

Hydrothermal hydrocarbon gases:

1, Genesis and geothermometry

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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 C₁-C₆ 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 C₆ 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 CH₄ 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 CH₄ require information about higher hydrocarbon gases ('C₂₊') and ¹³C 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 δ¹³C-CH₄; there are still too few data to consider broadening the approach to include δ²H-CH₄ 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 C₆ respectively. Methane/ethane (C₁/C₂) ratios within the range 10-100 are followed in a fairly linear way through C₁/C₃ and C₁/C₄ to C₁/C₅, which lies between 10² and 10³. C₆ data where available mostly indicate a slight rise in concentration relative to C₅. The average δ¹³C values of CH₄ 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 C₁/C₂-C₁/C₃-C₁/C₄-C₁/C₅ ('C₁/C₂ to C₁/C₅') 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 C₁/C₂ but virtually none for C₁/C₃ and C₁/C₄. The compositional range therefore occupies an area of the plot almost entirely separate from the sedimentary natural gases. There are few C₅ data for these gases and only one C₆ value, so it is not possible to draw conclusions regarding relative amounts of C₅ and C₆ compounds. These crystalline gases come from a variety of sources - diatremes, ophiolites and ancient shield rocks - and their averaged δ¹³C-CH₄ 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 C₆ 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 C₁/benzene and C₁/hexane distributions peak in the 10³-10⁴ 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 C₁/C₆ 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, C₁/C₂, C₁/C₃, C₁/C₄ and C₁/C₅ ratios are significantly higher in hydrothermal gases than in thermogenic sedimentary gases, though they may be similar to those in biogenic gases. Secondly, δ¹³C-CH₄ 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 C₁/C₆ 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 C₂/C₃/C₄/C₅ between hydrothermal and thermogenic natural gas hydrocarbons suggests a similar origin, and a comprehensive review of the δ¹³C-CH₄ situation by WELHAN (1988) shows this to be feasible from an isotopic viewpoint for virtually all hydrothermal gases. However, an explanation of the greater C₁/C₂ 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 C_1/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 CH_4 with a C_1/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 C_{2+} compounds to CH_4 stops, and where metagenetic production of 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 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. C_1/C_6 ratios may be useful in elucidating processes of 'excess' CH_4 production; as noted earlier, most of the C_1/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 C_1/C_{6+} is higher is it likely that directly-generated CH_4 is an important constituent.

If the elevated proportion of CH_4 in hydrothermal hydrocarbons were due to the addition of an abiogenic methane resulting from reaction at relatively shallow depths between deep CO_2 and H_2 formed by the dissociation of water at high temperature, some approach towards isotopic equilibrium between CO_2 and 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 CO_2 and CH_4 which have yet to achieve isotopic equilibrium. If higher C_1/C_2 values truly reflect the presence of synthetic 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 ~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 C_1/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 C_1/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 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 C_1/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.

Acknowledgements: I thank the referees (J.A. Welhan and anonymous) and Associate Editor B.R.T. Simoneit for their helpful comments and advice. This paper is published with the permission of the Director, British Geological Survey (NERC).

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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 _A	$T_{\Delta}^{13}C$ °C	Data Sources
Subduction							
El Ruiz, Colombia	N	1139	273 ^g	-	3.9	-	16, 31
Guanacaste, Costa Rica	W, N	22	241 ^g	-	7.0	-	13
Nisyros, Greece	W	9375	316 ^m	-	-	-	6, 42
Campi Flegrei, Italy	N	67	170 ^m	-	2.6	-	5, 33
Lardarello, Italy	W	335	232 ^m	-	3.2	-	5, 19
Vulcano, Italy	N	6526	200 ^m	-	5.0	-	2, 5
Matsukawa, Japan	W	223	230 ^m	-28.3	-	359	22
Cerro Prieto, Mexico	W	76	288 ^m	-33.7	6.3	252	10, 26, 39
Broadlands, New Zealand	W	1071	273 ^m	-26.1	6.2	393	11, 15, 25, 35
Rotorua, New Zealand	W, N	601	222 ^g	-30.5	-	307	14, 32, 35
Wairakei, New Zealand	W	131	261 ^c	-25.8	7.1	350	11, 15, 25, 35
Kamchatka, Russia	W, N	1811	280 ^m	-25.7	6.4	328	20, 32
Spreading Ridge							
Sao Miguel, Azores	W, N	76	230 ^m	-	-	-	5, 30
Asal, Djibouti	W	219	264 ^g	-25.9	12.3	322	7, 8
Oxarfjordur, Iceland	W	57	165 ^c	-39.5	10.3	-	27, 29
Bransfield Str, Antarctica	N ^a	5	150 ^c	-38.1	1.1	-	41
East Pacific Rise	N	1348	312 ^m	-16.3	7.8	689	37
Guaymas Basin, Gulf Calif	N	270	315 ^m	-46.4	7.0	119	38
Juan de Fuca, NE Pacific	N	783	285 ^m	-19.6	7.8	456	12
Red Sea	N	581	210 ^c	-	8.6	-	4, 24
Continental							
Aluto, Ethiopia	W	765	287 ^g	-25.8	11.5	345	7, 8
Olkaria, Kenya	W	906	292 ^g	-26.2	5.9	311	8, 9
Kibiro, Uganda	N	52	178 ^c	-36.2	-	300	1, 9
Yellowstone, USA	N, W	269	212 ^{c,m}	-23.5	4.8	350	17, 18, 21, 36, 40
Banza, L. Tanganyika	N	11	166 ^c	-50.4	-	138	3, 28, 34
Pemba, L. Tanganyika	N	117	214 ^c	-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 SiO₂ 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 C₆ in typical thermogenic sedimentary basin gasfields. Results from each field are averaged and expressed in relation to CH₄ (i.e. as C₁/C_n). 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 C₆ in low-temperature gases from predominantly crystalline sources. Results from each area are averaged and expressed in relation to CH₄ (i.e. as C₁/C_n). 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 C₆ in hydrothermal gases from subduction-related sources. Results for each system are averaged and expressed in relation to CH₄ (i.e. as C₁/C_n). 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 C₆ in hydrothermal gases from spreading zones and continental systems. Results for each system are averaged and expressed in relation to CH₄ (i.e. as C₁/C_n). 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 C₆ 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 C₁/benzene and C₁/hexane data for hydrothermal gases. Data from same sources as Fig 5.
- Fig 7 Plot of δ¹³C-CH₄ vs. methane/ethane ratio (C₁/C₂) 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 (C₁/C₂) 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

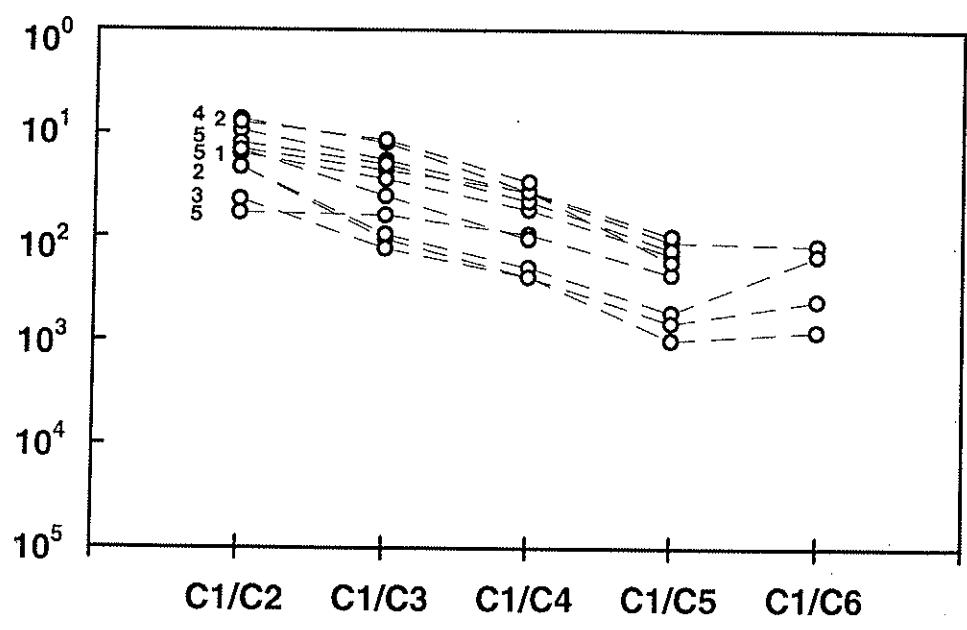


FIG. 2

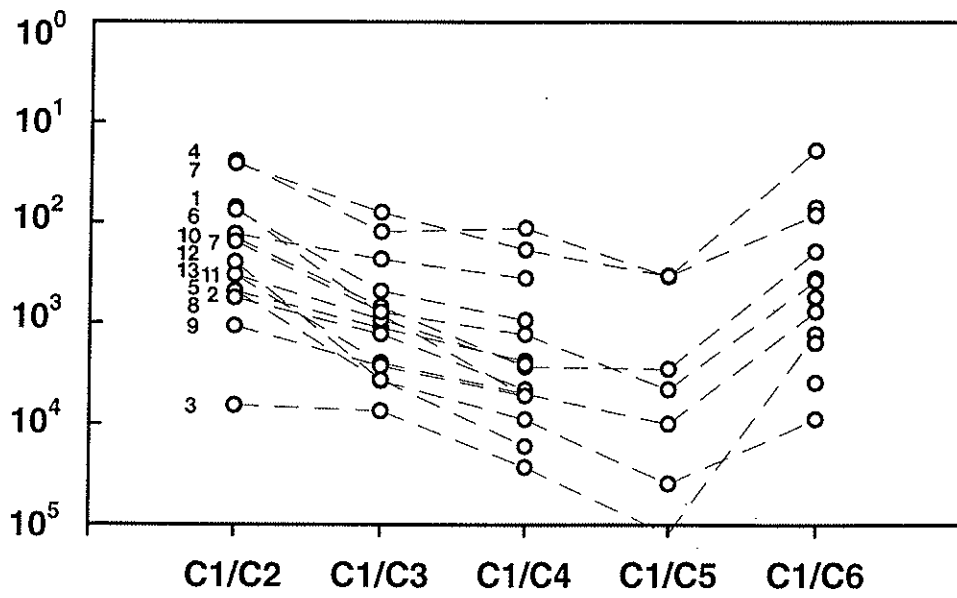


FIG. 2

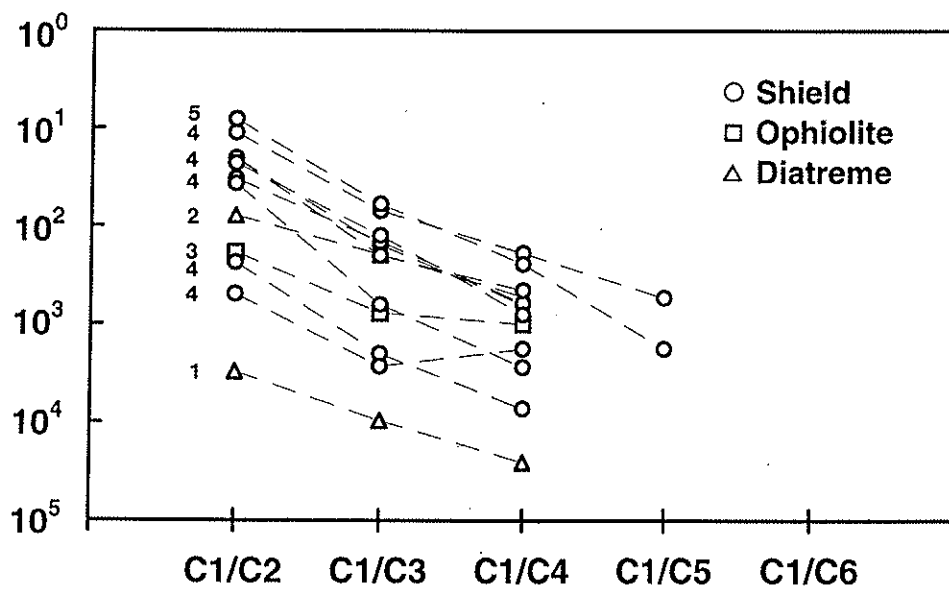


FIG. 4

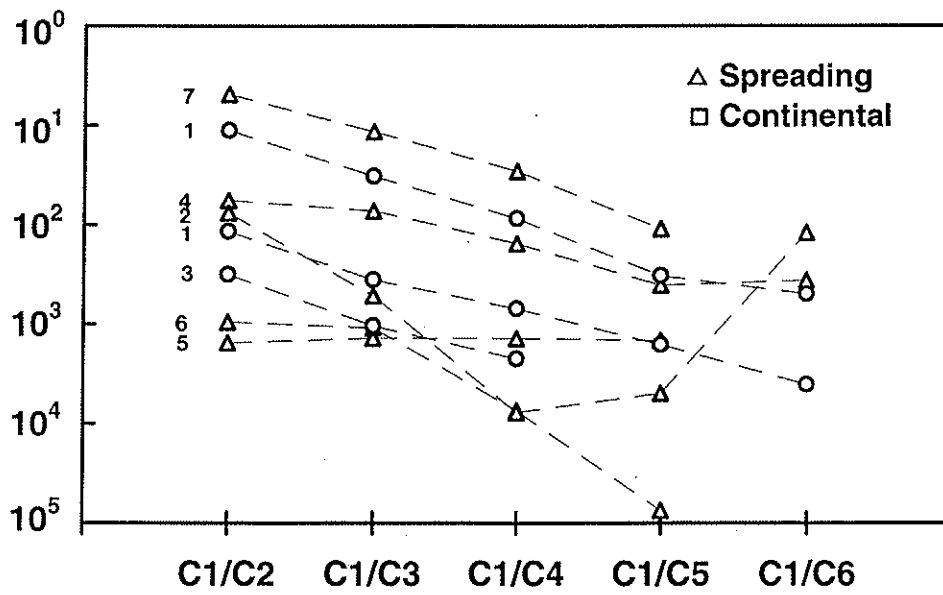
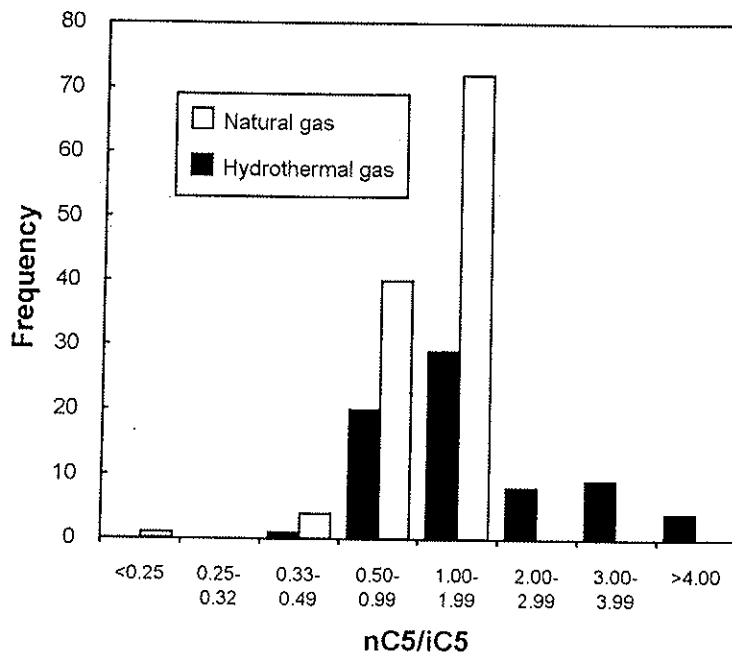
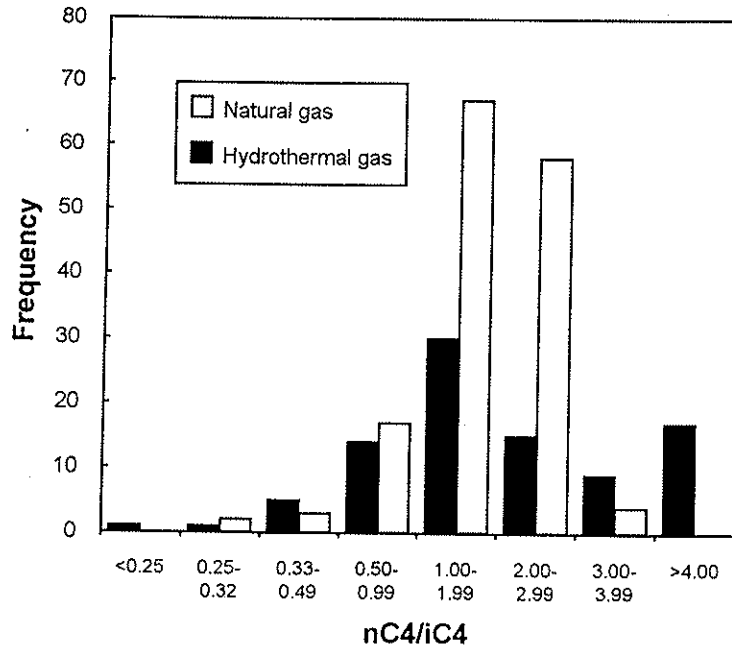


FIG. 5



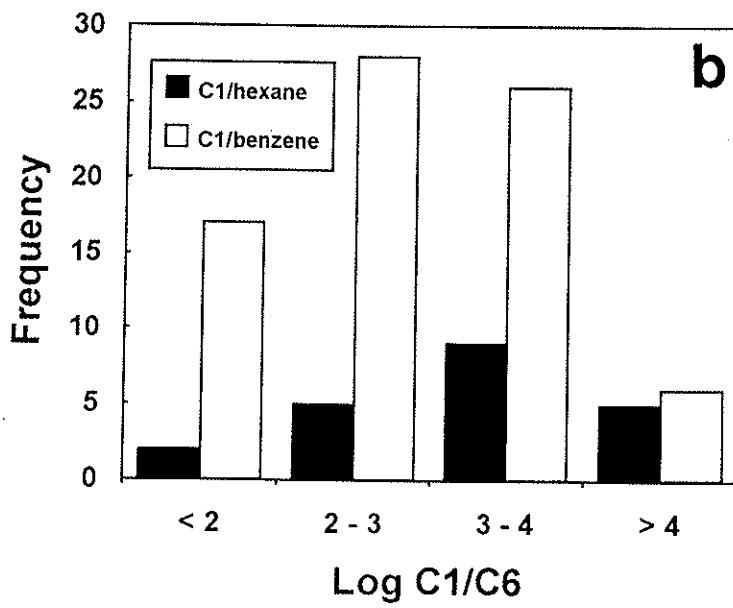
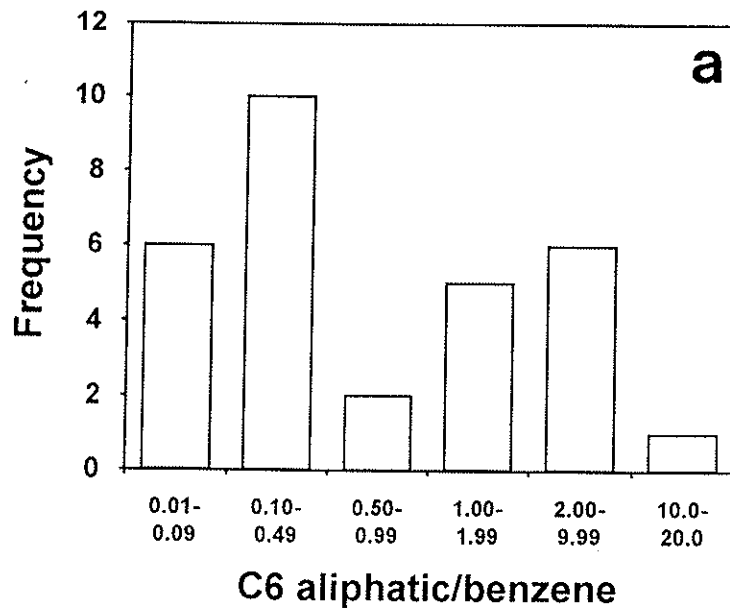


FIG. 7

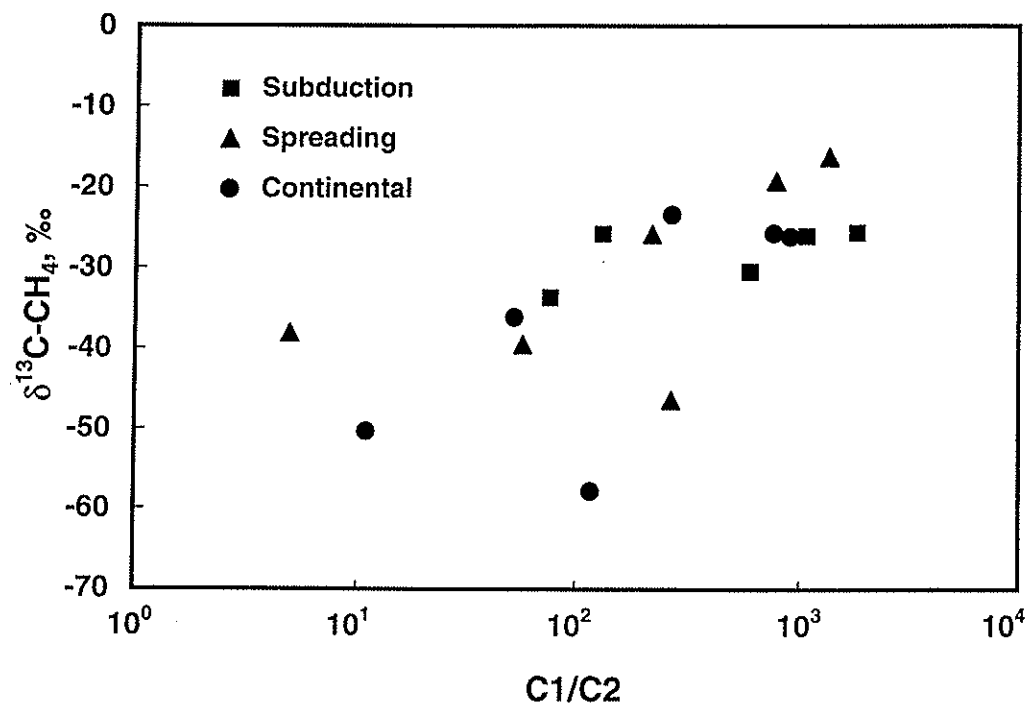


FIG. 8

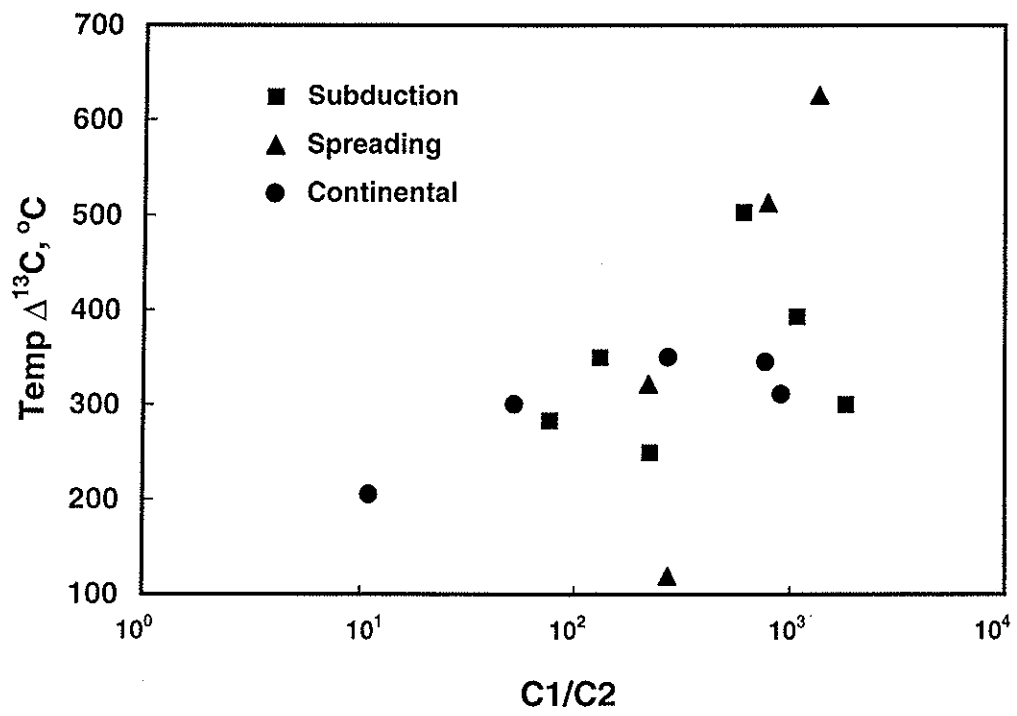


FIG. 9

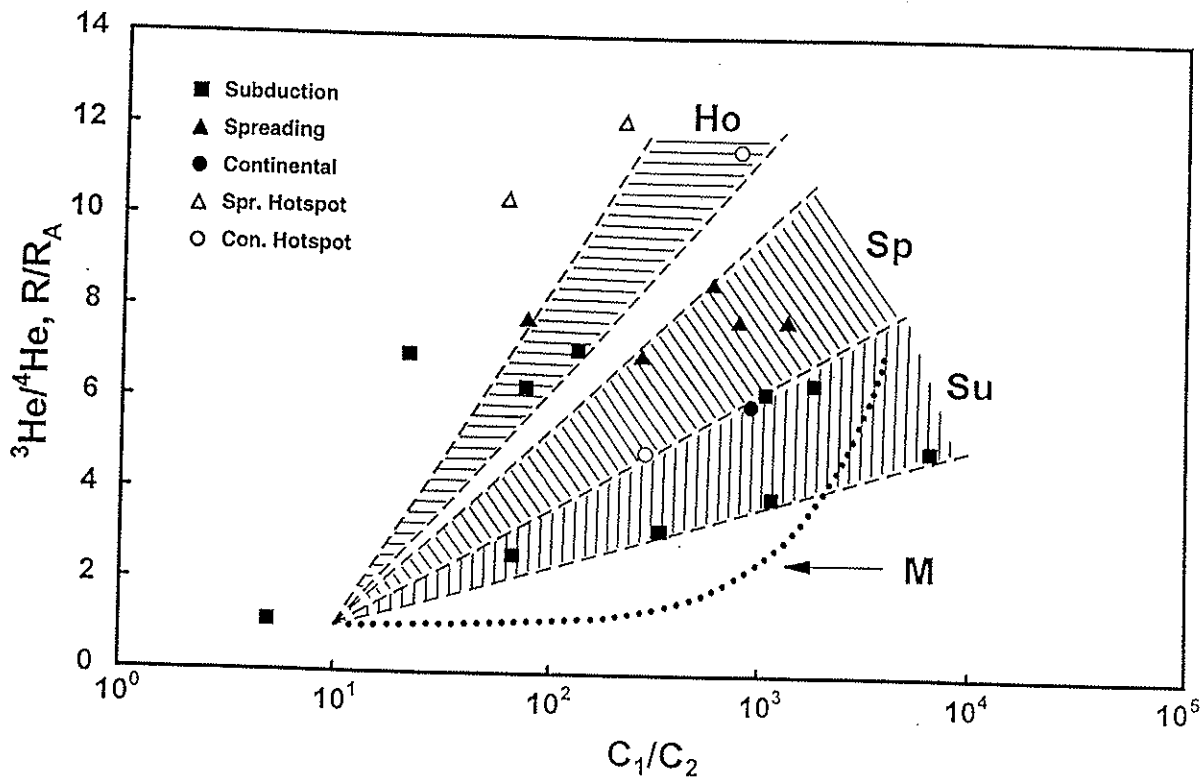


FIG. 10

