Identification Signs and Prospects of Hydrate Gas

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Abstract: Gas hydrate is a kind of icy crystal body formed by water and natural gas in special conditions. The discovery of gas hydrates provides a wide sphere and a new way of thinking for finding clean and effective energy resources to replace increasingly exhausted traditional energy resources. Moreover, in our country there are a wide realm and bright prospect in the exploration of gas hydrate. This paper has summarized the progress on the study of gas hydrate. And based on the former research about gas hydrates, the integrative identification signs of gas hydrates were summarized in the aspects of seismic data, geophysical well logging, sedimentary and rock, geochemistry, topography and morphology. In the end, the author hopes it may provide some useful clues to the exploration of gas hydrate.

Keywords: integrative identification signs; gas hydrate; exploration

Introduction

The initial evidence of gas hydrate occurrence is the saturated gas hydrates coring from the exploration bore in 1967, although it was found foremost in 1778. Under conditions of STDATM, one stere methane hydrates can create one hundred sixty-four stere methane and zero point eight stere water [1]. Messoyakha is the first gas field where gas hydrates were exploitated in the world. Subsequently the drilling core containing gas hydrates was sampled from the ever frozen layer in the north of Alaska. Gas hydrates, which occur under conditions of low temperature and high pressure, is an ice-snow crystalline, in which hydrocarbon and non-hydrocarbon gases are held within rigid cages of water molecules. Gas hydrates occur in sediments of seabed in layers, dip-dyes and delfs, distributing widely in shallow (> 300 m and > 500 m) sea areas, such as continental slope, island slope, marginal sea and inland sea, and so on, of oceans in the world. There are also hydrates in the Polar Regions with high latitude, permafrost zones and deep water lake on continents, where there exist appropriate temperature and pressure environments. It was confirmed that reserves of hydrate gas was enormous on the continental slope of South Japan Sea by the drilling result in Japan from 1999 to 2000. The drilling through ODP approved that there were abundant resources of gas hydrates on the Gulf of Mexico, the Black Ridge of East Coast, and the Oregon-Cascadia Ridge of West Coast. Gas hydrates have attracted considerable attention of the Chinese geological community since 1988 [2, 3]: Chinese translated version of *Gas Hydrates* has been published [4]; An *Advance in the Research on Gas Hydrate abroad* (compiling 339 pieces of Russia and

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English literatures) and *Special Volume of Gas Hydrate* have been translated and edited [5]; gas hydrates were synthesized in labs of glacial frozen ground institute of Academia Sinica in 1990 [6], the application for “the research of gas hydrates in the permanent frozen ground of Qinghai-Tibetan Plateau” was proposed [7]; and Chinese Institute of Geological and Mineral Information and Mineral Bed Institute of Chinese Institute of Geology had also surveyed and studied gas hydrates and proposed suggestions of erecting items [8]. Many specialists have also paid attention to the research and exploration of gas hydrate bosoms [9-11]. That Science and Technology State of Academia Sinica formed the *21st century energy resources development strategy symposium*, the topic of which was the prospect of exploration and exploitation of gas hydrate in China, in June 1998 shows that the leaders involved prepare to regard the research and development of gas hydrates as an aspect of energy developmental strategy. Lately Shi Dou and Lei Huaiyan have thoroughly talked about research progress and exploitation prospect [12, 13]. In October 2003, in Qingdao City, more than eighty specialists and scholar from America, Canada, Gemany, Russia, the republic of Korea, India, and China took part in the symposium on the new type of energy resources in future seafloor-gas hydrate, which China Geological Survey and Earth Science Department of National Natural Science Foundation of China auspiced, and unanimously agreed that there are huge total resources of “ignited ice”, which will hopefully become a new type of energy replacing oil and gas in the world. It is evaluated that the total resource of gas hydrate in oceans (with the exception of China) converted to methane is up to $(1.8\text{-}2.1)\times10^{16}$ m^3, organic carbon content of that is about two times the total resources of known coal, oil, and gas in the world [14]. So gas hydrates are generally regarded as clean energy minerals in the 21st century.

There are wide coastal areas and territorial seas and Qinghai-TIbetan Plateau claimed as the third almighty in the world in our country [15, 16]. And in the continental slope of the South China Sea alone, the resource of gas hydrates amounts to 845×10^8 t oil equivalent, which is more than that of oil and gas on land and offshore of our country [17]. It is deduced that there are huge resources of gas hydrates in wide sea area and the Qinghai-Tibetan Plateau. Moreover, it becomes an important assignment of our geological workers how to find and locate potential resources of gas hydrates. So it is of important theoretic and practical significance for the quick foundation of gas hydrates to generalize a series of synthetical identification signs of gas hydrate by use of preexisting data at home and abroad. In this article identification signs are analyzed aiming at proposing some clues to the gas hydrate research.

1 Identification sign of hydrate gas

1.1 Identification sign on the seismic section

Gas hydrates occur under specific conditions of pressure and temperature, but the temperiture-pressure gradient is quite immobile in limited regions. So the gas hydrate stability zone is limited to the regions of same depth in sea floor. There are mainly the following features.

1.1.1 The bottom-simulating reflector (BSR)

The reflection from the bottom of the gas hydrate stability zone approximately parallels the seafloor, usually being named a bottom-simulating reflector (BSR), which is the first signature of hydrate gas occurrence.

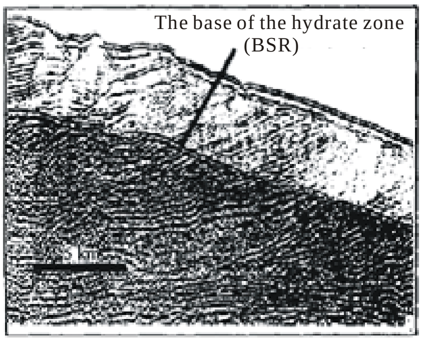

Fig. 1 BSR in a typical seismic reflection

A high-amplitude, negative polarity reflector, which approximately parallels the seafloor bathymetry, cuts discordantly across the stratigraphic section, and is irrelevant to the real sedimentary formation reflection, coincides with the base of the hydrate zone [18] (Fig.1). In addition, the hydrated layer usually displays “blanking” effects of the sedimentary section, i.e., reduced acoustic impedance contrasts caused by the cementation of the host sediments by the gas hydrate molecules. At present, BSRs are the most credible, intuitionistic and widely used indicators. This is becaused the heretofore affirmed hydrate gas in the ocean has been diagnosed from seismic sections. BSRs are generally interpreted as a very apparent transitional zone between the sediments containing gas hydrates (the P-wave velocity increase) and the underlying unhydrated strata frequently containing free gas. And in this zone there is likely free methane, as a result, the velocity of seismic wave may fall down. BSR is easily identified with the following obvious features: (1) it often parallels approximately the seafloor, and cuts discordantly across the stratigraphic section; (2) it shows a high-amplitude and negative polarity reflector as compared with the surrounding sediments, and that it is a reflective sign of interface, of which the velocity drops from high to low; (3) it presents a twig “bright trace” zone and the underlying reflection blind zone is commonly observed for the screening effect of strong reflection interface; (4) it often distributes under highland in seafloor and continental slope; and (5) its scale extends from several kilometres to several hundred kilometres.

BSRs can be used to diagnose the hydrate gas, but the following need to be noticed: (1) there does not exist the one-to-one corresponding relation between hydrate gas and BSR; (2) BSR is affected by tectonism, sedimentation, carbon contents, hydrate content ,and so on, so that both 20 % hydrated content of layers and not less than 10 % free gas content of layers beneath it are needed if BSRs can be observed; and (3) tectonic uplift, high depositional rate, high carbon content, and high hydrated content help the occurrence of BSR [19, 20].

1.1.2 Amplitude scotoma

The second feature of hydrate gas occurrence is seismic amplitude “blanking” effects, i.e., reduced acoustic impedance contrasts within the hydrated sediments, presumably due to the cementation of the stratal interfaces by the gas hydrate molecules. The effect is always observed in deposits containing gas hydrate.

The phenomenon that the seismic amplitude above BSRs is greatly reduced due to the evenly blend of deposit and hydrate continuously appears in the deposit containing hydrate gas is named blanking reflection [21]. This zone appears on the seismic data as a layer with reduced amplitudes and pronounced high velocity relative to the surrounding sediments.

1.1.3 Velocity reversal

The third feature of hydrate gas occurrence is the reversion of compressional wave velocity. That is to say, the compressional wave velocity abruptly decreases when the compressional wave spreads from a consolidated or “frozen” layer (the gas hydrated sediments) to a zone of unconsolidated sediments (under BSR).

1.2 Identification sign of geophysical logging

Now data concerned with stable zones of hydrate gas may qualitatively be acquired from several types of geophysical logging data, most of which helps qualitatively denote the hydrate gas occurrence in a specific area. In the course of drilling hydrate in NWEileenState-2 well of the Prudhoe Bay Oilfield in Alaska province, Collett T S put forward four conditions of identifying special layers utilizing geophysical logging methods [22-24]: (1) high resistivity (approximately 50 times more than water); (2) short time of acoustic waves propagating (131μs/m lower than water); (3) obvious emission of gases during the exploration drilling (the volume content of gas ranges from 5% to 10%); and (4) the features above occurring in two wells or more two wells .

Fig. 2 shows the logging curve of NWEillenState-2 core of the Prudhoe Bay Oilfield in Alaska [23]. It shows the following features in the reservoir hydrate gas occurrence (C , D , E): (1) relatively higher deviation of resistivity than the strata saturated with water; (2) relatively lower negative deviation of gamma curve than the strata saturated with water; (3) relatively lower acoustic travel time than the strata saturated with water or free gas; (4) gentle rise of neutron porosity just contrary to the strata with free gas (a marked decrease of neutron porosity); and (5) gentle decrease of density as compared with the strata saturated with water.

Tab. 1 shows the physical properties, which are measured by the ordinary well logging, of the massive hydrate, deposit containing hydrate, deposit saturated with water, and deposit containing gas. Generally because the hydrate displaces the seawater with high resistivity in hole, the resistivity from resistivity log of strata containing hydrate is greater than that of strata saturated with water. As the cement between the deposit of hole with high velocity and the particle, the hydrate stiffens the deposit, the P-velocity and S-velocity of which will increase. If there exists free gas, the value of acoustic logging and VSP-velocity will decrease, and the value of gamma, neutron porosity, and volume density well logging will decrease by a small margin.

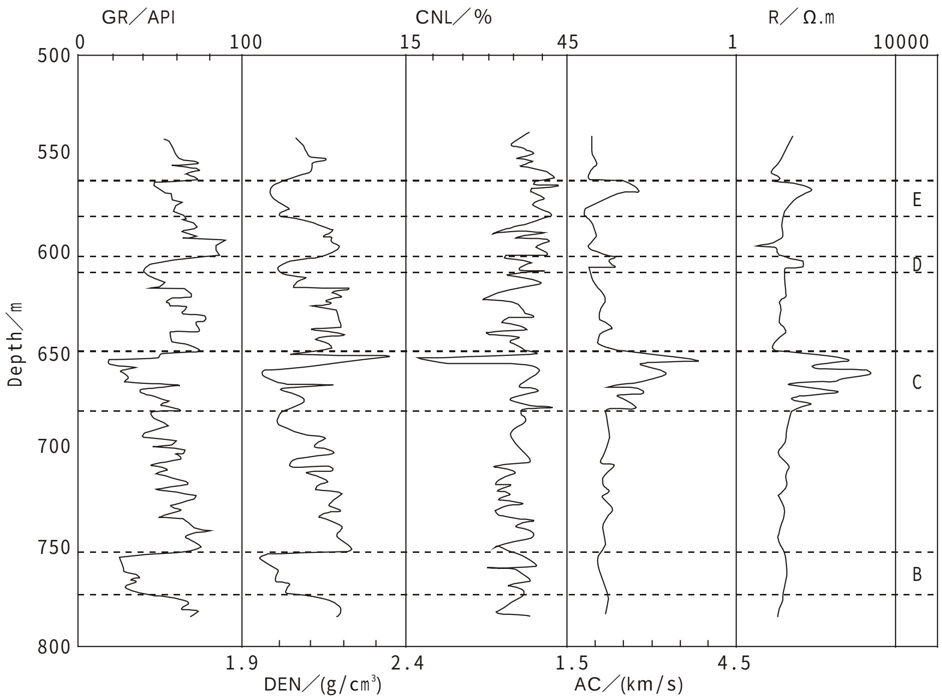

Fig. 2 Logging curve of NWEillenState-2 core of the Prudhoe Bay Oilfield in Alaska (Collett,1998)

Tab. 1 Common ranges of in situ log properties [25]

	Massive hydrate	Deposit containing hydrate	Deposit saturated with water	Deposit containing gas
V_p / km·s^{-1}	3.2 - 3.6	1.7 - 3.5	1.5 - 2.0	1.4 - 1.6
V_s / km·s^{-1}	1.6-1.7	0.4 - 1.6	0.75 - 1.0	0.4 - 0.7
R / Ω·m	150 - 200	1.5 - 175	1.0 - 3.0	1.5 - 3.5
P / g·cm^{-3}	1.04 - 1.06	1.7 - 2.0	1.7 - 2.0	1.1 - 1.5
Φ / %	20 - 50	35 - 70	35 - 70	50 - 90
γ / API	10 - 30	30 - 70	50 - 80	30 - 80

1.3 Sedimentary and lithologic identification signs

1.3.1 Composition and color

The hydrate gas found in nature generally presents white, canary, amber, and dust-colours in the form of sub-equidimensional, formational, spiculate, and scattered crystal [26-29]. It may exist in ambient temperature from below zero centigrade to above zero centigrade. Judging from the core samples acquired, hydrate gases may occur in following forms: (1) occupation of large pore space among rock particles; (2) the spherulitic scattered in the granule rock; (3) solid filled in fissure; and (4) solid hydrate in concomitance with a little deposit.

1.3.2 Lithologic features

By far, the hydrate gas found in the sea area in the world mainly distributes in the fine graded deposit in lentoid, tubercular, particle, and flaky shapes [30, 31]. The lithology of deposit containing hydrate gas is mainly siltstone and clay. The sedimental character controls the formation and distribution of hydrate gas [32].Part of findings shows that diatom fossil is abundant in deposit from stable zones of hydrate gas [33].It is presumed that there is more hole space, which makes the hole space and permeability of deposit increases in the diatom fossil. Because the deposit with more diatom fossil occurs in the environment of palaeoclimatic optimum and higher palaeoproductivity, it is also a source of organic carbon. So lithologic features may also denote hydrate gas occurrence.

1.3.3 Sedimentation rate

Sedimentation rate, which is the main factor controlling the accumulation of hydrate gas, is generally higher than 30 m/Ma [34, 35]. Because sedimentary areas, where sedimentation rates are higher, easily form the undercompaction region, where the favorable fluid conducting system will form. This will favor the formation of hydrate gas.

1.3.4 Sedimentary environments and sedimentary facies

The sites of gas hydrate distribution suggest that many types of sedimentation of gravity flows, such as delta, fan delta, turbidity fan, slope fan, contour currents, and so on, where there are higher sedimentation rate, thick sediments accumulation, and moderate ratio of sandstone to mudstone, are the more favourable facies for gas hydrate development. High ratio of sandstone to mudstone and pore space and more pore water favour gas hydrate development. If the ratio of sandstone to mudstone is too high, the sealing ability will become weak, which is disadvantageous to the gas hydrate accumulation. As to the thickness of deposits, it is generally larger in sites with higher sedimentation rates. But in the site with the thickest deposits (sedimentary center), the ratio of sandstone to mudstone is too low, so there is little pore space and pore water, which is disadvantageous to the development of gas hydrate. Contour currents, which present the features, such as coarse grained lithologies, well pore space, ample gas source, excellent fluid migration condition, and etc, favour the development of gas hydrate, so the sites, where sedimention of contour currents is more intensive, is always the favourable area of gas hydrate concentration. Blake outer ridge is the famous area containing hydrate gas. Now it is proved that there is a close relation between the deposits containing hydrate gas and the contour currents in seafloor, and the deposits containing hydrate gas are formed by the activity of contour currents (the sedimentary rate was about 350 m/Ma) [38,39].

1.4 Geochemical identification sign

The geochemical anomalies of pore water chlorinity, oxygen isotope, and sulfate concentration gradient in sediments prove to be excellent indicators of the presence of gas hydrates. Many successful examples show the obvious pore water chlorinity decrease, and the $\delta^{18}O_{SMOW}$ increase downward, linear and sharp sulfate gradient, and shallow sulfate-methane interface（SMI）are all the signs of gas hydrate occurrence.

1.4.1 Chlorinity in pore water of sediments

Chlorinity in pore water of sediments is one of the indicators of the presence of gas hydrates. Measurements of chlorinity for samples of gas hydrate from Guatemala offing show porewater chlorinity values of 0.051 % to 0.32 %, and that of 0.18 % to 0.82 % from Peru sea [40]. These are greatly lower than the average seawater chlorinity (1.98 %).

1.4.2 Organic carbon content in sediments

Organic carbon content in sediments is the key element of gas hydrate formation. In the littoral zone of Guatemala, organic carbon content is 2.0 % to 3.5 % in sediments containing gas hydrate [41]. In Black outer ridge, organic carbon content is 1 % on the average in sediments containing gas hydrate. So it is presumed that organic carbon content in sediments might be higher in the time of gas hydrate formation.

1.4.3 Indicator of oxidation-reduction electric potential, sulfate content, and oxygen isotope in pore water of sediments

Some indicators, such as low oxidation-reduction electric potential, low sulfate content, high oxygen isotope, and so on in pore water of sediments, may be depended on to guess the presence of gas hydrates [42, 43].

1.4.4 Typomorphic minerals

Typomorphic minerals, which can indicate the presence of gas hydrates, are generally some specially designated constituents and morphologic carbonate, sulfate, and sulfide, which are a series of typomorphic minerals which form in the interaction of mineralizing fluid with seawater, porewater, and sediments in the course of sedimentation, diagenesis, and post-diagenesis [44]. After the gas hydrate decomposes, for example, carbonate will subside. Then whether gas hydrate occurs or not may be suspected by the specially isotopic geochemical character. And that some characteristic fossil aggregations, such as the presence of Calyptogena generic mollusca occur, occur in rock is a proof of presence of gas hydrates.

In the 1990s, the discovery of authigenic carbonates minerals one after another in marine bottom sediments from offshore Oregon of western North America, the western Indian continental margins, and United Nations sea plateau of the Mediterranean, aroused people’s great attention to the authigenic minerals. As a result, the distribution of gas hydrate is linked with the presence of authigenic carbonates, which serves as the symbol of gas hydrate formation. Generally, these authigenic minerals are in the form of carbonate buildup, carbonate crusts, carbonate nodules, and carbonate chimney, in associated with which there are also Mussels, Tube Shape Worms, Fungus, and Methane Air Bubble. All these are the result of the fluid body containing wealthy methane venting upward [45]. So they often occur in clay diapirs and mud volcanos.

1.4.5 Thermoluminescence of offshore sediments

Thermoluminescence of offshore sediments is a potential method for gas hydrate exploration. As one of the nucleus-exploration technics, detection objects of thermoluminescence are typomorphic minerals generated by the formation and decomposition of hydrocarbons. The number, shape, and absorptivity of thermoluminescence peaks are not the same for the minerals which form in different enviroments. After the gas hydrate forms and decomposes, some typomorphic minerals will occur and serve as a good clue to prospecting. Moreover, some carbonate minerals, such as calcite and aragonite, are the main components of the shell of marine organisms, and there is a relation between some molluscs and gas hydrate.So the prescence of gas hydrate may be suspected by the exploration method of thermoluminescence [46] .

1.4.6 Anomalously increased sea-surface temperature

During the instantaneous tectonic activities, seafloor gas hydrate and conventional gas reservoirs may decompose and vent gaseous hydrocarbon, for example, mathane, which upward migrates and diffuses to sea surface due to the pressure decrease and temperturte increase. These gaseous hydrocarbons may act as a heat-carrying agent due to the effort of instantaneous mother earth electric field and sun [47]. According to the observation of the sea-surface temperature scanned by the satellite-based thermal infrared,the seafloor gas vent may be qualitatively investigated, so that the potential regions for gas hydrate formation may be preliminarily delineated in the early stage of investigation.

1.5 Topography and morphology identification signs

Gas hydrate distributes not only in the polar zone and continental permafrost but also in the ocean floor. In-depth study shows gas hydrate is generally found in sediments from continatal slope, island slope, offshore seafloor and seamount, and marginal basins along active and passive continental margins, inland seas, and lakes [48]. Moreover there is a relation in terms of space and formation condition between gas hydrate and some specially designated typical geological structures, such as plate subduction zones, slumps, accretional wedges, clay diapirs, and so on.

1.5.1 Slip block

The development of slip block contributes a situable environment of temperature and pressure for gas hydrate occurrence. First, slump results in rapid deposits in local area, so that local pressural screening effects come into being. Then, gas hydrate easily forms if there exists ample water and gas in the interior of screening body. Moreover, the slump in itself may be the tectonic effects resulted from the decomposition of gas hydrate (As the pressure increases, gas venting from the underling stable zones makes the upper of gas hydrate break, which causes suspended deposit in the continental slope to glide along the gentle boundary).The alteration of sea level causes a series of incidents to happen repeatedly, so that the thick chaotic melange forms in the continental slope toe [49]. During the marine regression in Late Pleistocene（about 220-170 ka）, the sea level decreased by about 100-120 m, so that total pressure loadings of seafloor decreased by about 1 000 kPa. Moreover, the decrease of total pressure caused the gas hydrate to discompose, venting a large amount of methane and water and causing submarine slides. So it is guessed that submarine slides, which took place during the last glacial maximum period in the late Pleistocene, serves as an important clue to searching the gas hydrate.

In the 1980s, the large submarine landsliding relevant to the gas hydrate was found on the continental shelf in the west of Norway [50]. It was mainly made of three slides in different periods, whose total area amounts to 5 580 km^2. The scale of No.2 slide (8-5 ka), which extends from the continent slope to deep sea basins (the slippage distance exceeds 800 km and the water depth being influenced reaches 3 500 m), is the largest among the slides. It should be noted that BSR is found around the slides. Investigations show the earthquake and the decomposition of gas hydrate caused by the earthquake are the main reasons for the occurrence of the above large types of submarine slides.

1.5.2 Clay diapirs

There is a relation between clay diapirs and gas hydrate: firstly, clay diapirs itself may be the result of the sealed gas venting due to pressure release; secondly, clay diapirs can serve as the passage of gas migration upward, which helps the gas release; finally, clay diapirs can also form a local high pressure, which helps the formation of gas hydrate. Gas hydrate was found in five samples containing clayey breccia from the Sonokin Trough in the northern part of the continental slope of the Black Sea during TTR-6 Cruise of Gelendzhik (1996) [51], which demonstrates the relative relation between clay diapir and gas hydrate.

The combination of sediment loading and methane promotes the mud volcanic development and helps the evolution of clay diapirs around the detachment zone, while the accumulation of mathane results in the formation of gas hydrate [52]. So there is a close relation between mud volcano (Clay diapirs) and gas hydrate. But it should be noticed that gas hydrate does not always coincide with BSR. By now samples containing gas hydrate have been gathered from sediments in the Gulf of Mexico, Okhotsk Sea, Caspian Sea, Black Sea, Mediterranean Sea, and off Nigeria, where BSRs were not detected. The research on the distribution of gas hydrate in these sites shows gas hydrate is universally situated around the top of mud volcano and clay diapers [1].

1.5.3 Accretional wedges

The geologic body formed by the stripped sediments growing into the fault zone is named accretional wedges in the subduction process of oceanic plate with certain thickness sediment. Accretional wedges, which have a close relation to its typical mineralizational geologicl enviroment, is the commonly special structure of gas hydrate development. That gas hydrate formsa in stable shallow strata needs two preconditions: (1) The ocean crust containing organic substance is continuously stripped down and accumulates in the deformed front due to structure underplating of subducting plate, so that the deep attains the ample gas source; and (2) sediment thickening, loading increase, and tectonic compression result in sediment dehydration, deaeration and the formation of imbricate thrust fault, then the pore fluid taking along the deep mathane quickly vents upward [53] .

2 Conclusion

a) Gas hydrates can be identified by the sign of BSR, seismic “blanking” effect, and velocity reversal in the seismic section.

b) Gas hydrate mainly shows three electric features: high resistivity (approximately 50 times more than water), short time of acoustic waves propagating (131 μs/m lower than water), and obvious emission of gases during the drilling (the volume content between 5 % and 10 %).

c) Gas hydrates mainly distribute in granule deposits in the lentoid, tubercular, particle, and flaky shapes. And that many types of sedimentation of gravity flows, such as delta, fan delta, turbidity fan, slope fan, contour currents, and so on where there higher sedimentation rate, thick sediment piles, and moderate ratio of sandstone to mudstone (35 % - 55 %), are the more favourable facies in which the gas hydrate forms.

d) Many geochemical abnormalities, such as obvious chlorinity decrease, $^{18}O_{SMOW}$ increase downward of the pore water, linear and sharp sulfate gradients, shallow sulfate-methane interface (SMI), idiographic concomitant carbonate mineral (calcium carbonate and siderite etc), thermoluminescence of offshore sediments, and anomalously increased sea-surface temperature, can all indicate the gas hydrate occurrence.

e) There is a relation in terms of space and formation conditions between the gas hydrate and some specially designated typal geological structures, such as plate subduction zones, slumps, accretional wedges, clay diapirs, and so on.

f) Gas hydrates occurrence, which cannot be judged neither only by some identity symbol, or is negated due to lack of some identity symbol, should be synthetically analyzed and judged during the exploration of gas hydrates.

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天然气水合物的识别标志及研究进展

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摘 要：天然气水合物是天然气和水在特定条件下形成的一种透明的冰状结晶体。天然气水合物的发现为寻找清洁高效的新型能源，以取代日益枯竭的传统能源提供了一个广阔的领域和新的思维方式。我国天然气水合物具有广阔的勘探领域和良好的勘探前景。本文对天然气水合物的研究现状进行了综述。在总结前人关于天然气水合物研究的基础上，总结归纳了天然气水合物的地震、地球物理测井、沉积岩石、地球化学、地形地貌等识别标志。企望对加速天然气水合物的勘探提供一些有益的线索。

关键词：天然气水合物；识别标志；勘探