An abiogenic hydrocarbons of mantle-derived in Songliao Basin, China

The 2nd Deep Carbon Cycle International Conference (Beijing, April 21-25, 2010)

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Songliao Basin, located in northeast China, covers an area of $24\times10^4 km^2$ and is the biggest oil reservior in China. The natural gas prospecting in the basin has provided good chance for the investigation of and search for abiogenic commercial gases.

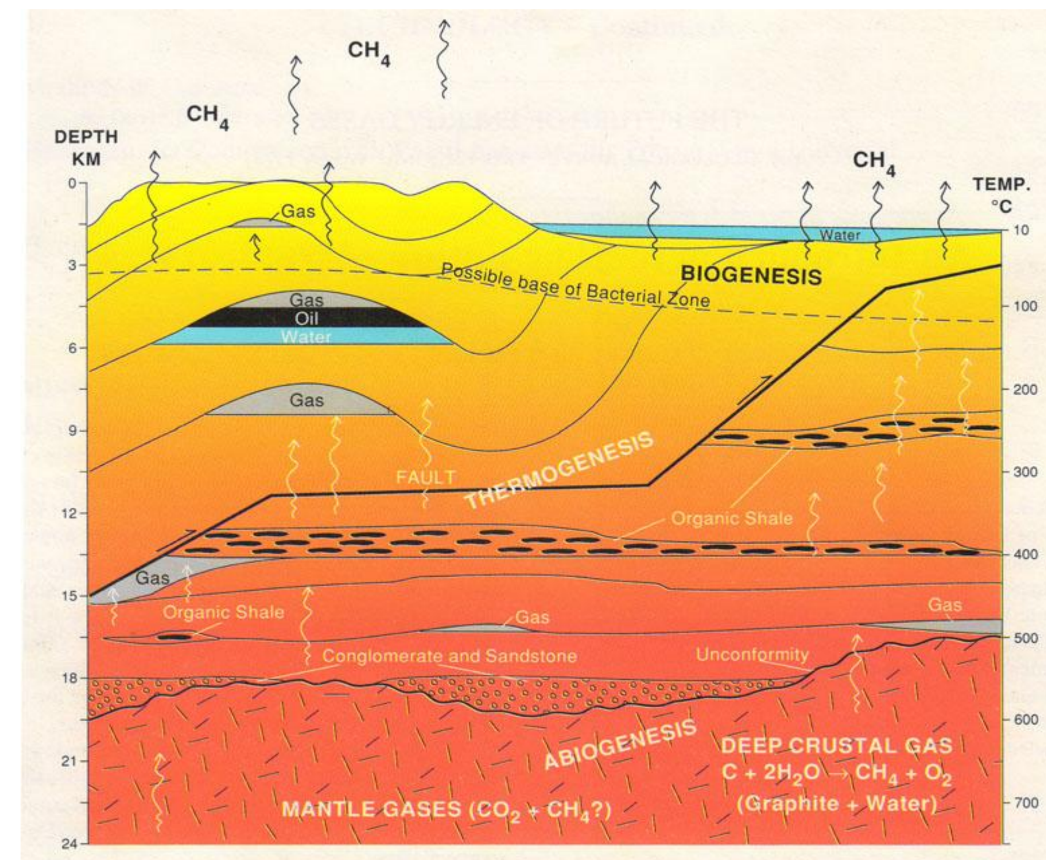


Fig.1 Schematic cross section of the Earth's crust, showing origin, migration, and accumulation of methane. (From Howell,D G,et al.,1993)

The biodegradation or thermodegradation of complex high-molecule sedimentary organic material can form microbial gas or thermogenic gas.

- **Microbial gas : The $\delta^{13}C_1$ value ranges from -110‰ to -50‰**
- **Thermogenic gases: The $\delta^{13}C_1$ value ranges from -50‰ to -35‰**
- **both gases have $\delta^{13}C$ and δD: $\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3<\delta^{13}C_4$ and $\delta D_{CH4}<\delta D_{C2H6}<\delta D_{C3H8}<\delta D_{C4H10}$**
- **Simple carbon-bearing molecules (CH_4, CO and CO_2) can form abiogenic alkane gases via plymerization in abiological chemical process in nature, with $\delta^{13}C_1$ heavier than -30‰.**
- **abiogenic alkane gases are characterized by a reverse distribution of $\delta^{13}C$ values and a normal trend of δD values, namely $\delta^{13}C_1>\delta^{13}C_2>\delta^{13}C_3>\delta^{13}C_4$ and $\delta D_{CH4}<\delta D_{C2H6}<\delta D_{C3H8}<\delta D_{C4H10}$.**
- **The $\delta^{13}C$ values and δD values are negatively correlated.**

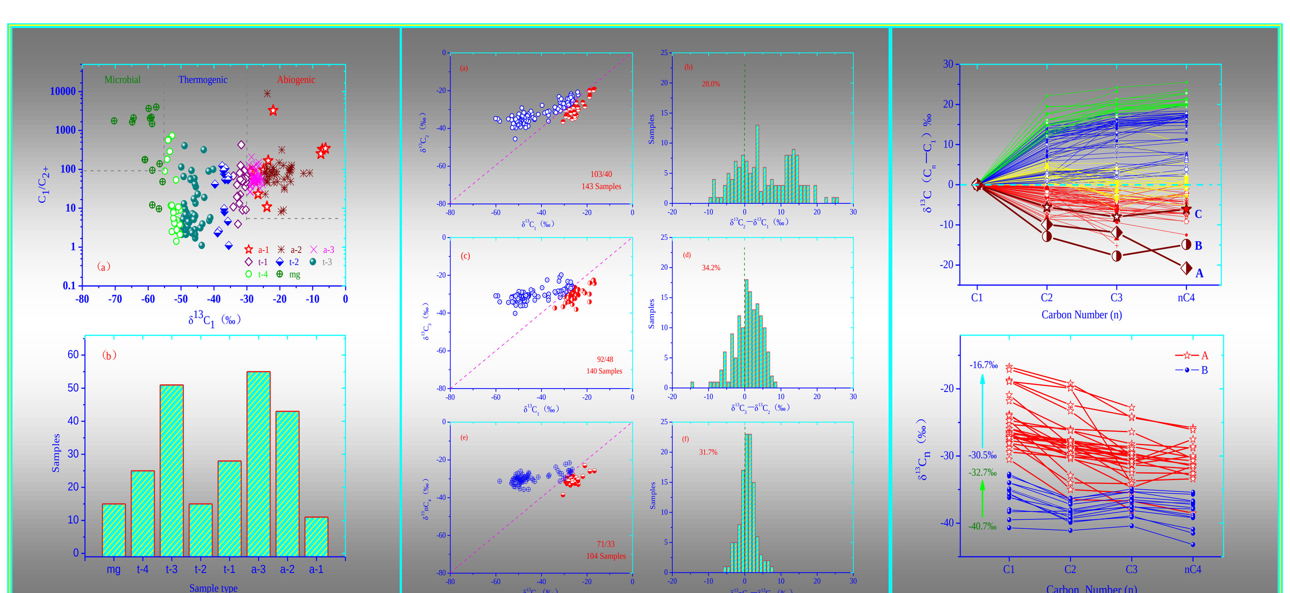


Fig.1 $\delta^{13}C_1$ distributions of natural gases from Songliao Basin..

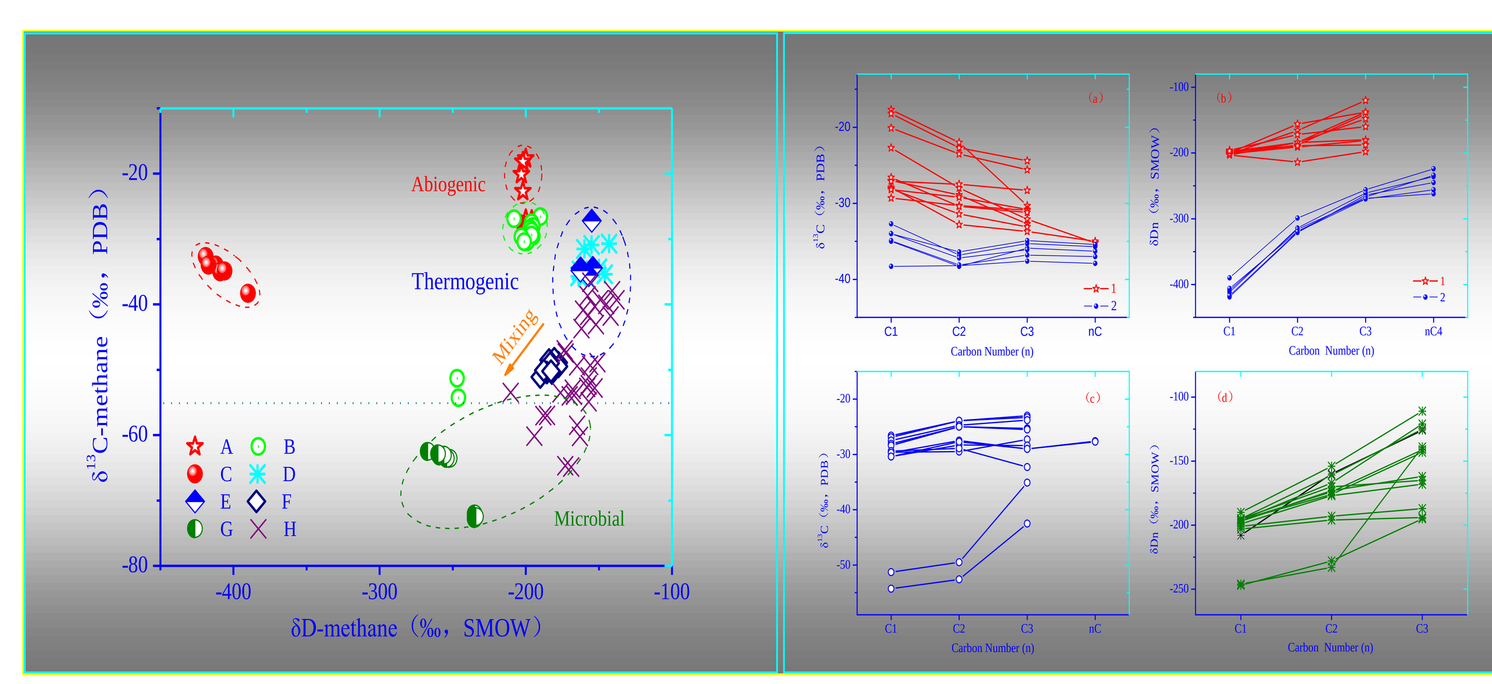
Fig. 2 $\delta^{13}C$ value distributions for methane, ethane, propane and butane in natural gases from Songliao Basin.

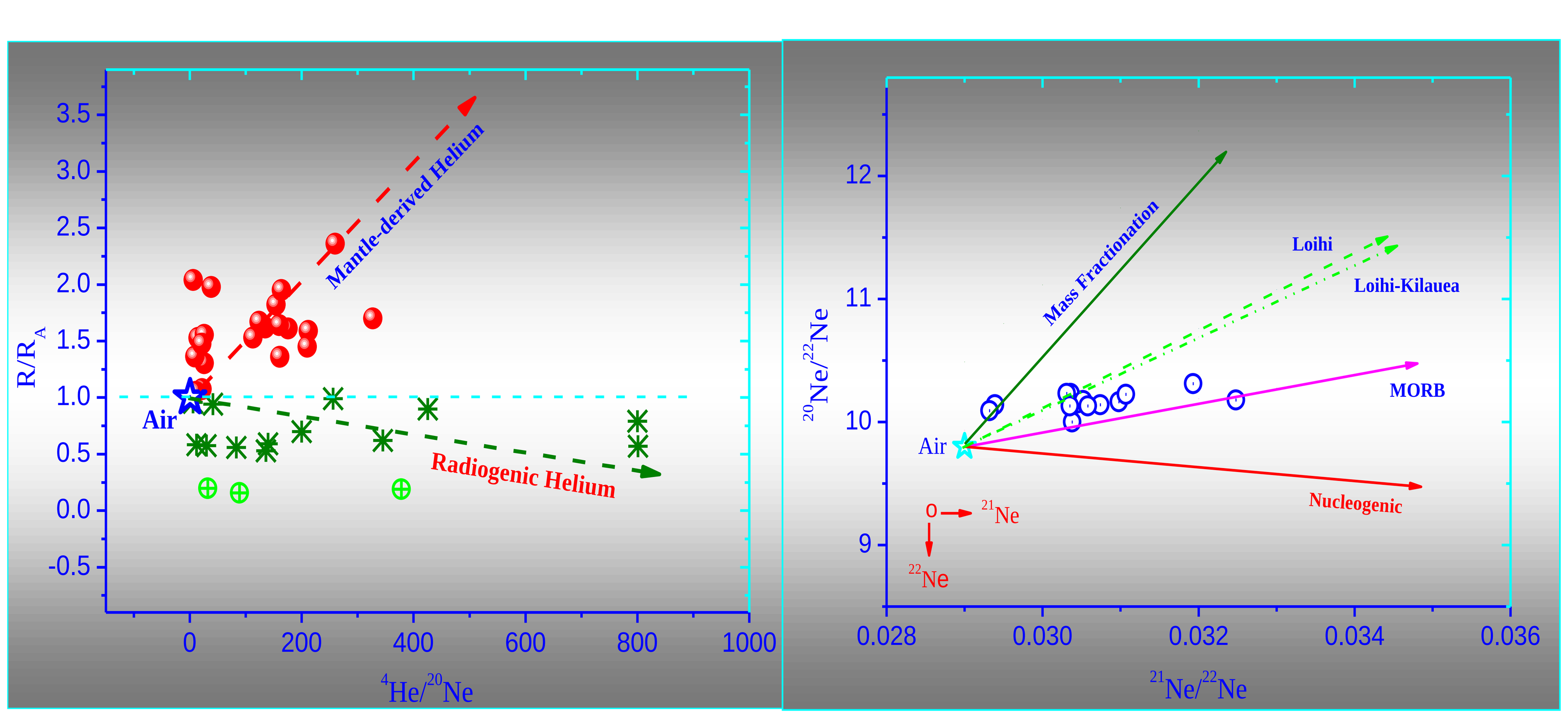
Fig. 3 Distribution of alkane carbon numbers versus the difference in $\delta^{13}C$ value ($\delta^{13}C_n-\delta^{13}C_1$) for natural gases from Songliao Basin.

Natural gases from 26 commercial gas wells distributed in the Xujiaweizi and Yingshan-Miaotaizi faulted depressions in Songliao Basin,China show $\delta^{13}C_1$ values ranging from -30.5‰ to -16.7‰ with a very narrow δD range between -203‰～-196‰. These gases are characterized by a reverse distribution of $\delta^{13}C$ values but a normal distribution of δD values, and a negative correlation between their $\delta^{13}C$ and δD values, indicating an abiological origin.

A-1: Distribution of $\delta^{13}C$ values versus carbon numbers of alkanes (C_1-nC_4); A-2: Distribution of δD values versus carbon numbers of alkanes (C_1-nC_4); (Sherwood et al., 2002),.

B-1: Distribution of $\delta^{13}C$ values versus carbon numbers of alkanes (C_1-nC_4); B-2: Distribution of δD values versus carbon numbers of alkanes (C_1-C_3).





The R/R_A values of helium isotope composition of samples are between 1.05 and 2.36, shows significant contribution of helium from mantle. These samples have $^{21}Ne/^{22}Ne$-$^{20}Ne/^{22}Ne$ values between Loihi line and MORB line, and have enriched ^{129}Xe with respect to the atmosphere (0.15%-2.16%). The existence of mantle origin noble gases provides isotope evidence of mantle degassing in Songliao Basin.

The prospecting practice in Songliao Basin has demonstrated that abiogenic alkane gases are of a promising resource, and it provides an example for the investigation and search for abiogenic commercial natural gases worldwide.

The Degassing from hot-springs In Volcanic Geothermal Areas

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The presence of a large amount of gases in the deep Earth has long been an interesting problem. It provides a common basis for explaining some puzzling natural processes, such as the degassing of the earth, the formation and evolution of atmosphere and the possible existence of abiogenic methane in deep Earth. Volcanic activity is a generally known phenomenon to cause the emission of gases, including H_2O,CO_2,CO,CH_4,N_2,NH_3,H_2,H_2S etc., from the inner Earth. Geochemical investigation of gases from hot-springs can not only provide some important information about these gases of the earth, but also evidence subsurface magmatic activity.

The net accumulation rate of organic carbon in sedimentary rocks is approximately $3.2x10^9$kg/yr (Tissot and Welte,1984). **An overall thermal alteration reaction of the form**

$$CH_{1.0}(kerogen) \rightarrow 0.75C(graphite)+0.25CH_4$$

The maximum annual production of biogenic methane cannot exceed $1.5x10^9 m^3$($0.8x10^9$ kgC). In comparison , roughly $26x10^9$kg of mantle carbon ($48x10^9 m^3 CO_2$) are annually degassed into the ocean at spreaing ridges (Des Marais,1985;Marty and Jambon,1987) **, and an additional large amount（$65×10^9$kg C） is released by subaerial volcanism and geothermal activity.**

These data suggest that if methane composed only 1 percent of the total flux of carbon out of the mantle, the biogenic and abiogenic methane production rates would be of comparable magnitude.

Mud-Volcanic Degassing Process

Table 1 Gas and Isotopic Composition of Springs in Tibet and Tengchong Geothermal Areas

采样位置（No.）	温度（℃）	He (ppm)	CH_4 (%)	CO_2 (%)	Ar (%)	N_2 (%)	N_2/Ar	R/Ra	$^4He/^{20}Ne$	^3He (ppt)	$\delta^{13}CO_2$	$\delta^{13}CH_4$	$CO_2/^3He$ ($x10^8$)	$CH_4/^3He$ ($x10^8$)
4-1	25	792	0.377	0.26	0.868	91.5	105	0.12	57.8	120	/	/	0.21	3.1
4-2	85	28.48	0.006	23.9	0.693	60.4	87.2	0.11	670	4.5	-5.0	/	530	1.3
4-3	88	93.08	0.027	57.46	0.581	36.1	62.1	0.12	584	15	-6.3	/	380	1.8
4-4	26	27.95	0.008	34.35	0.594	53.31	89.7	0.12	813	4.7	-5.9	/	730	1.8
4-5	75	25.98	0.005	14.62	0.767	66.82	87.1	0.13	127	4.6	-5.8	/	320	1.1
4-6	85	67.21	0.015	37.05	0.588	50.78	86.4	0.13	53.7	11	-4.2	/	330	1.4
4-7	/	21.75	0.026	34.66	0.622	53.01	85.2	0.13	65.8	11	-4.2	/	930	7.0
4-8	/	25.02	0.02	60.47	0.609	55.57	91.2	0.11	48.1	3.8	-5.5	/	800	5.3
4-9	86	9	0.001	1.07	0.925	79.58	86	0.71	0.866	2.9	-16.9	/	36	0.2
4-10	/	94.87	0.018	12.1	0.844	70.57	83.6	0.13	137.9	17	-7.5	/	71	1.0
4-11	/	45.44	0.015	89.74	0.182	9.02	49.6	0.12	154	7.3	-6.2	/	1200	2.0
4-12	86	3.01	0.001	21.19	0.763	62.95	82.5	0.93	0.704	3.7	-6.7	/	570	0.2
4-13	77	4.86	0.001	34.85	0.316	51.55	163	0.86	0.578	4.6	-3.9	/	760	0.2
4-14	60	181	3.83	63.75	0.437	28	64.1	0.28	154	70	-0.3	/	92	54.7
4-15	83	2.85	0.016	13.56	0.724	68.18	94.2	0.44	131	1.7	-3.3	/	780	9.2
4-16	86	49.3	0.049	79.03	0.273	14.53	53.2	0.25	114	17	-11.2	/	450	2.8
4-17	50	15.41	0.009	26.97	0.629	57.96	92.1	0.25	104	5.4	0.1	/	500	1.7
4-18	79	2.53	0.011	22.54	0.667	61.56	92.3	0.57	2.4	1.8	-0.9	/	1250	5.8
4-19	10	7.17	0.091	43.51	0.514	45.95	89.4	0.25	30.7	2.4	-0.7	/	1800	38
4-20	56	13.2	0.092	28.38	0.586	57.54	98.2	0.27	200.8	4.9	-0.4	/	580	19
4-21	/	514	0.04	29.92	0.61	68.93	113	0.23	166	170	-6.7	/	18	0.2
4-22	45	48.28	0.024	83.04	0.28	14.45	51.6	0.21	80	14	-2.6	/	600	1.7
4-23	/	292	0.014	4.3	1.026	90.4	88.1	0.17	32.2	68	-10.3	/	6.3	0.2
5-1	90	99.61	0.926	25.08	0.769	61.35	80	4.3	1	814	-2.87	-19.24	3.1	1.1
5-2	86	129.4	1.033	46.69	0.557	41.83	75	3.58	4.8	681	-2.81	-20.21	6.8	1.5
5-3	96	5.81	0.007	3.09	0.875	76.97	88	2.86	0.7	36	-3.49	-16.16	8.6	0.19
5-4	95	31.54	0.344	32.41	0.633	56.33	85	3.28	50	145	-2.68	/	22.4	2.4
5-5	25	150	0.018	26.62	0.782	62.47	80	3.2	20	678	-5.23	-13.50	3.9	0.03
5-6	/	57	0.48	55.56	0.28	38.63	138	4.11	193	328	-2.7	-19.60	16.9	1.5
5-7	/	51	0.41	64.1	0.3	28.76	96	4.21	128	301	-3.7	/	21.3	1.4
5-8	/	57	0.48	66.6	0.25	24.65	98.6	4.02	17	326	-3.0	-19.41	20.4	1.5
5-9	/	41	0.33	35.26	0.61	54.75	89.6	3.86	6	233	-3.0	-20.03	15.1	1.4
5-10	/	39	0.33	55.2	0.4	38.08	95.2	3.9	9	220	-2.9	-21.44	25	1.5
5-11	/	47	/	81.91	0.01	6.02	602	4.92	30	327	/	/	137	/
5-12	/	5.2	0.04	42.38	0.56	47.67	85.1	2.35	0.7	31	-4.9	-19.64	12.1	1.3
5-13	/	91	/	80.13	0.18	14.52	80.7	5.13	24	661	/	/	33	/
5-14	/	7.4	0.06	20.12	0.78	67.12	86.1	2.34	0.44	61	-5.0	-19.78	68.9	1
5-15	/	3.5	/	10.33	0.83	71.23	85.8	2.29	1.1	15	/	/	133	/
5-16	71	70.56	0.02	62.51	0.42	30.68	73	0.49	25	47	-3.87	-13.65	18.8	0.4
5-17	85	128	0.03	49.77	0.56	41.83	74.7	0.49	33	265	-4.01	/	299.4	0.11
5-18	25	3.32	0.01	62.89	0.4	32.35	81	0.66	0.76	2.1	-3.25	-16.60	0.4	4.7

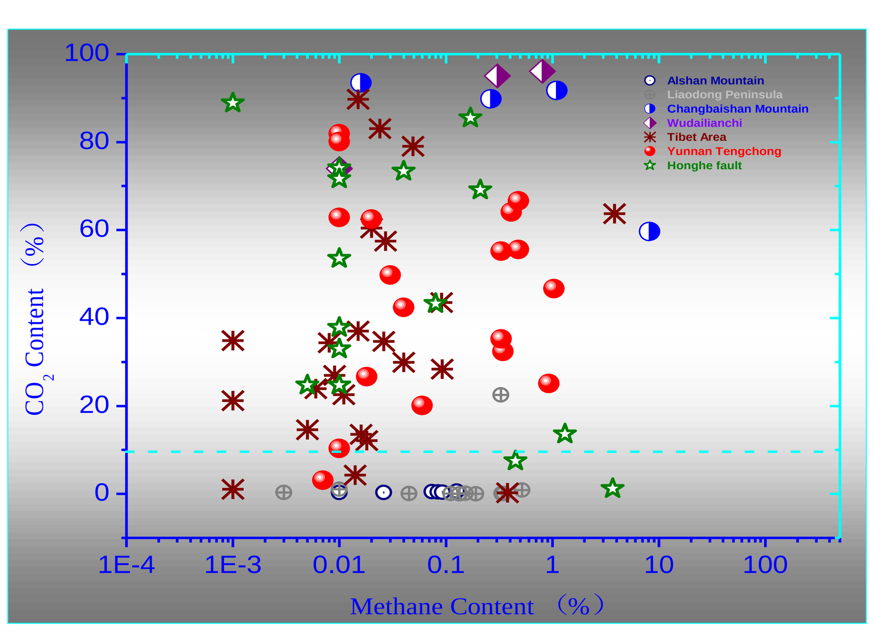

Fig. 1 Distribution of CH_4 ~ CO_2 from springs in geothermal Areas,China

Chemical and isotopic composition of free gases springs in Tibet and Tengchong geothermal areas is shown in table 1.

Fig.1 show distribution of CO_2~ CH_4 of 81 samples from sprengs in geothermal areas,China.

Fig.2 and Fig.3 show distribution of R/Ra~ $^4He/^{20}Ne$ of 81 samples from sprengs in geothermal areas, China.

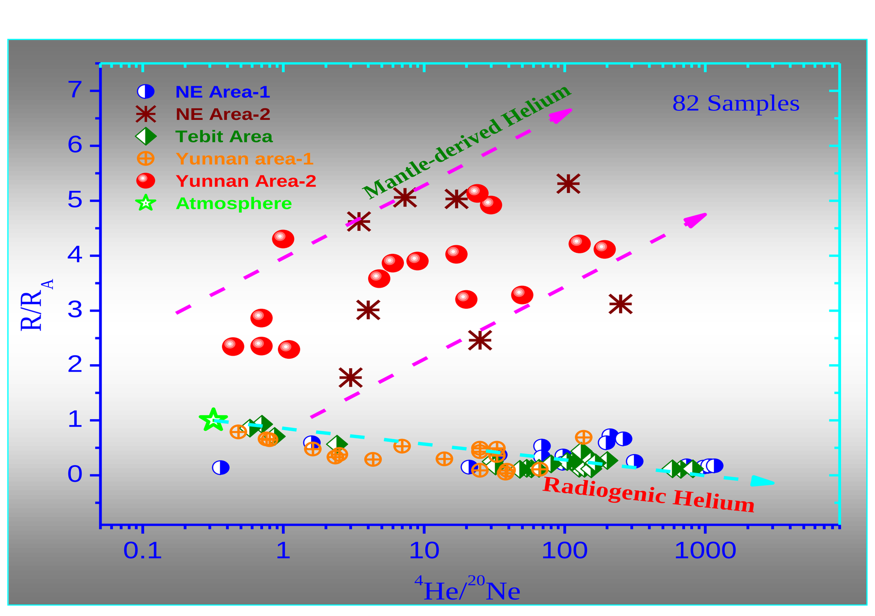

Fig.2 Relation between $^3He/^4He$ (*R/Ra*) and $^4He/^{20}Ne$ ratios in geothermal areas,China

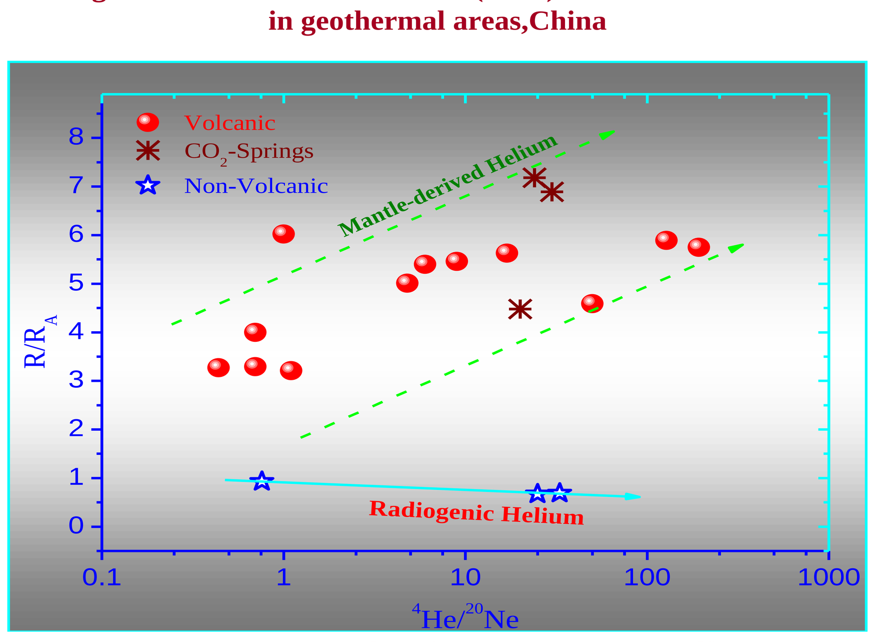

Fig.3 Relation between $^3He/^4He$ (*R/Ra*) and $^4He/^{20}Ne$ ratios in Tengchong volcanic geothermal area

NS-NNE tension and tense-shear fault zones exist in Tengchong volcanic area of Yunnan Province, China,formed by the collision and compression of Indian and Eurasian plates. Hot-springs extensively distribute in the area. The study of gas geochemistry of hot-springs and low temperature CO_2-springs indicate that He,CH_4 and CO_2 are mainly of manle origin possessing the following characteristic values :

- $^3He/^4He = 3.21x10^{-6} \sim 7.17x10^{-6}$ (or R/Ra = 2.29 ~ 5.13),
- $\delta^{13}C_{CH4}$ = -16.6‰ ~ - 21.4 ‰,
- $\delta^{13}C_{CO2}$ = -2.7‰ ~ - 6.7 ‰,
- $CH_4/^3He = 1.5x10^7 \sim 2.4x10^7$

The relationship between He/CO_2,$^3He/^4He$, $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ suggest that the He, CH_4 and CO_2 in Tengchong volcanic geothermal system is the same source(mantle) .