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Geochemical anomaly of pore waters from marine sediments in the Chinese continental margins and their implications for gas hydrates

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1 Introduction

Gas hydrate is a potential new energy source, which occurs both in marine sediments and in permafrost regions. Gas hydrates posses vast amounts and show potential economic and environmental significance. In recent years, natural gas hydrates have increasingly attracted the attention worldwide and a vast amount of research work has been conducted regarding the occurrence, distribution, and formation mechanism of marine gas hydrates in the world's ocean. However, the gas hydrate research and exploration in China is just starting.

2 Gas hydrates in the South China Sea

In the South China Sea, several lines of evidence have shown favorable conditions for gas hydrate occurrences, including the geologic and tectonic settings, the temperature-pressure conditions, and the thick organic-rich sediments. Direct evidence for gas hydrate, such as the bottom-simulating reflector (BSR) on seismic-reflection profiles, has already observed in many regions of the South China Sea. Furthermore, initial geological, geophysical and geochemical investigations in the South China Sea have suggested great promise for the occurrences of gas hydrates.

3 Geochemical anomalies

Gas hydrates are formed at low temperatures and high pressures. When conditions of temperature and pressure change, the gas hydrates in the marine sediments begin unstable and dissociation and escape of methane may occur. As a result, the chemistry of marine sediments and pore waters may alter. In general, three major factors are involved in these processes: (1) change of pH values, it will result in re-distribution and equilbration of elements between sediments and pore waters, and lead to fractionations of isotopes such as Li and B. (2) change of redox condition, it may lead to change of SO_4^{2-} and other cations such as Mn and NH_4^+. (3) change of chemistry of pore fluids, including anions, cations, and isotopes. All these factors may lead to fractionations of S and C isotopes, and precipitaion of authigenic minerals such as calcite, siderite, barite, gypsum, and pyrite. It has been proven that the most useful indicators for the presence of gas hydrates include the downward chlorinity decrease combined with δ^{18}O increase. Other indicators include the sharp interstitial sulfate gradients, increase of methane concontrations, dilutions of major ion concentrations, and stable isotope variations of δD, δ^{13}C, δ^{11}B, and ^{87}Sr/^{86}Sr.

In this paper, we discuss all available geochemical parameters that have been used and proved to be diagnostic tools for the search of gas hydrates. They include gaseous hydrocarbon contents (mainly methane and ethane) in the marine sediments, carbon isotopes of the methane, downward and spatial profiles of Cl^-, SO_4^{2-} and major cations (e.g., Ca, Mg, Ba, Sr, B, and NH_4) contents, and δ^{18}O, δD, δ^{11}B, and ^{87}Sr/^{86}Sr ratios of the pore waters. There are also many other potential indicators for the gas hydrates, such as thermoluminescence anomaly, reflectance spectra using diffuse reflectance spectrometry, and biogeochemical evidence.

Our results on Cl and SO_4 anion concentrations show that several sites in the north margin of South China Sea display high chlorinity in pore waters. It is suggested that the salt exclusion effect during hydrate formation will cause a salinity increase of pore waters in the hydrate roof zone and shallow subseafloor sediments due to fluid diffusion. Therefore those sites with elevated chlorinity in the South China Sea deserve a further examination for gas hydrate occurrence. Analysis of sulfate concentrations in pore waters reveals a steep sulfate gradient decrease with depths, and the calculated SMI values are around 10 mbsf, which is similar to the SMI values of those well-known gas hydrate occurrences as revealed by ODP-164 and ODP-204 drilling samples. The data suggest that those sites hold a great potential for gas hydrate presence at depths and warranty a further detailed exploration.

A comparison of ammonia and phosphate concentrations in pore water of shallow marine sediments shows that in the gas hydrate occurrence area the pore water show significantly higher ammonia and phosphate concentrations. We also found an increasing trend of pore water phosphate concentrations with depths, which match the SMI curve of SO_4^{2-} gradients in pore water. Therefore, we suggest that the anomalies of ammonia and phosphate concentrations in pore water may be used as a new geochemical tracer to prospect marine gas hydrate. We further discussed the possible mechanisms that cause the anomaly of ammonia and phosphate concentrations in pore water, and developed a simple and useful method to analyze concentrations of these ions in pore water and seawater.

4 Conclusions

In summary, the geochemical anomalies in the shallow sediments and pore waters are all coupled with the geological and geophysical evidence, and pointed out possible gas hydrate occurrence in the South China Sea. We believed that in the near future, the gas hydrate will be actually drilled out in the South China Sea, and we expect that day will come soon.

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