Measurement of dissociation heat of N_2, O_2, and Ar hydrates

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Gas hydrates are crystalline clathrate compounds composed of gas and water molecules, and stable under low temperature and high pressure conditions. Dissociation heats (enthalpies) of gas hydrates have been obtained from their phase diagrams using the Clapeyron equation; however, the application has also been difficult due to low quality of the phase data. Dissociation heat of N_2 hydrate was reported by Kang *et al.* (2001), but the value is thought to be overestimated because it is larger than that of methane hydrate. Dissociation heat of O_2 and Ar hydrates have not reported yet. In this study, we applied calorimetric technique to determine their dissociation heat.
The samples of gas hydrates were synthesized from fine ice powder and guest gases at 273.2 K and the pressure condition of 20MPa (N_2) and 16MPa (O_2 and Ar). The ice powder started to melt and formed these gas hydrates. Approximately 1 g of each hydrate sample was set in a pressure cell specially designed for a Tian-Calvet type heat-flow calorimeter, and its dissociation monitored. The experimental setup and technique were the same as the one that was used previously by Hachikubo *et al.* (2009; 2012).
Dissociation heats of N_2, O_2, and Ar hydrates from hydrate to gas and ice are 12.8±0.2 [kJ mol^{-1}], 12.6±0.1[kJ mol^{-1}], and 13.2±0.1[kJ mol^{-1}], respectively. Yoon *et al.* (2003) reported that dissociation heats of N_2 and O_2 hydrates are 12.18 [kJ mol^{-1}] and 11.52 [kJ mol^{-1}], respectively, using the Clausius-Clapeyron equation. Therefore, our data are several percent smaller than the previous report.

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Keywords: gas hydrate, dissociation heat, hydration number, calorimetry

Isotopic fractionation process of guest gas at the formation of nitrogen hydrate

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Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperature, high partial pressure of each gas component, and high gas concentration. Nitrogen hydrate exists in Greenland and Antarctic ice sheets as an air (N_2 and O_2 mixed gas) hydrate. Recently, existence of nitrogen hydrate has been expected in the Titan (the largest moon of the Saturn). On the other hand, isotopic fractionation of carbon and hydrogen in methane and ethane during the formation of gas hydrates was reported by Hachikubo *et al.* (2007). In this study, we report isotopic fractionation of nitrogen during the formation of nitrogen hydrate. The samples of nitrogen hydrate were experimentally prepared in a pressure cell and isotopic compositions of both residual and hydrate-bound gases were measured. $d^{15}N$ of hydrate-bound molecules was about 0.2 permil higher than that of residual gas molecules in the formation processes. Temperature effect on the isotopic fractionation was small between 226K and 273K.

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Keywords: gas hydrate, stable isotope, nitrogen

Raman spectroscopic analysis of mixed-gas (methane and hydrogen sulfide) hydrate

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Natural gas hydrates in subsurface marine sediment encage hydrogen sulfide. Microbial community produces hydrogen sulfide from methane ascending from deeper sediment layer and sulfate supplied from sea water. The existence of hydrogen sulfide decreases the equilibrium pressure of natural gas hydrate. Therefore, near-surface gas hydrates might exist in shallower area (i.e. less than 300m below sea level). On the other hand, hydration number decides the amount of gas in an unit volume/weight of crystal. In the case of ideal full-occupation of hydrate cages, the value of hydration number is 5.75 (Sloan and Koh, 2008). However, actual hydration number is estimated to be around 6, because small amount of empty cages decrease the free energy and stabilize the crystal. The cage occupancies and the hydration numbers can be estimated from these Raman peak intensities using a statistical thermodynamic model (Sum et al., 1997); however, the effect of hydrogen sulfide on the estimation has not examined yet. In this study, we synthesized methane and hydrogen sulfide mixed-gas hydrate and obtained their Raman spectra.

The mixed-gas hydrates were synthesized in a pressure cell, and retrieved the crystals at the temperature of liquid nitrogen. Hydrate-bound and residual gases were also sampled and their gas compositions were determined using gas chromatograph. Raman spectra were obtained at 123 K in the range 2,800-3,000 cm-1 and 2,500-2,700 cm-1 for the C-H stretching peaks of methane and the S-H stretching peaks of hydrogen sulfide, respectively. The Raman peaks were fitted using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane and hydrogen sulfide encaged in the large and small cages of the cubic structure I.

The methane peak ratio of large to small cages first increased with the composition of hydrogen sulfide (up to several percent), and then decreased and converged with the number of 3.2. On the contrary, The hydrogen sulfide peak ratio distributed from 2.4 to 2.8, increased with the composition of hydrogen sulfide, and then converged with the number of 3.2. These results suggest that molecules of hydrogen sulfide prefer to be encaged in small cages, although the molecular diameter of hydrogen sulfide is larger than that of methane.

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Keywords: gas hydrate, hydrogen sulfide, Raman spectroscopic analysis

Gas hydrate dissociation behavior from temperature monitoring data

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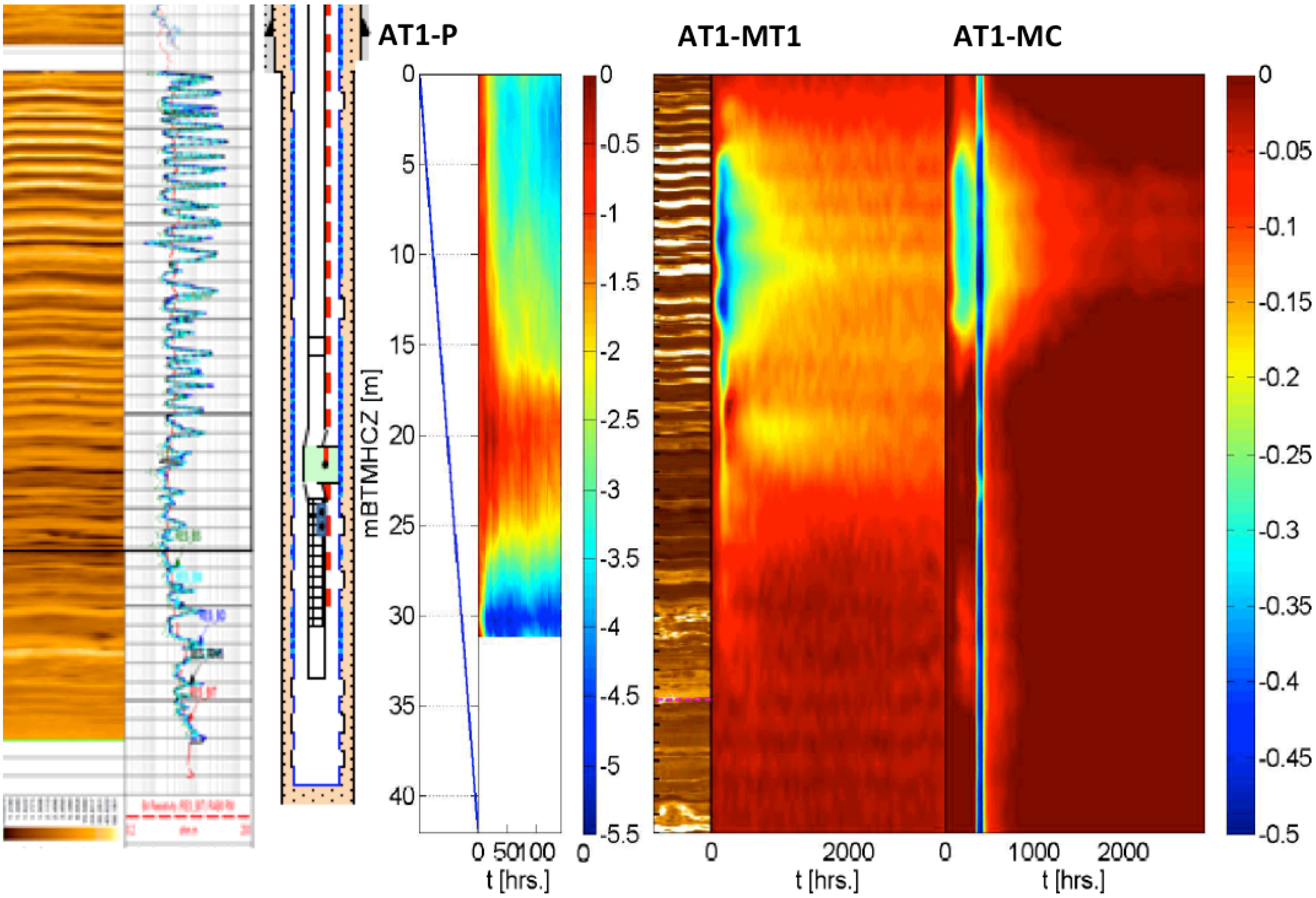
Because the gas hydrate dissociation is an endothermic process, temperature measurement is an important way to know the response of gas hydrate reservoir to the application of some gas production techniques. Furthermore, a heat source, and how efficiently the heat is supplied form the formation are critical knowledge to evaluate effectiveness of the depressurization method as a practical gas production technique that depends on natural heat supply from formations.

The program of the 2013 first offshore production test of methane hydrate in the Eastern Nankai Trough included temperature monitoring in the production hole (AT1-P) and monitoring holes (AT1-MT1/MC). In all wells, some degree of temperature drop was observed.

During the six-days of the depressurization operation, maximum 5 K and 0.5 K in P and MT1 wells respectively. The vertical profiles of the temperature drop show high degree of heterogeneity, and the dissociation process reached in a localized region of the monitoring well. The water production zone in the production well was also concentrated at a specific depth.

Rapid temperature changes were observed in every well when the sand production event happened and terminated the flow in the seventh day of the test. The data show that the sanding occurred at a specific depth with strong water flow, and effect of it reached the monitoring hole location of 20 to 30 m far away.

Keywords: Gas hydrate, Thermal behavior, Depressurization, Downhole measurement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4-Component seismic survey in the second offshore production test of methane hydrate

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JOGMEC carries out 4-component seismic surveys before and after an offshore production test and grasps a change in physical properties by dissociation of methane hydrate (MH) three-dimensionally and evaluates MH dissociation behavior from those data comparisons.
The 4-component seismic survey data was acquired three times in August, 2012 before the production test, in April and August, 2013 after the test in the first offshore production test. The result could show the change in physical properties by the data comparison between before and after the test. On the other hand, improvements of quality of acquired data such as a design of receiver and source points, accuracy of source points and cause of a change in physical properties by data comparison between before and after the test were mentioned as a problem. So, the problems experienced in the first production test were improved for a data acquisition of the second offshore production test. A preliminary simulation was carried out. As a result, it was confirmed that the improvement of the resolution of MH around the production well was possible by the following matters;
・One OBC (Ocean Bottom Cable) would be manufactured additionally and two OBCs would be used.
・Two OBCs would be set in east and west so as to insert the production well. Those direction would be made north and south.
・Source points would be arranged in the range of 4 km north and south and 3 km east and west centering on the production well.
・In order to improve the accuracy of the source points, GPS antenna would be installed at the center of the float hanging an air-gun.
So, one OBC was produced additionally in FY2016 and the 4-component seismic survey data before the test was acquired by the specifications according to the results of the simulation around the production well of the second offshore production test in August, 2016.
From the comparison of the profiles between the acquired data and the data of Daini Atsumi Knol in the geophysical survey project in ‘Tokaioki to Kumanonada ‘took in 2002, it could be confirmed that the resolution in the MH reservoir, below BSR (Bottom Simulating Reflector), and between the sea bed and the top of the MH reservoir was improved. Therefore, more accurate reservoir structure grasp and the evaluation of MH dissociation behavior by comparing to the data after the test will be expected.
This study shows an example of interpretation of the profile before the test.
This study is performing as part of resources assessment of MHs offshore surrounding Japan that JOGMEC is conducting as a member of a research group for resources assessment of Research Consortium for Methane Hydrate Resources in Japan (MH21).

Keywords: 4-Component seismic survey, OBC, Methane Hydrate

Methane Hydrate Potential of the Hidaka Trough, Offshore Japan

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JOGMEC, as a member of research group for resources assessment of Research Consortium for Methane Hydrate Resources in Japan (MH21), has been conducting resources assessment of methane hydrate (MH) offshore surrounding Japan.
This study aims to investigate the gas hydrate potential by the analysis of the 3D seismic reflection survey. In terms of resources assessment, it is important to understand the character and distribution of the BSR (bottom simulated reflector), sand distribution, high velocity anomaly and strong amplitudes above BSR to interpret the methane hydrate concentrated zones (MHCZ) quantitatively.
The 3D seismic reflection data (4800 m streamer, 384 channels, 48 fold) acquired in 2013 and 2014 by geophysical vessel ‘Shigen’, which is owned by Agency for Natural Resources and Energy. We investigated the potential of methane hydrate as resources in the Hidaka trough by the 3D data in Hidaka trough which located in the south Hokkaido government, Japan.
The BSR exists in quaternary sediment and extends over a broad area of the Hidaka trough. Amplitudes of BSR are various and some of them associate with amplitude versus offset (AVO) anomaly. Quaternary sediment is interpreted as hemipelagic and gravity flow deposit. Low amplitude anomaly below BSR associated with low interval velocity and pull down effect are observed as large gas chimney.
Topographical anomalies like small diapir with high amplitude indicates hydrate mounds on the water bottom. They suggest that hydrocarbon matured and generated in deep area, then it migrated and trapped to shallow sediment through several faults caused by tectonics in the foreland basin. It is obvious that hydrate in the basin are closely related to the petroleum system.
Even the focused area has not been drilled, the analysis of 3D seismic data and its interpretations are useful to understand thermal structure, fluid migration, and estimation of the MHCZ in the basin.

Keywords: Methane Hydrate, Seismic Reflection

Methanogenesis and methane consumption within the gas chimney structure in Hidaka Trough, offshore Hokkaido: implications from pore water and gas geochemistry

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Hidaka Trough, offshore Hokkaido, is characterized by gas chimney structures, methane plume, and degassing structures that indicate gas migration from deep sediments to the surface area. This methane is strongly associated with microbial mediated chemical reactions in shallow sediments. This study aims to figure out the microbial processes such as methanogenesis and methane consumption, characterizing geochemical environment in shallow sediments, by analyzing concentrations of dissolved ions and hydrocarbons, and stable isotopic composition ($\delta^{13}C$) of dissolved carbons collected from mounds with gas chimney structures in Hidaka Trough.

Sulfate is depleted strongly near the seafloor at the sulfate-methane interface (SMI), indicating the domination of reductive environment near the seafloor. Sharp negative peak of $\delta^{13}C$ of dissolved inorganic carbon (DIC) locates at the SMI, indicating the anaerobic methane oxidation predominates for the sulfate consumption at this interval. We examined $\delta^{13}C$ of methane and dissolved hydrocarbon composition to distinguish the gas source. Although the biogenic methane is transported from deep sediments, it receives a certain amount of methane of thermogenic origin. In addition, by comparing $\delta^{13}C$ of methane with DIC, biogenic methane produced by microbial mediated CO_2 reduction pathway is also significant. Methane produced by microbial mediated CO_2 reduction within upper methanogenesis zone and biogenic and/or thermogenic methane derived from deep sediments contributes to the shallow reductive environment within gas chimney structures in Hidaka Trough.

This study used data collected during the academic researches and expeditions conducted under the commission from AIST as a part of the methane hydrate research project funded by the Ministry of Economy, Trade and Industry, Japan.

Geochemistry of methane in surface sediment of shallow gas hydrate deposits in the Oki Trough and Joetsu Basin, Japan Sea

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Shallow gas hydrate deposits have been developed, often accompanying subsurface gas chimney structures and gas seepage on the seafloor, in the Oki Trough and Joetsu Basin areas in the Japan Sea. High gas concentration, mainly methane, is a key for characterizing and constraining the reaction and behavior of carbon in the seafloor˜sub-seafloor environments. Here we present the analytical results of sulfate concentration and isotopic composition and concentration of gases dissolved in pore waters collected from the intensive shallow gas hydrate coring program in 2015 (PS15) in order to discuss the biogeochemical processes around the sulfate-methane interfaces (SMI) in these fields.
The depths of SMI are shallow and $\delta^{13}C$ values of methane below the SMI are high in the Joetsu Basin compared to the Oki Trough, reflecting that higher methane flux is caused by higher contribution of thermogenic gas. The $\delta^{13}C$ values show negative peaks around the SMI, which are relatively large in the Joetsu Basin, reflecting the carbon recycling between anaerobic methane oxidation and microbial methane production around there. The rapid decreases of C1/(C2+C3) ratios around the SMI are also caused by the anaerobic oxidation of methane. The C1/(C2+C3) ratios are entirely high in the Joetsu Basin, resulting mainly from ethane enrichment in the Oki Trough. Differences of gas source is one of the important factors controlling shallow biogeochemical processes.
This study was conducted under the commission from AIST as a part of the methane hydrate research project funded by the Ministry of Economy, Trade and Industry, Japan.

Keywords: shallow gas hydrate, Japan Sea

Ionic analusis of seawater and interstitial water in methane hydrate fields off Sain'in region of estern Honshu, Japan

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In order to assess geochemical condition, we measured dissolved ion of seawater and interstitial water in methane hydrate fields off San’ in region of western Honshu, Japan. Sediment samples were obtained in Tsushima Basin, Yamato Basin and Oki Trough using in July 2016. The methane flux in study area is comparatively high. Although methane hydrate has not been recovered in study sites, methane hydrate is probably embedded in deeper horizons, as indicated by chloride concentrations.

Keywords: Methane hydrate, Interstitial water

Geochemical characteristics of hydrocarbon gases within gas chimney structures in the Tsushima Basin and the Oki Trough, Japan Sea

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Shallow gas hydrate often develops in gas chimney structure with mound/pockmark in the Japan Sea, however, the distribution and reaction of gas inside the chimney is not well understood. We retrieved cores from the well-develop gas chimneys with mound in the southeastern margin of Tsushima Basin and western and eastern Oki Trough to examine the relationship between the geochemical composition of gas and geological structure of gas chimney in the Japan Sea of Southwest Japan.

Concentrations of sulfate dissolved in pore waters rapidly decrease with depth to the sulfate-methane interface (SMI). Contrarily, concentrations of methane increase downward from the depth of the SMI. Methane/ethane ratios are low (<100) above the SMI, however, those rapidly increase below the SMI. This is because methane was preferentially oxidized by the sulfate at the depth of SMI and methane was generated by methanogenic bacteria above the SMI. The highest methane flux is observed in the western Oki Trough area where the thermogenic methane are most dominant below the SMI among sites. This site is characterized by the subsurface structure of a large-scaled gas chimney complex and the thermal gradient as high as 57mK/m, indicating that thermogenic methane is produced in relatively shallow sediment and is efficiently delivered to the near-surface environments.

Keywords: gas chimney, hydrocarbon gas, Japan Sea

Biogeochemistry of the seawater-seafloor of Oki trough

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Recently, Shallow methane hydrates near the seafloor has been found in the Japan Sea including Oki Trough area, there are also found characteristic submarine topography such as mound/pockmark topography and chimney structure indicate shallow methane hydrates existence. Some of these features often accompany active methane seepage (methane plume), they cause the local changes of biogeochemical environments near the seafloor. Understanding impact shallow methane hydrates work seafloor environment and water column play important role in understanding ocean environment including shallow methane hydrate areas. We have collected seawater and sedimentary pore water samples in order to characterize the biogeochemical processes associated with the high methane delivery and accumulation. The sampling sites are focused in an area where mound-gas chimney structures are well developed at water depths of 760 m, situated in the Oki Trough of the Japan Sea, ~120 km offshore Tottori.
Concentrations of methane dissolved in water columns collected from fixed point observation of offshore Tottori show little variations near the seafloor, but some variations near depth from 200 meters below the sea-level (mbsl) to 400 mbsl. The concentration of methane dissolved in the seawater is high between 200 and 400 mbsl, which may reflect the formation of shell-like methane hydrates on the surface of the methane bubbles near the seafloor and its dissociation around the upper limit of the hydrate stability around 400 mbsl, and subsequent methane release into the seawater.
Concentrations of methane and ethane dissolved in the sedimentary pore waters collected from the same location are relatively high, comparable to the sites in Offshore Joetsu, and the concentration of sulfate rapidly decrease downward to the sulfate-methane interface at <1.5 meters below the seafloor, methane flux is as high as those in the Offshore Joetsu sites. The chemical compositions of these gases are similar to the sites where bacterial mats and carbonates with frequently high concentrations of methane are widely observed in other areas of Oki Trough.
This study was conducted as a part of the shallow methane hydrate exploration project of METI and the expeditions by the Tottori Prefecture Fishery Research Center.

Investigation of Gas Hydrate Petroleum System in the Miyazaki-oki Forearc Basin, Japan: Preliminary Results

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JOGMEC Methane Hydrate R&D Group has been conducting long-term feasibility studies to assess the available gas hydrate resources in the eastern Nankai Trough, Japan. In order to understand methane generation, migration and accumulation mechanism of gas hydrate, petroleum system modeling (PSM) approach has been utilized for the resource assessment study of the eastern Nankai Trough with provable results. We have applied the modeling approach of the eastern Nankai Trough study in exploring methane hydrate resource assessment of Miyazaki Oki area. This study presents preliminary results of 1D and 2D modeling study of Miyazaki Oki area in investigating sensitivity of lithology and petroleum systems parameters to simulate gas hydrate stability zone (GHSZ) to match with interpreted bottom simulating reflectors (BSRs).

Study area comprises lower Miocene to Pleistocene, deep to shallow marine sedimentary successions of Hyuganada group and Miyazaki Group overlain the basement Shimanto Group. Based on 6 interpreted sequence boundaries from 3D migration seismic and velocity data, construction of a depth 3D framework model is made and distributed by a conceptual submarine fan depositional facies model derived from seismic facies analysis and referring existing geological report. In contrast to the eastern Nankai Trough, the Miyazaki Oki area is lack of calibration data such as pressure and temperature but an exploratory well, Udo Oki-1X, was drilled in the vicinity of the study area. The exploratory well covers most of Miyazaki group where geochemical data, lithology, temperature and vitrinite reflectance are available. Referring to this well, pseudo wells are constructed and sensitivity analyses of lithology and petroleum system parameters are performed. These 1D pseudo well results are applied to 2D modeling and migration simulation. Biogenic methane generation models, Gaussian distribution with peak temperature (model applied in the eastern Nankai Trough models) and Middleburg model based on sedimentation rate, were applied to generate biomethane. PetroMod compaction and permeability curves are assigned for each lithology and hybrid algorithm (combination of Darcy and Flowpath) were used in migration simulation process.

The 2D modeling study has confirmed that lower boundary of GHSZ at pseudo wells has been simulated with sensitivity of a few tens of meters in comparing with interpreted BSR. Furthermore in terms of geological properties, as gas hydrate accumulation increases, trends of reducing effective porosity and permeability are also observed accordingly. Preliminary results of 1D and 2D modeling will be applied to 3D model to investigate migration of biomethane and accumulation of methane hydrate in spatial distribution. As the future works, simulation run of 3D base case model, investigation of structural development and updating facies distribution are planned to perform.

Keywords: Miyazaki Oki, Gas Hydrate Stability Zone, Petroleum System Modeling, BSR

