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The Isotope Geochemistry of N_2 in Natural Gas Pools

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Abstract The isotopic compositions of N_2 (δ 15N,‰,ATM) imply the geochemical origins of molecular nitrogen in gas pools . N_2 with $-19‰ \leq \delta^{15}N_{N_2} \leq -10‰$ may be from immature sedimentar y organic matter.$-10‰ < \delta^{15}N_{N_2} \leq -2‰$ may indicate the N_2 origina tes from mature (including high mature) sedimentary organic matter.$-2‰ < \delta^{15}N_{N_2} < +1‰$ implies the N_2 may be from the deep crust or mantle. N_2 with $\delta^{15}N_{N_2}=0‰$ and $N_2/Ar=38\sim84$ suggests to come from the atm osphere.$-1‰ \leq \delta^{15}N_{N_2} < +4‰$ characterizes N_2 from ammonium clay m inerals in shale and mudrock during metamorphism. $\delta^{15}N_{N_2}=+4‰$ is t he typical feature of N_2 from saltpeter in evaporite.$+4‰ < \delta^{15}N_{N2} \leq +18‰$ indicates N_2 may derive from post-mature sedimentary organic matter, which is the main source of N_2-high gas ($N_2 > 60\%$) pools.N_2-high gas pools ,which occurs in a large scale in peroliferous basin, suggests that it is mainly the post-mature gas trapped in the reservoir. N_2 with $\delta^{15}N_{N_2}$ varying from -10‰ to -2‰ is the main source of N_2-rich gas (N_2>15%) pool s,and with $\delta^{15}N_{N_2}$ varying from +1‰ to +4‰ may form either the N_2-high or the N_2-rich gas pools.

Key words nitrogen isotope origin of nitrogen natural gas ammomia sedimentary organic matter

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INTRODUCTION

gas pools (Zhu,1994).N_2-rich gas pools have been discovered in many petroliferous basins all over the world (Headlee,1962),such as Mid-Europea n basin(Littke et al.,1995;Krooss et al.,1995),Volga-Ural basin(Prasolov et al. ,1990),Zhungaer basin (Wang and Jiang,1997), Yinggehai basin, Sanshui basin (Zeng ,1986),Subei basin (Xu,1994),Songliao basin (Huang,1995),Great Valley basin (Jen den et al.,1988a) and Western Interior basin (Hoering and Moore,1958;Jenden et a l.,1988b).

However, the isotope geochemistry of N_2 in gas pools is still poorly known (K rouse,1979;Prasolov et al.,1990;Xu,1994;Witicar,1994;Littke et al.,1995;Krooss e t al.,1995; Du et al.,1996). We believe that this is due to multiple origins whic h are often mixed together and lead to irregular variations of $\delta^{15}N$ of N_2 in gas pools. In order to unravel the molecular nitrogen isotopic composit ions in gas pools,the isotope geochemisty of single and typical sources of N 2 has to be studied.

In order to elucidate the geochemical implications of isotopic compositions of m olecular nitrogen in gas pools,we chose four typical basins(i.e. the West-Sibe rian basin in Russia,the Yinggehai basin of China,the Californian Great Vall ey basin of USA and the Mid-European basin) among the numerous N_2-bearing ba sins in the world.The four basins have significantly different isotopic char acteristics of gases,which may provide insight into the isotope geochemistry of N_2 in natural gas pools.

EXPERIMENTAL AND RESULTS

Thirty five gas samples were collected at high pressure in steel bot tles with stopcocks at both ends from the gas-producing wells in Yinggehai basin ,offshore and southwest of Hainan Island, China. In the laboratory,chemical com positions of major,minor and trace components (CH_4、C_{2+}、CO_2、N_2、Ar and He) were analyzed using a gas chromatograph system.Peak heights of chemical components in the samples were calibrated against those of the in-house standa rd gases.Overall anlytical errors were estimated to be <5% for most samples.

Purification of He and Ar was carried out by a two-stage Ti-Zr getter in a speci al high vacuum stainless steel system. An activated charcoal trap was held at li quid N_2 temperature in order to separate Ar from He. A VG-5400 static mass spe ctrometer was used for the measurements of $^3He/^4He$ and $^{40}Ar/^{36}Ar$ ratios. The precision of the measurement was less than 1% for most samples.

Separation of the gas samples into pure gas components(CH_4、CO_2 and N_2) an d oxidation of CH_4 to CO_2 were performed in a glass vacuum line using a tra p held at liquid N_2 temperature,another trap at acetone-liquid N_2 sherbet te mperature,and a CuO furnace.

The δ ^{13}C and δ ^{15}N were determined by a MAT-251 mass spectrometer(Finnigan). The

respectively.

FOUR TYPICAL N_2-BEARING BASINS

West-Siberian basin

The West-Siberian province is a great gas-bearing basin formed in Mesozoic tim e. More than 20 giant and super-giant gas fields have been discovered in the nor thern part of the basin.Both the two sets of the source rocks and reservoirs are from the Cretaceous (Dai,1985;Zhang,1990).

The Cenomanian reservoirs contain a huge gas accumulations of either bacterial or early thermogenic origin.The source rock is a coal-bearing series of Lowe r Cenomanian,Abbian and Aphian age with immature organic matter (Ro<0.6%). Sand stones in the Upper Cenomanian are the principal gas reservoirs, which produce dry gas (C_1/C_{1-2}>0.99, CH_4=95.5%～99.7%,C_2H_6=0.02%～0.08%,C_3H 8=0.03%～0.025%).N_2 and CO_2 also exist commonly in these gas reservoirs,whic h the volume content of N_2 (0.1%～1.2%) being higher than that of CO_2 (0.1%～0.3%).The carbon isotope values of methane are light (δ ^{13}C=- 68‰～-55‰,PDB) (Dai,1985) and the nitrogen isotope values of N_2 are also l ight (δ ^{15}N=-19.0‰～-10.7‰) with a variability from -16‰ to -12‰. The associated ^{3}He/^{4}He ratios are at 10^{-8} order of magnitude(Prasolov et al.,1990).

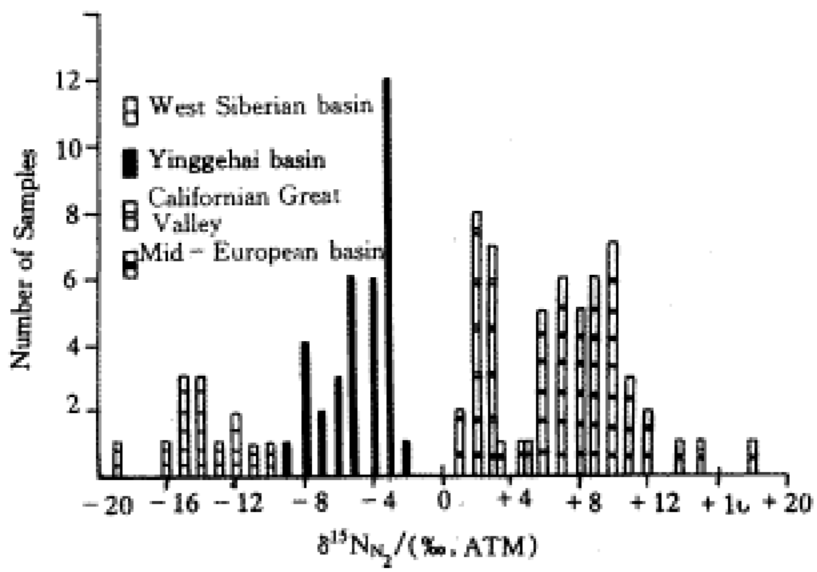

Fig.l Histograms of $\delta^{15}N_{N2}$ of natural gases
from the West Siberian basin (Prasolov et al.,1990),
Yinggehai basin,Calif ornian Great Valley (Jenden et al.,
1988a)and Mid-European basin (Boigk et al.,
1976;Weinlich,1991)

Yinggehai basin

Yinggehai basin is a gas-rich basin formed in Cenozoic times. Three giant gas f ields have been discovered in its southern part.The source rock is a neritic an d bathyal dark mudstone in the Pliocene Yinggehai formation with mature (mainly high mature) humic organic matter.According to the stratigraphy of the Qiongdon gnan basin adjacent to Yinggehai basin,other potential source rocks are marine dark mudstones of the Miocene Meishan formation and Oligocene limnic mudstones a nd coal-bearing series.

The detected natural gas in Yinggehai basin is primarily produced from marine sa ndstones of the Pliocene Yinggehai formation.Hydrocarbon composition in natural gas varies in a wide range, the contents of CH_4,C_2H_6 and C_3H_8 vary ing from 6.47% to 90.99%,0.013% to 2.09%,and 0.002% to 0.55%, respectively,and $C_1/C_{1\sim5}$ ratios varying from 0.96 to 1.00. CO_2(0.10%～88.93%) and N_2(2.93%～33.48%) are common in the natural gas,which appear to be inversely correlated to each other.Methane $\delta^{13}C$ values vary from -63.14‰ to -29. 08‰,but usually from -40‰ to -30‰,and nitrogen $\delta^{15}N$ values vary mainl y from -9‰ to -2‰.

Californian Great Valley basin

The Californian Great Valley basin is rich in oil and gas,which was formed in th e late Mesozoic times. It is separated into two main basins,the Sacramento to th e north and the San Joaquin to the south by Stockton arch.The northern San Joaqu in basin and the Sacramento basin are dry gas regions,where many gas fields have been discovered (Jenden et al.,1988a).Fraciscan metasedimentary complex is the basement of this basin and Cretaceous and Tertiaty siltstones,shales and sandsto nes were deposited above.Gases reservoirs are primarily from the Cretaceous,Mioc ene and Pliocene (Jenden et al.,1988a).

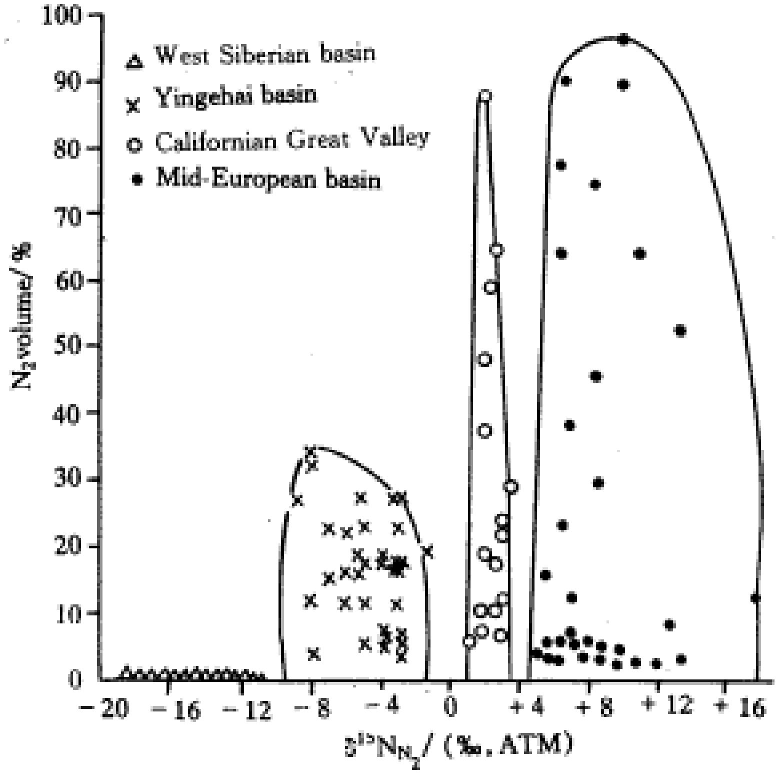

Fig.2 Plot of N_2 versus $\delta^{15}N_{N2}$ of nat ural gases from the West Siberian basin (Prasolov et al.,1990),Yinggehai basin,Californian Great Valley (Jenden et al.,1988a) and Mid-European basin (Boigk et al.,1976;Weinlich,1991)

The concentrations of methane in natural gas vary from 12% to 96%,C_{2+}~0.02% to 5.1%,CO_2~0.001% to 0.6%,and N_2~1.0% to 87%.Meth ane $\delta^{13}C$ values vary from -52.4‰ to -15.2‰,and nitrogen $\delta^{15}N$ val ues vary from +0.9‰ to +3.5‰ with a main range from +1.0‰ to 3.0‰(Jenden et al.,1988a).

Mid-European basin

The Mid-European basin is a gas-rich basin formed in late Paleozoic to Cenozoi c times. Lots of N_2-rich gas fields have been discovered in its northern part. The source rocks are coal-bearing series in the Upper Carboniferous with post-mature organic matter.Gas reservoirs are primarily in Permian Rotliegend a nd Triassic Buntsandstein formations.Main components of natural gas are CH_4 an d N_2. The content of N_2 is more often greater than 50% in the gas accu mulations in the northern part of the basin. The gas occurrence with N_2 higher than 50% is consistent with the high maturity of the source rocks with vitrini te reflectance values higher than 3.0%(Littke et al.,1995;Krooss et al.,1995).T he content of CO_2 is less than 1%.Methane $\delta^{13}C$ values are greater than -36‰,and can be as high as -15%.Molecularnitrogen $\delta^{15}N$ values vary from +6.5‰ to +18.0(Maksimov et al.,1975; Stahl,1977).

DISCUSSION

Heoring and Moore(1958) discovered the $\delta^{15}N$ values of N_2 in Oklahoma,M ississippi and Texas to vary from -10.5‰ to -2.1‰,but to vary from +1.3‰ to +11.9‰ in Arkansas. They gave no interpretation for the geochemical implications of the two groups of molecular nitrogen $\delta^{15}N$ values. Bokhoven and Theeu ween(1966) measured the molecular nitrogen $\delta^{15}N$ values in Dutch gas reser voirs,but they could not affirm the origin of molecular nitrogen.Maksimov et al. (1975) studied the molecular nitrogen $\delta^{15}N$ values in N_2-high gas reserv oirs of Mid-European basin,which vary from +4.28‰ to +18‰, and surpposed the origin of molecular nitrogen should be derived from deep crystalline rocks.But this inference was denied by Littke et al.(1995) and Krooss,et al.(1995).Jenden et al.(1988a) thought the molecular nitrogen with $\delta^{15}N$ values varying fro m +0.9‰ to +3.5‰ in gas reservoirs of the California Great Valley originated f rom the upper Jurassic Fraciscan metasedimentary complex,according to studies on the isotope ratios of carbon,nitrogen and helium. Prasolov et al.(1990) discove red that the molecular nitrogen $\delta^{15}N$ values in the former USSR could be divided into two groups.One of them has $\delta^{15}N$ values of about -10‰,the other about +14‰. The “ light ” nitrogen originates from organic matter and pre sumably from ammonia salts via the gaseous ammonia stage.

Fig.1 shows the features of isotopic compositions of the molecu lar nitrogen in the four typical N_2-bearing basins. It appears that the molec ular nitrogen $\delta^{15}N$ values differentiate among those basins and have mult iple central distribution patterns different from the two group patterns sugges ted by Prasolov et al.(1990).Fig.2,3,and 4 show the plots of volume content of m olecular nitrogen vs molecular nitrogen $\delta^{15}N$ values,the molec ular nitroge $\delta^{15}N$ values vs the associate methane $\delta^{13}C$ values,and N_2/Ar ratios vs the molecular nitrogen $\delta^{15}N$ va lues, respectively,which also reflect multiple central distribution patte rns.

In order to understand the implications of the multiple central distribution pa tterns of molecular nitrogen $\delta^{15}N$ values in petroliferous basins, it is n ecessary to introduce the possible origins of molecular nitrogen in subsurface. The possible nitrogen sources include: (1) at mosphere,(2) immature sedimentary o rganic matter,(3) mature (including high-mature) sedimentary organic matter,(4) post-mature sedimentary organic matter,(5) ammonium clay minerals in sedimentar y rocks,(6) radiogenic nuclear reaction,(7) nitrogen-bearing salt in evaporite; (8) magmatic rocks,and (9) the deep crust or mantle degassing.

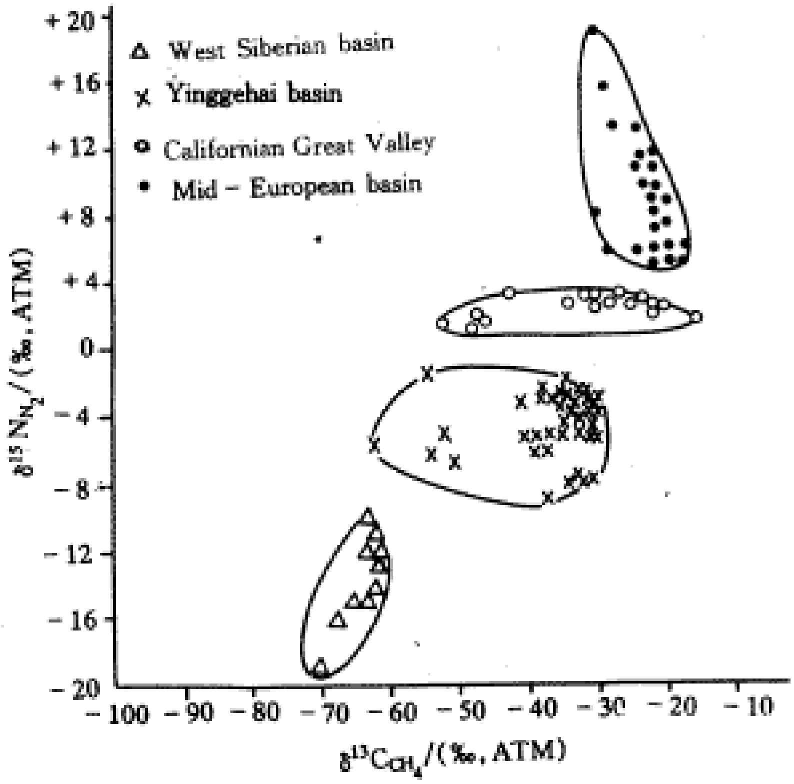

Fig.3 Plot of $\delta^{15}N_{N_2}$ versus $\delta^{13}C_{CH_4}$

of natural gases from the West Siberian basin (Dai,1985;Zh-ang,1990;Pra solov et al.,1990), Yinggehai basin,Californian Great Valley (Jenden et al.,1 988a),and Mid-European basin(Boigk et al.,1976,Stahl 1977;Weinlich,1991)

The molecular nitrogen from the atmosphere is characterized by the δ +15Nvalues=0‰ and N_2/Ar ratio=38～84.This feature is considered to be unc hanged in the past 3 billion years (Sano and Pillinger,1990).The atmospheric N 2 is not the main source for N_2 in natural gas accumulations,which the evidenc e is that the isotopic compositions of N_2 in N_2-rich gas reservoirs over th e world have no signs of atmospheric characteristics (Heoring and Moore,1958;Bok hoven and Theeuween,1966;Maksimov et al.,1975;Prasolov et al.,1990;Littke et al. ,1995;Krooss et al.,1995).The radiogenic molecular nitrogen can be neglected bec ause of its little contribution to gas pools,and magmatic rocks-derived N_2 al so has little significance for it (Krooss et al.,1995) because nitrogen content in magmatite is the lowest in all crust rocks (Littke et al.,1995).Primordial N -2 from the deep crust or mantle can migrate along the active deep-setting fau lts and accumulate (Krooss et al.,1995). The δ^{15}N values of primodial N 2 should be similar to that of N_2 in the atmosphere,because atmospheric N_2 i s mainly from the upper mantle degassing during the earth early evolution

(Zhan g and Zindler,1989). Primordial $\delta^{15}N$ values of N_2 are supposed to vary from -2‰ to

by Prasolov et al.(1990). The N values of molecular nitrogen derived from reduction of nitrogen-bearing salt minerals in evaporite are typically equal to +4‰(Prasolov et al.,1987).Littke et al.(1995) and Krooss et al.(1995) infered that sedimentary organic matter and ammonium-clay minerals are the main sources of N_2 in gas accumulations

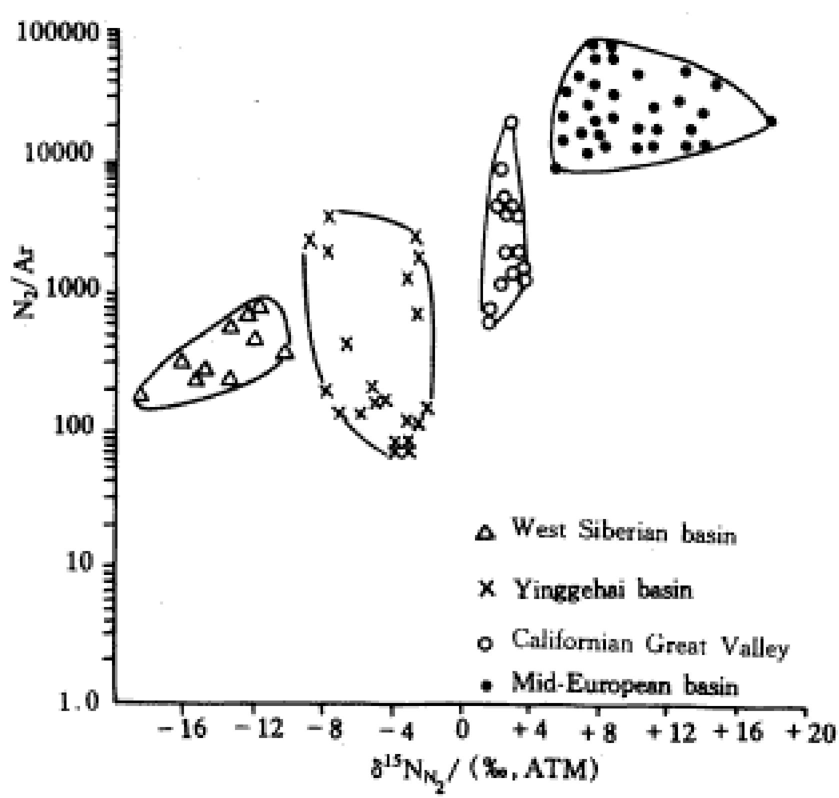

Fig.4 Semilogarithmic plot of N_2/Ar ratios versus $\delta^{15}N_{N_2}$ of

natural gases from the West Stberian (Prasolov et al.,1990), Yi nggehai basin,Californian Great Valley (Jenden et al., 1988a) and Mid-Europ ean basin (Boigk et al.,1976; Stahl,1977;Weinlich 1991)

N_2 from immature sedimentary organic matter

The immature sedimentary organic matter contains proteins and ami no-ac ids in high concentration. Proteins can easily form amino-acids by hydrolysis, such as COOH-CH_2-NH_2, and amino-acids are unstable and ammoniated by micr oorganism:

COOH-CH_2-NH_2microorganismCO_2+H_2+NH_3+Energy (1)

The NH_3 in this reaction is unstable.Part of it is absorbed by cl ay minerals, such as illite. Another part can transform into molecular nitroge n through the following reactions:

$$8NH_3+CO_2 \rightarrow CH_4+4N_2+6H_2O \quad \text{(Kreuler and Schuiling,1982)} \qquad (2)$$

$$2NH_3+2Fe_2O_3 \rightarrow 6FeO+N_2+3H_2O \quad \text{(Getz,1987)} \qquad (3)$$

The N_2 from immature sedimentary organic matter is depleted in h eavy nitrogen (Macko et.al.,1987).

The molecular nitrogen of gas pools in the Upper Cretaceous of West-Siberian basin is a typical one from immature sedimentary organic matter.$^3He/^4He$ rat ios of the associated helium (10^{-8}) suggest that no significant N_2 from the atmosphere or the deep crust or mantle is present.The $\delta^{15}N$ values d o not indicate a contribution from nitrogen-bearing salt minerals in evaporite (Prasolov et al.,1990).

Thus the molecular nitrogen in the Upper Cretaceous of the West-Siberian basi n should be derived from immature sedimentary organic matter,with typical $\delta^{15}N$ values varying from -19‰ to -10‰.N_2 with similar $\delta^{15}N$ va lues has also been discovered in the Quaternary of the Qaidamu basin, China . The $\delta^{15}N$ values of N_2 from immature sedinentary organic matter should vary from -19‰ to -10‰.

N_2 from mature sedimentary organic matter

Although part of sedimentary organic nitrogen has been depleted during the imm ature stage,quite some organic nitrogen still exists in mature sedimentary orga nic matter,such as protein, amino-acid,pyride and pyrole,etc (Baxby et al.,1994),which is the reason why the nitrogen content in sedimentary rocks is the highe st in the crustal rocks.During the mature stage,especially in the high mature s tage,temperatures are high and approach those necessary to reach the activ ation energy (40 to 55 kcal/mol) to break nitrogen bonds in mature kerogen (Kro oss et al.,1995).

Except for a small part of NH_3 generated during this stage which is absorbed by authigenic clay minerals such as illite and montmorillonite in sedimentary ro cks (Cooper and Erans,1983;Oh et al.,1988),large volumes molecular of nitrogen are also generated through reaction (2) and (3) mentioned in section 4.1. These transformations are the possible reasons of N_2-rich gas pools associated wit h “ red beds ” and the low content of CO_2 in nature. Via the NH_3 stage,the g enerated molecular nitrogen is also depleted in heavy nitrogen (^{15}N),but is heavier than that from immature sedimentary organic matter. In general, the molecules with the light isotope would decompose more readily,enriching ^{14}N in the gas phase relative to the remaining nitrogen-bearing organic mat ter(Hoering and Moore,1958).

The natural gases in the Pliocene Yinggehai formation of Yinggehai basin have t he basic feature of an origin from mature (including high mature) sedimentary o rganic matter.$^3He/^4He$ ratios of the associated helium vary from 5.0×10^{-8} to 6.79×10^{-7},which suggests that there is little contribution of mantle-derived gas.No trace of magmatism or nitrogen-bearing salt mineral s has been discovered up to now in the basin.

mature (including high mature) sedimentary organic matter,with a typic al isotopic feature of $\delta^{15}N$ values varying from -9‰ to -2‰. The N_2 w ith this origin has been discovered in the Lower Cretaceous of the West Siberia n basin (Prasolov et al., 1990) and Western Interior basin (Hoering and Moore,1 958; Jenden et al., 1988b).Thus,the range of $\delta^{15}N$ values of N_2 from mat ure organic matter should vary from -10‰ to -2‰.

N_2 from post-mature sedimentary organic matter

The geothermal energy at the mature stage of sedimentary organic matter i s not high enough to release all organic nitrogen.Therefore organic nitrogen st ill exists in postmature sedimentary organic matter in high concentration. During the postmature stage,the geothermal energy is high enough to generate mol ecular nitrogen through pyrolysis(Krooss et al.,1995). Thus, a large amount of m olecular nitrogen can be generated during this stage.

Littke et al.(1995) and Krooss et al.(1995) investigated the N_2 generation fro m post-mature sedimentary organic matter at high temperature by laboratory pyr olysis experiments . They discovered that the peak of N_2-high gas generation was after that of methane-rich gas generation,and using the chemical dynamics m ethod, they concluded that the essential geotemperature to generate N_2-high gas from organic matter should be at least 300℃ in nature.

Natural gases reservoired in Permian Rotliegend and Triassic Buntsandstein forma tions of the Mid-European basin,especially in its northern part, have typic al features of the generation from post-mature sedimentary organic matter.Marin e evaporates were deposited in this basin, but there are no saltpeter or othe r nitrogen-bearing salt minerals in significant amount (Littke et al.,1995). Th erefore the hypothesis of evaporite-derived N_2 (Prasolov et al.,1990) has be en denied.Although the magmatism is obvious,its contribution to gas accumulation can neglected. On the contrary,the magma heat should have had accelerated the N_2 generation from sedimentary organic matter at high temperature (Krooss et al .,1995).

Most of the molecular nitrogen, in Permian Rotliegend and Triassic Buntsandste in formations, should be generated from the Upper Carboniferous post-mature s ource rocks. The typical feature of molecular nitrogen $\delta^{15}N$ values from this type of generation should range from +4‰ to +18‰. The occurrence of N_2 with this origin in a large scale may indicate that it is mainly the post-mat ure gas reservoired in petroliferous basins (Littke et al,.1995; Krooss et al.,1 995). Heavy N_2 ($\delta^{15}N \approx$+5‰～+18‰) discovered in the rift basin systems of eastern China, American Arkansas and Volga-Ural basin may be of the same or igin.

N_2 from ammonium clay minerals

The inorganic fixed nitrogen (NH^{+}_{4}) in sedimentary rocks is primarily deri ved from organic matter. Some part of NH_3 from immature and mature sedimentar y organic matter can be absorbed by clay minerals generating during the diagenes is of sedimentary rocks.In

in clay minerals (Cooper and Erans,198 3; Oh et al.,1988;Baxby et al., 1994; Littke et al.,1995; Krooss et al., 1995).T he fixed nitrogen in clay minerals shows a high thermal stability and cannot rel ease molecular nitrogen unless at a high temperature.This temperature should be higher than 1000℃ during laboratory pyrolysis experiment and higher than 500℃ under geological conditions according to chemical dynamic calculation (Whelan e t al.,1988). Thus, molecular nitrogen can be generated from metamorphism of ammo nium clay mineral-bearing sedimentary rocks,with the $\delta^{15}N$ value varying from +1‰ to +4‰.

The natural gases in the Cretaceous and Tertiary of the Californian Great Valley have complex origins involving mixing of multiple sources,with a narrow range o f molecular nitrogen $\delta^{15}N$ values from +0.9‰ to +3.5‰.Jenden et al (1988 a) suggested this kind of molecular nitrogen should originate from Upper Jurassi c Fraciscan metasedimentary complex. The isotopic composition of N_2 from ammo nium clay mineral may vary from +1‰ to +4‰.

CONCLUSIONS

There are multiple origins of N_2 in the subsurface and they often mi x together in N_2-bearing gas reservoirs in petroliferous basins. Therefore wi dely ranging $\delta^{15}N$ values of N_2 have been observed and are puzzling for scientists.Based on analyzing and contrasting four typical N_2-bearing basins ,West-Siberian basin,Yinggehai basin,Mid-European basin and Great Valley,and t he study of the molecular nitrogen possible origins and the corresponding isotop ic composition features,we can conclude on the isotope goechemistry of molecula r nitrogen. Values between $-19‰ \leq \delta^{15}N_{N2} \leq -10‰$ represents the N_2 from immature sedimentary organic matter.N_2 with $-10‰ < \delta^{15}N_{N2} \leq -2‰$ originates from mature (including high-mature) sedimentary organic matter. $-2‰ < \delta^{15}N_{N2} < +1‰$ may reflect the N_2 from the mantle. $\delta^{15}N_{N2}=0‰$ and $N_2/Ar=38$～84 characterizes N_2 from atmosphere. $+1‰ \leq \delta^{15}N_{N2} < +4‰$ indicates N_2 metamorphism of ammnium clay mineral-b earing sedimentaryrocks. $\delta^{15}N_{N2}=4‰$ is the isotopic composition feat ure of N_2 from saltpeter in evaporite. Values between $+4‰ < \delta^{15}N_{N2} \leq +18‰$ imply that N_2 may originate from post-mature sedimentary organic ma tter.The isotopic compositions of N_2 from mutiple origins appear irregular.

Gas pools containing N_2-high ($N_2 > 60\%$) and N_2-rich($N_2 > 15\%$) may be do minantly from post-mature sedimentary organic matter.The occurrence of N_2-h igh gas pools in a large scale may indicate that this gas is mainly derived fr om post-mature source rocks in petroliferous basins.N_2-rich gas (N_2＞15%) may also originate from mature,especially high

be formed by metamorphism of ammonium clay mineral-bearing sedimentary rocks.

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