each field, among which the number of data points can vary considerably.) If the magnitude of  $C_1/C_2$  is a function of  $C_{2+}$  breakdown with increasing temperature, a correlation should be

seen with  $\delta^{13}\text{C-CH}_4$ , because this should be rising back towards the initial kerogen source composition (presumably in the range -20 to -30‰ PDB) from the more depleted initial composition resulting from the spread of fractionation factors between  $\text{C}_1\text{-C}_5$  which attends the initial production from kerogen (e.g. DES MARAIS et al, 1981). The correlation is seen to be a straight-line relationship when  $\text{C}_1/\text{C}_2$  is plotted on a log scale, which suggests that it is indeed related to thermal effects rather than to mixing with a mantle  $\text{CH}_4$  with a  $\text{C}_1/\text{C}_2$  value of, say,  $10^3 - 10^4$  and a  $\delta^{13}\text{C-CH}_4$  of -15‰. The few exceptions to the trend are from the relatively unusual situations of recent organic-rich sediments invaded by thermal fluids, in Lake Tanganyika and the Guaymas basin of the Gulf of California.

However, it is not possible from examining Fig 7 to see where the cracking of  $\text{C}_{2+}$  compounds to  $\text{CH}_4$  stops, and where metagenetic production of  $\text{CH}_4$  direct from kerogen begins, if it occurs at all. It is traditionally considered (e.g. by TISSOT and WELTE, 1984) that the beginning of metagenesis is signalled by  $\delta^{13}\text{C-CH}_4$  values more enriched than -30‰. Based on this somewhat arbitrary value, it appears from Fig 7 that rather more hydrothermal  $\text{CH}_4$  is directly generated from source material than from cracking. However, what holds for natural gas may not be applicable to hydrothermal systems. For example, it is not known with certainty for most systems whether organic precursors are in solid or dissolved form - whether kerogen in sediments is invaded episodically by thermal fluids, or if dissolved organics are continuously being drawn through hydrothermal convective cells. Most hydrothermal systems may contain greater or lesser proportions of both; neither situation is comparable to the slow evolutionary processes that occur in subsiding sedimentary basins.  $\text{C}_1/\text{C}_6$  ratios may be useful in elucidating processes of 'excess'  $\text{CH}_4$  production; as noted earlier, most of the  $\text{C}_1/\text{C}_6$  ratios in Figs 1 and 3 overlap, implying that the reduced proportions of  $\text{C}_2\text{-C}_5$  species arise from cracking. Only in those cases where  $\text{C}_1/\text{C}_{6+}$  is higher is it likely that directly-generated  $\text{CH}_4$  is an important constituent.

If the elevated proportion of  $\text{CH}_4$  in hydrothermal hydrocarbons were due to the addition of an abiogenic methane resulting from reaction at relatively shallow depths between deep  $\text{CO}_2$  and  $\text{H}_2$  formed by the dissociation of water at high temperature, some approach towards isotopic equilibrium between  $\text{CO}_2$  and  $\text{CH}_4$  reflecting the temperature of formation might be expected. When carbon isotopic equilibrium geothermometry is applied to hydrothermal systems the indicated temperatures are frequently implausibly high (Table 1), suggesting separate origins for the  $\text{CO}_2$  and  $\text{CH}_4$  which have yet to achieve isotopic equilibrium. If higher  $\text{C}_1/\text{C}_2$  values truly reflect the presence of synthetic  $\text{CH}_4$ , then these should be associated with lower, more realistic carbon isotope geothermometer temperatures. However, a plot (Fig 8, based on data compiled in Table 1) shows no clear tendency towards this relationship; indeed the opposite is suggested, which is not too surprising since  $\delta^{13}\text{C-CO}_2$  varies comparatively little between systems, while  $\delta^{13}\text{C-CH}_4$  has already been shown in Fig 7 to have a positive correlation with

$C_1/C_2$ . Therefore while a synthetic  $CH_4$  contribution cannot be ruled out (for example, the purity of synthetic  $CH_4$  may vary substantially according to the formation temperature and availability of suitable catalytic minerals - Szatmari, 1989), it seems unlikely to play a major role in most systems.

A test of the possibility of mixing between thermogenic and 'deep'  $CH_4$  can be performed by plotting  $^3He/^4He$  versus  $C_1/C_2$  (Fig 9). There is no sign of a mixing relationship between low  $^3He/^4He$  – low  $C_1/C_2$  and high  $^3He/^4He$  – high  $C_1/C_2$  end members: any such trend would result in a curve on Fig 9 because of the  $C_1/C_2$  log scale. Instead, the data points are better explained by assuming that the hotter the hydrothermal system (or part thereof), the greater the input of mantle helium. Zones are delineated on Fig 9 which show the kind of compositions expected if there is a temperature-controlled evolution between a starting composition with a  $C_1/C_2$  ratio of around 10 and an  $R/R_A$  value of 1, and a high-temperature end product with a  $C_1/C_2$  ratio between  $10^3$  and  $10^4$ , with the relevant  $^3He/^4He$  ratios for the geological situation concerned, i.e.  $R/R_A \sim 5-7$  for subduction, 7-9 for spreading and  $>9$  for hotspots. (The magnitude of the hypothetical mantle  $C_1/C_2$  ratio is admittedly speculative, but at mantle temperatures it is difficult to see how  $C_{2+}$  molecules could be stable enough to exist to any significant extent.) With the exception of Yellowstone, where the available  $C_1/C_2$  data are not from the high  $^3He/^4He$  areas of the Caldera, samples fall either within their expected zones, or in some cases outside their zone but on the lower  $C_1/C_2$  side, suggesting that local enrichments in organic precursors are responsible for the shift. It is noteworthy that samples never fall outside their zones on the higher  $C_1/C_2$  side, which they would tend to do if derived from a straightforward mixing process and not near to an end-member composition.

Given the above evidence, it appears that (except for biogenic gases) the ratio of methane to ethane could reflect substantially the maximum temperature reached during evolution. Tendencies towards re-equilibration on cooling seem likely to be limited by kinetic factors (SUGISAKI and NAGAMINE, 1995).

## GEOTHERMOMETRY

The data reviewed in the previous section suggest that hydrothermal hydrocarbon gases are mostly of thermogenic origin and share with natural gases a tendency towards a rise in the methane/ethane ratio with increasing temperature. This characteristic temperature-related breakdown to methane may be of only passing interest to gas producers but could be of greater significance to geothermal development. Geothermometry in geothermal systems has usually depended on the deployment of aqueous cation and silica geothermometers (e.g. FOURNIER, 1981), which have been proved in many locations worldwide. However, in more arid areas where regional groundwater levels are low, most reliance must be placed

on gas geothermometry. Several relationships between subsurface temperature and 'inorganic' gas concentrations or ratios have been proposed, based on assumed gas-mineral equilibria controls (e.g. ARNORSSON and GUNNLAUGSSON, 1985). The evidence for whether  $\text{CH}_4/\text{C}_2\text{H}_6$  could also be used in a predictive capacity is now considered.

Fig 10 shows a plot of  $\text{C}_1/\text{C}_2$  versus reservoir temperature based on direct measurement or solute geothermometry using the data compiled in Table 1. Over half the data are derived from geothermal wells while the remainder are from spring and fumarolic sources. Where there are two or more data points for a geothermal field, these have been averaged to avoid over-representing any particular system. There is a clear tendency for an increase in  $\text{C}_1/\text{C}_2$  with rise in temperature. A regression line with the form

$$t^{\circ}\text{C} = 57.8 \log (\text{C}_1/\text{C}_2) + 96.8$$

and an  $r^2$  of 0.75 can be drawn through the data with the exception of the four outlying points representing Cerro Prieto, Guanacaste, Guaymas and Vulcano. The  $\pm 35^{\circ}\text{C}$  band around this regression line is also shown. Most of the hydrothermal systems fall within this band. Two of the exceptions, Cerro Prieto, situated in northern Mexico and the relatively nearby Guaymas offshore field further south in the Gulf of California, lie on the same rift/transform fault system. In both cases there is an excess of  $\text{C}_2$  for the temperature. Both fields are basically sediment-hosted and abundant organic remains are present (DES MARAIS et al, 1988; WELHAN and LUPTON, 1987). This could be the source of the discrepancy. GIGGENBACH and CORRALES (1992) speculated about the involvement of sediments at Guanacaste also. Perhaps these systems represent an end-member of a series of sub-parallel trends from different hydrothermal systems, but as yet there are too few data to test this. Only Vulcano plots significantly below the band, probably because of the influence of volcanic gases, which are generally devoid of higher hydrocarbons because of their extremely high temperatures ( $>500^{\circ}\text{C}$ ).

Apart from these somewhat specialised exceptions, it appears that geothermometry based on the methane/ethane ratio of hydrothermal gases can be a reasonably accurate predictor of subsurface temperatures. The analysis of these gases is simple, and no information about absolute gas concentrations relative to steam or knowledge of reservoir salinity is necessary (as required by e.g. ARNORSSON and GUNNLAUGSSON, 1985), or measurements of/assumptions about multiple gas concentrations (see e.g. SIMONEIT, 1982). This means that the  $\text{C}_1/\text{C}_2$  geothermometer may be useful during reconnaissance of geothermal prospects based on fumarolic surface features, or for oceanic hydrothermal systems where solute geothermometry could be difficult to apply.



## CONCLUSIONS

The origin of hydrocarbon gases in hydrothermal systems has been considered from several points of view, based on evidence provided by published studies. It is concluded that most, if not all, hydrothermal hydrocarbon gases are generated in the shallow subsurface by the action of heat on organic precursors. Apart from being present at much lower concentrations, the resulting gas mixtures differ from those produced in sedimentary basins chiefly by possessing a higher proportion of methane. While a conventional interpretation of carbon isotope data would indicate that this is of metagenetic origin, consideration of the  $C_1/C_6$  evidence suggests that at least in some cases the 'excess' methane is simply due to the extension of an initial catagenetic process.

As would be predicted by the assumption of a thermal breakdown mechanism, the ratio of  $CH_4$  to  $C_{2+}$  in hydrothermal systems appears to show a correlation with deep temperatures where these have been determined by direct measurement or solute geothermometry. Using the ratio  $CH_4/C_2H_6$  as an approximation, a geothermometric relationship has been developed which is simple to apply and works within certain limits for most geothermal systems.

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Table 1. Averaged methane/ethane ( $C_1/C_2$ ) and other data for hydrothermal systems worldwide. Data sources as credited in footnotes.

Hydrothermal System	Sample Source	$C_1/C_2$	T res °C	$\delta^{13}C\text{-CH}_4$ ‰ PDB	$^3\text{He}/^4\text{He}$ R/R <sub>A</sub>	$T_{\Delta}^{13}C$ °C	Data Sources
<b>Subduction</b>							
El Ruiz, Colombia	N	1139	273 <sup>g</sup>	-	3.9	-	16, 31
Guanacaste, Costa Rica	W, N	22	241 <sup>g</sup>	-	7.0	-	13
Nisyros, Greece	W	9375	316 <sup>m</sup>	-	-	-	6, 42
Campi Flegrei, Italy	N	67	170 <sup>m</sup>	-	2.6	-	5, 33
Lardarello, Italy	W	335	232 <sup>m</sup>	-	3.2	-	5, 19
Vulcano, Italy	N	6526	200 <sup>m</sup>	-	5.0	-	2, 5
Matsukawa, Japan	W	223	230 <sup>m</sup>	-28.3	-	359	22
Cerro Prieto, Mexico	W	76	288 <sup>m</sup>	-33.7	6.3	252	10, 26, 39
Broadlands, New Zealand	W	1071	273 <sup>m</sup>	-26.1	6.2	393	11, 15, 25, 35
Rotorua, New Zealand	W, N	601	222 <sup>g</sup>	-30.5	-	307	14, 32, 35
Wairakei, New Zealand	W	131	261 <sup>c</sup>	-25.8	7.1	350	11, 15, 25, 35
Kamchatka, Russia	W, N	1811	280 <sup>m</sup>	-25.7	6.4	328	20, 32
<b>Spreading Ridge</b>							
Sao Miguel, Azores	W, N	76	230 <sup>m</sup>	-	-	-	5, 30
Asal, Djibouti	W	219	264 <sup>g</sup>	-25.9	12.3	322	7, 8
Oxarfjordur, Iceland	W	57	165 <sup>c</sup>	-39.5	10.3	-	27, 29
Bransfield Str, Antarctica	N <sup>a</sup>	5	150 <sup>c</sup>	-38.1	1.1	-	41
East Pacific Rise	N	1348	312 <sup>m</sup>	-16.3	7.8	689	37
Guaymas Basin, Gulf Calif	N	270	315 <sup>m</sup>	-46.4	7.0	119	38
Juan de Fuca, NE Pacific	N	783	285 <sup>m</sup>	-19.6	7.8	456	12
Red Sea	N	581	210 <sup>c</sup>	-	8.6	-	4, 24
<b>Continental</b>							
Aluto, Ethiopia	W	765	287 <sup>g</sup>	-25.8	11.5	345	7, 8
Olkaria, Kenya	W	906	292 <sup>g</sup>	-26.2	5.9	311	8, 9
Kibiro, Uganda	N	52	178 <sup>c</sup>	-36.2	-	300	1, 9
Yellowstone, USA	N, W	269	212 <sup>c,m</sup>	-23.5	4.8	350	17, 18, 21, 36, 40
Banza, L. Tanganyika	N	11	166 <sup>c</sup>	-50.4	-	138	3, 28, 34
Pemba, L. Tanganyika	N	117	214 <sup>c</sup>	-57.9	-	86	3, 28, 34

T res - Reservoir temperature, provided in data source (either measured [m] or calculated by solute geothermometry [c], as indicated) or calculated for this study from the average of the Na/K and SiO<sub>2</sub> solute geothermometers (g) in FOURNIER (1981).

$T_{\Delta}^{13}C$  - Carbon isotope geothermometry temperature calculated from the equation in LYON and HULSTON (1984).

Sample source: N - natural (spring or fumarole etc); W - well; a - based on the samples with most  $\delta^{13}C\text{-CH}_4$  enrichment from stations 1347 and 1357 of ref. 41 below.

Data sources : 1 - ARMANNSSON (1994); 2 - BOLOGNESI and D'AMORE (1993); 3 - BOTZ and STOFFERS (1993); 4 - BURKE et al (1981); 5 - CAPACCIONI et al (1993); 6 - CHIODINI et al (1993); 7 - DARLING (1996); 8 - DARLING (this issue); 9 - DARLING et al (1995); 10 - DES MARAIS et al (1988); 11 - ELLIS and MAHON (1977); 12 - EVANS et al (1988); 13 - GIGGENBACH and CORRALES (1992); 14 - GIGGENBACH and GLOVER (1992); 15 - GIGGENBACH et al (1988); 16 - GIGGENBACH et al (1990); 17 - GUNTER (1978); 18 - GUNTER and MUSGRAVE (1971); 19 - HOOKER et al (1985); 20 - KAMENSKY et al (1976); 21 - KENNEDY et al (1984); 22 - KIYOSU et al (1992); 23 - KONONOV (1992); 24 - LUPTON et al (1977); 25 - LYON and HULSTON (1984); 26 - NEHRING and D'AMORE (1984); 27 - OLAFSSON et al (1993); 28 - PFLUMIO et al (1994); 29 - POREDA et al (1992); 30 - RODRIGUES et al (1994); 31 - SANO et al (1990); 32 - STEWART et al (1992); 33 - TEDESCO et al (1990); 34 - TIERCELIN et al (1993); 35 - TORGENSEN et al (1982); 36 - TRUESDELL et al (1977); 37 - WELHAN and CRAIG (1983); 38 - WELHAN and LUPTON (1987); 39 - WELHAN et al (1979); 40 - WELHAN et al (1988); 41 - WHITICAR and SUESS (1990); 42 - gas results used by permission of the Public Power Corporation, Athens.

## FIGURE CAPTIONS

- Fig 1 Distribution of ethane, propane, butane, pentane and undifferentiated C<sub>6</sub> in typical thermogenic sedimentary basin gasfields. Results from each field are averaged and expressed in relation to CH<sub>4</sub> (i.e. as C<sub>1</sub>/C<sub>n</sub>). Sources of data: IGARI and SAKATA (1988), Japan (1); JAMES (1990), Canada (2), USA (3) and UK North Sea (4); JENDEN et al (1988), USA (5).
- Fig 2 Distribution of ethane, propane, butane, pentane and undifferentiated C<sub>6</sub> in low-temperature gases from predominantly crystalline sources. Results from each area are averaged and expressed in relation to CH<sub>4</sub> (i.e. as C<sub>1</sub>/C<sub>n</sub>). Sources of data: GIGGENBACH et al (1991), Laacher See, Germany (1) and Mt Gambier, Australia (2); NEAL and STANGER (1983) Oman (3); SHERWOOD-LOLLAR et al (1993) and SALVI and WILLIAMS-JONES (1997), areas of the Canadian Shield (4); KONERUP-MADSEN et al (1979), S Greenland (5).
- Fig 3 Distribution of ethane, propane, butane, pentane and undifferentiated C<sub>6</sub> in hydrothermal gases from subduction-related sources. Results for each system are averaged and expressed in relation to CH<sub>4</sub> (i.e. as C<sub>1</sub>/C<sub>n</sub>). Sources of data: CAPACCIONI et al (1993), Campi Flegrei (1), Lardarello (2) and Vulcano (3), Italy, El Chichon, Mexico (4) and S Kamchatka, Russia (5); DES MARAIS et al (1988) Cerro Prieto, Mexico (6); GIGGENBACH and CORRALES (1992), Guanacaste-Miravalles, Costa Rica (7); GIGGENBACH and GLOVER (1992), Rotorua, NZ (8); GIGGENBACH et al (1988), Broadlands (9) and Wairakei (10), NZ; GIGGENBACH et al (1990), Nevado del Ruiz, Colombia (11); GIGGENBACH et al (1992), Zunil, Guatemala (12); KIYOSU et al (1992), Matsukawa, Japan (13).
- Fig 4 Distribution of ethane, propane, butane, pentane and undifferentiated C<sub>6</sub> in hydrothermal gases from spreading zones and continental systems. Results for each system are averaged and expressed in relation to CH<sub>4</sub> (i.e. as C<sub>1</sub>/C<sub>n</sub>). Sources of data: BOTZ and STOFFERS (1993), L. Tanganyika (1); CAPACCIONI et al (1993), Azores (2); GUNTER (1978), Yellowstone, USA (3); OLAFSSON et al (1993), Oxarfjordur, Iceland (4); WELHAN and CRAIG (1983) East Pacific Rise (5); WELHAN and LUPTON (1987), Guaymas Basin, Gulf of California (6); WHITICAR and SUESS (1990), Bransfield Strait, Antarctica (7).
- Fig 5 Histograms showing the distribution of butane and pentane isomers in hydrothermal and sedimentary gases. Data from references given in captions to Figs 1, 3 and 4, plus SIMONEIT et al (1988).
- Fig 6 (a) Histogram showing the distribution of C<sub>6</sub> aliphatic/benzene in hydrothermal gases. Data from CAPACCIONI et al (1993), OLAFSSON et al (1993) and DARLING (this issue) (b) Histogram showing the distribution of C<sub>1</sub>/benzene and C<sub>1</sub>/hexane data for hydrothermal gases. Data from same sources as Fig 5.
- Fig 7 Plot of δ<sup>13</sup>C-CH<sub>4</sub> vs. methane/ethane ratio (C<sub>1</sub>/C<sub>2</sub>) for hydrothermal gases of all types, based on data compiled in Table 1 (results for each system averaged). Data from references quoted in footnote to Table 1. *Subduction* and *Spreading* categories refer to both terrestrial and marine systems, while *Continental* refers to systems in the continental interiors, which do not readily fit into either of the first two categories.
- Fig 8 Plot of carbon isotope geothermometer temperatures vs. methane/ethane ratio (C<sub>1</sub>/C<sub>2</sub>) for hydrothermal gases of all types, based on data compiled in Table 1 (results for each system averaged). Data from references quoted in footnote to Table 1.

- Fig 9 Plot of  $^3\text{He}/^4\text{He}$  as  $R/R_A$  (ratio in the sample compared to the ratio in air, e.g. TORGERSEN et al, 1982) vs. methane/ethane ratio ( $C_1/C_2$ ) for hydrothermal gases of all types, based on data compiled in Table 1 (results for each system averaged). Symbols as for Fig 8, but with the addition of empty symbols to indicate cases where hotspot (lower mantle) helium is present. Ho - hotspot zone; Sp - spreading and dormant rifting outside hotspot areas; Su - subduction; M - theoretical mixing line between crustal and putative mantle methane of general spreading-subduction type (i.e. non-hotspot). Data from references quoted in footnote to Table 1.
- Fig 10 Plot of geothermal reservoir temperature vs. methane/ethane ratio ( $C_1/C_2$ ) for hydrothermal gases of all types, based on data compiled in Table 1 (results for each system averaged). Data from references quoted in footnote to Table 1. Regression line for all points except Cerro Prieto (C), Guanacaste (G), Guaymas (Gs) and Vulcano (V) is shown, together with the  $\pm 35^\circ\text{C}$  band.

FIG. 1

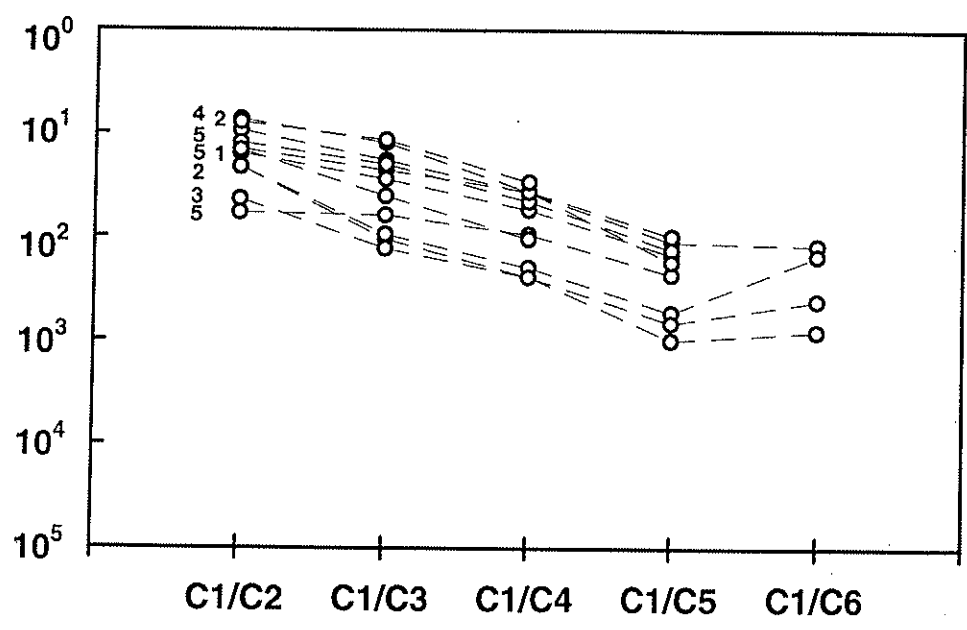


FIG. 2

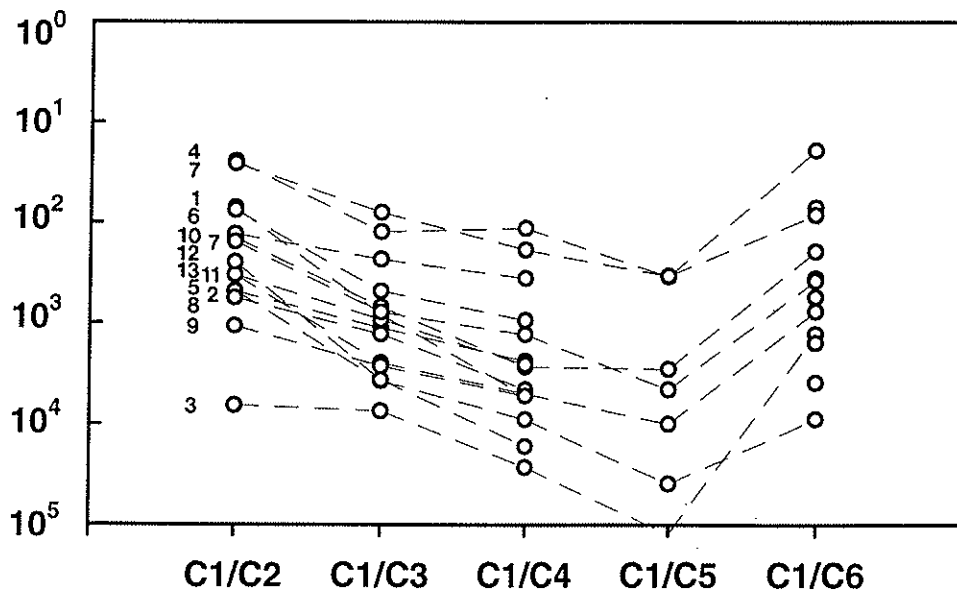


FIG. 2

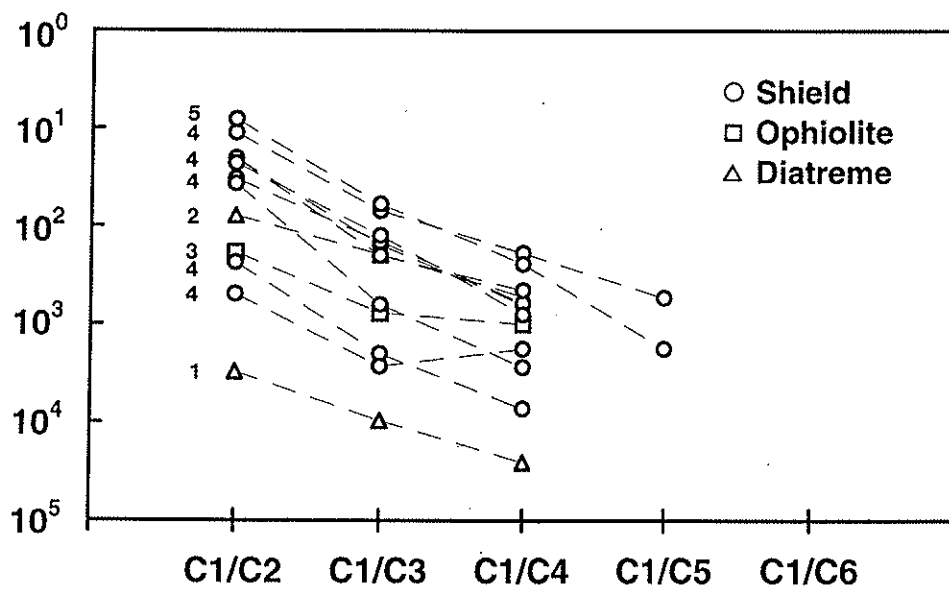


FIG. 4

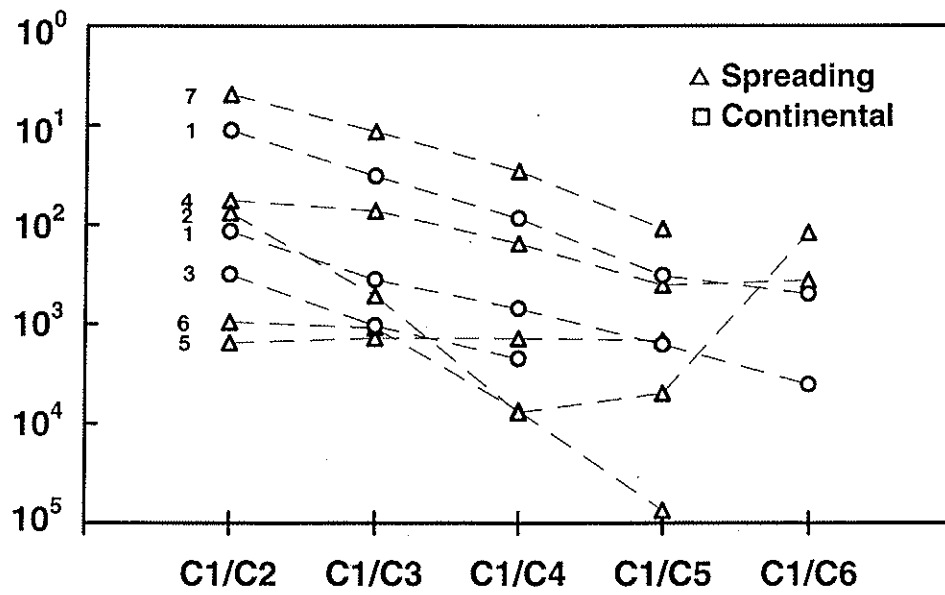
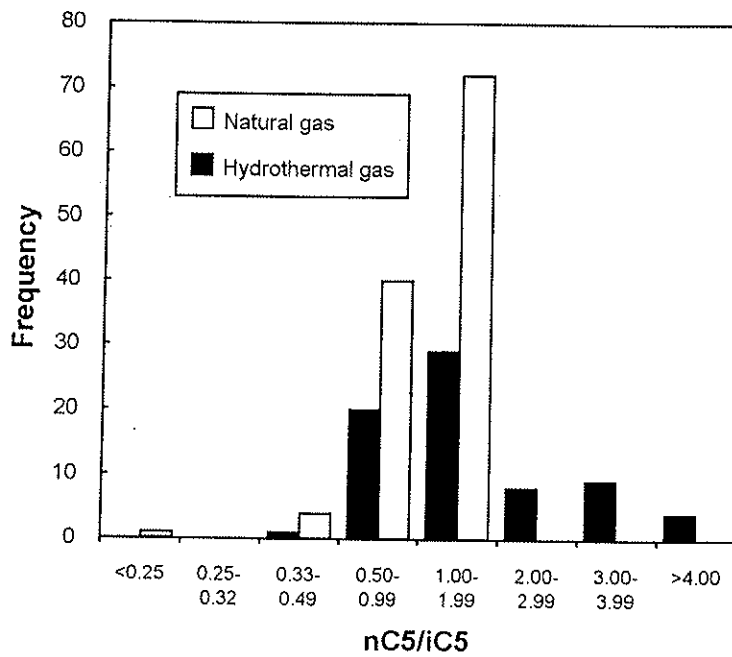
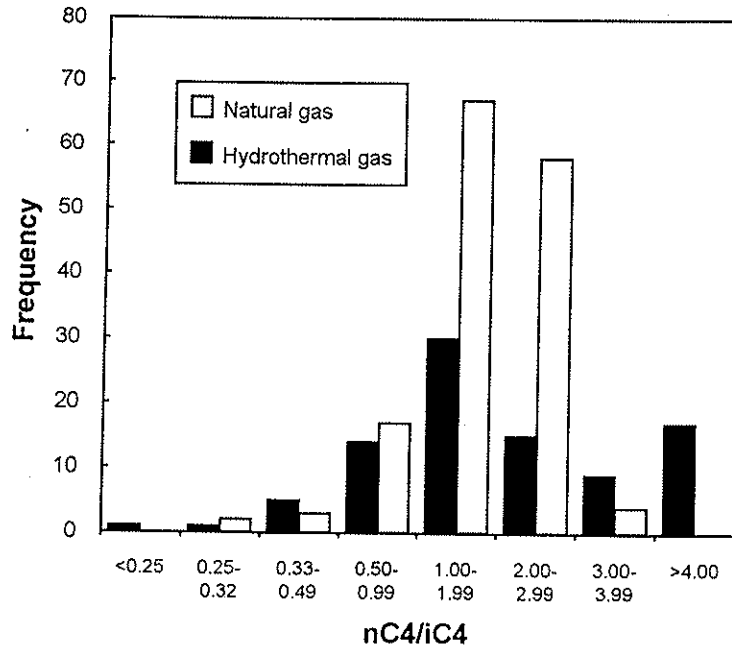


FIG. 5





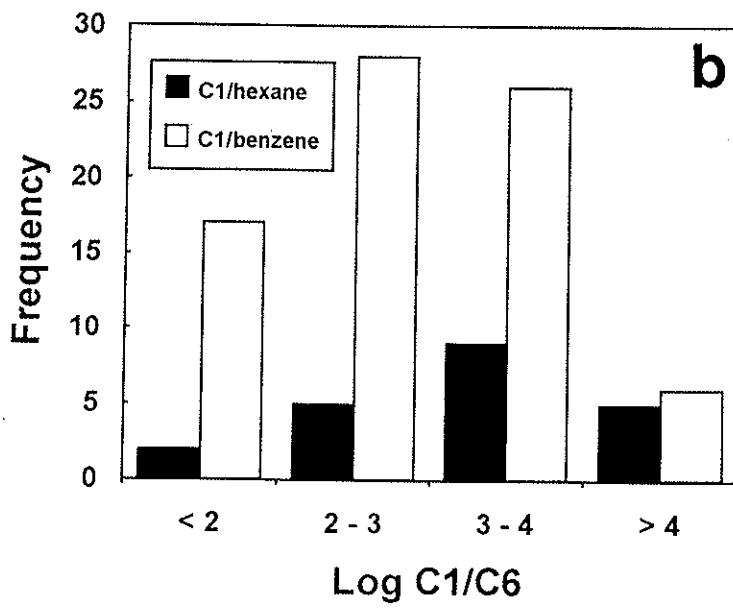
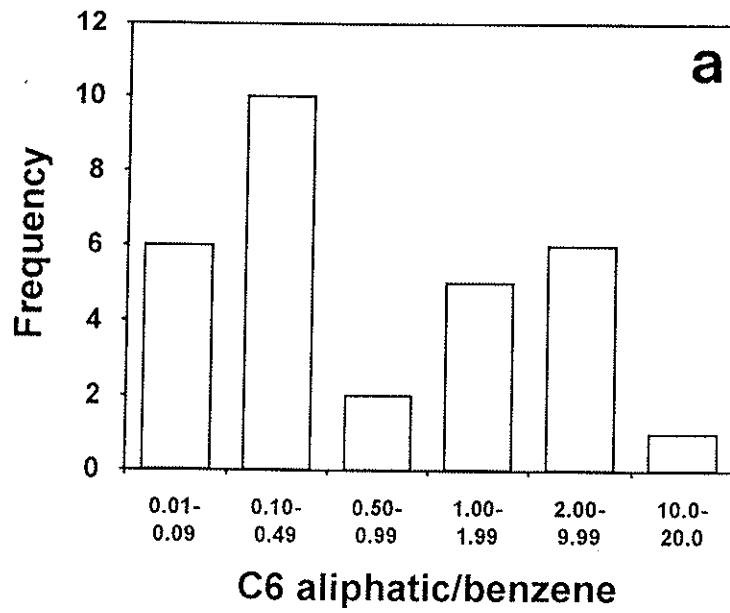




FIG. 8

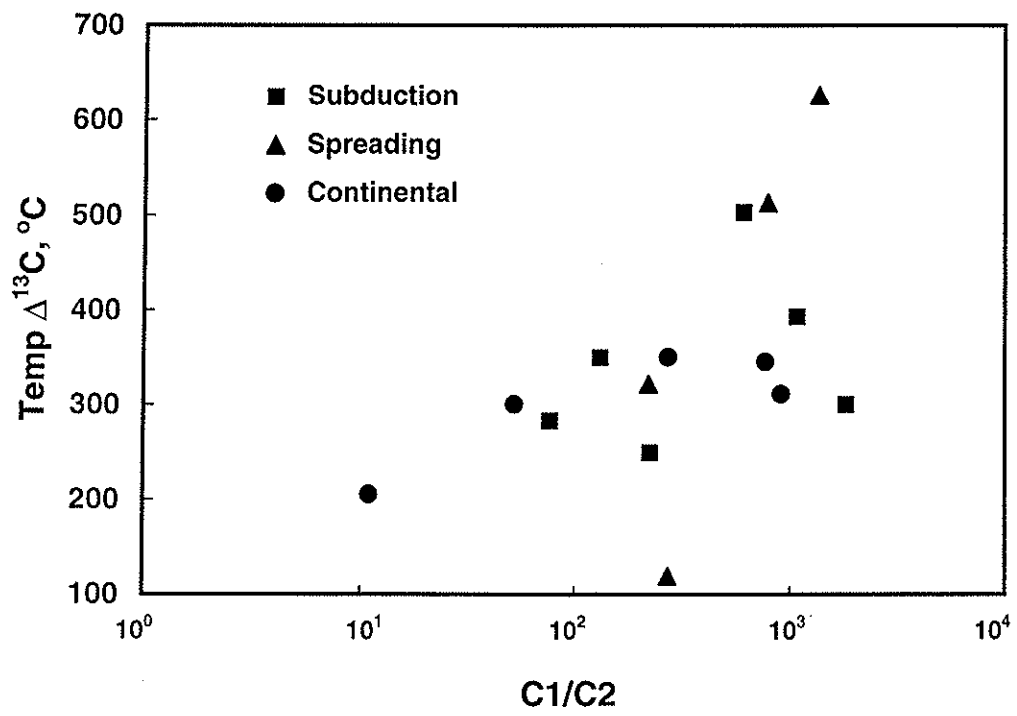


FIG. 9

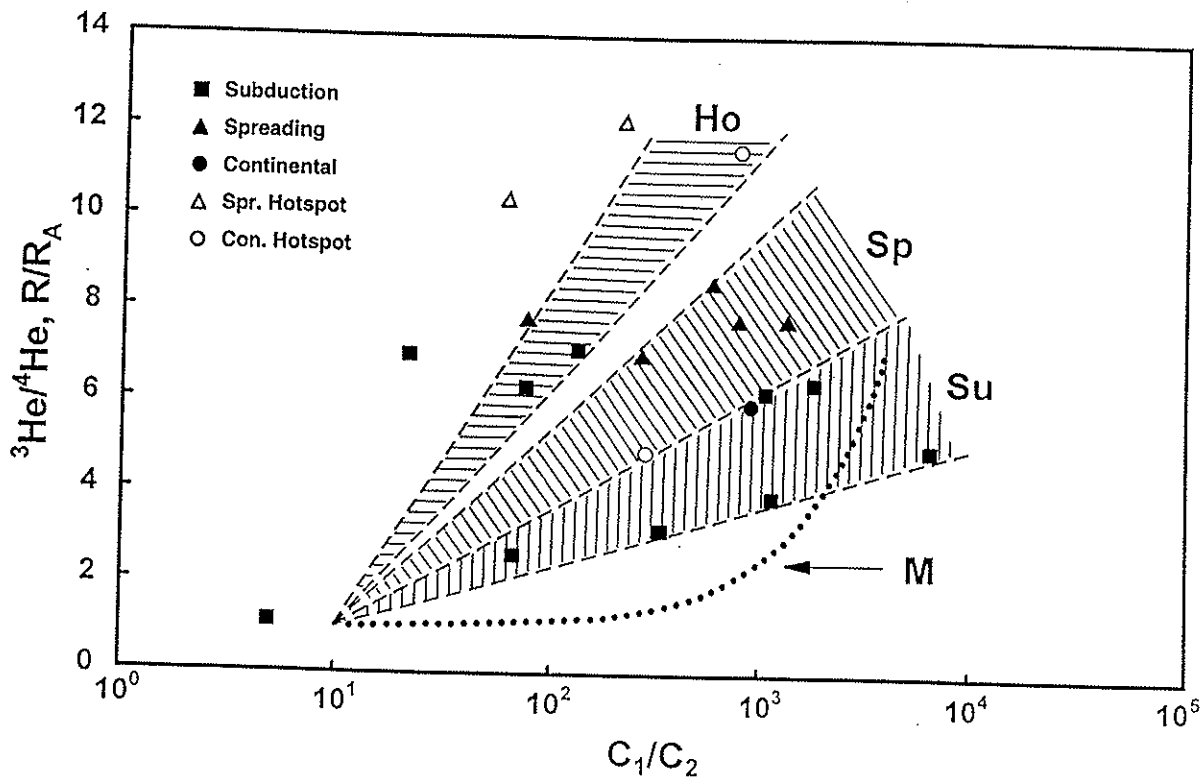


FIG. 10

