Minutes
Sedimentary and Geochemical Processes Panel
Lamont Doherty Geological Observatory, NY
4 - 6 June 1991

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Executive Summary

DATE: 4 - 6 June 1991

PLACE: Lamont Doherty Geological Observatory, NY

HOST: R. Jarrard, Borehole Group

List of Attendees

SGPP members

Jeffrey Alt	Jacques Boulegue
Nicholas Christie-Blick	Shirley J. Dreiss
Rodger Flood	William W. Hay
Richard Hiscott	Makoto Ito
Judith McKenzie	Jürgen Mienert
Frederick Prahl	Dorrik A. V. Stow
Erwin Suess, SGPP chair	Peter Swart

Apologies from Henry Elderfield

Liaisons & guests
R. Zierenberg LITHP
M. Langseth PCOM
A. Fisher ODP
M. Coffin

The meeting was dominated by the joined session with DMP during the second day; this session was preceded and followed by regular SGPP business. Highlights of the numerous agenda topics were as follows:

1. SGPP supports revival of Red Sea drilling as initiated by LITHP and requests PCOM to inquire with the appropriate authorities and/or other connections. SGPP regrets that no geochemist has been appointed co-chief for Leg 146 (Cascadia) but urges ODP staffing of the shipboard scientific party should take this situation into account. SGPP suggests that the organizers of the Gas Hydrate Workshop consider expanding the existing report and perhaps submit an article for publication in addition to publishing the WG- Report in the JOIDES Journal. SGPP has formulated a request for proposals to drill a dedicated gas hydrate leg; this request will appear in the JOIDES Journal and in EOS and results from a lack of current proposals on SGPP's highest ranked theme.

2. The proposed ship track and duration of stay in the Atlantic and an unsatisfactory outcome of SGPP's global ranking done at the College Station meeting in March prompted much discussion of ways and means of voting/ranking proposals, taking into account scientific themes and practical logists. SGPP decided to draw up a revised ranking by eliminating non-Atlantic proposals, eliminating the Gas Hydrate "non-proposal" and adding the new Atlantic/adjacent seas proposals. The purpose and rational for this revision is to provide PCOM with input for the immediate Atlantic drilling:

			(average scores)
	348	New Jersey Margin	13.36
2	391	Mediterranean Sapropels	12.86
3	378	Barbados accretion	12.29
4	330	Mediterranean Ridge	11.60
5	380	VICAP	11.53
6	361	TAG hydrothermalism	10.60
7	354/339	Benguela current	10.47
8	388	Ceara Rise	10.47
9	59	Madeira Abyssal Plain	9.53
10	323	Atlantic/Mediterranean Gateway	8.71
11	372	N Atlantic Water Masses	7.53
12	345	W. Florida margin	7.47
13	332	Florida Escarpment	7.33
14	379	Mediterranean Drilling	6.80
15	313	Equatorial Atlantic pathway	4.27
16	327	Argentine Rise	3.87
17	341	Global Climatic Change	2.93

3. The discussion during the joint session with DMP was initiated by seven questions formulated to express SGPP's thematic needs:

What is the accuracy of geochemical logging tools including uses of new logging tools?
What are the logging characteristics and log interpretation of gas hydrates?
How to make maximum use of sealed bore holes and collect samples at in situ temperature and pressure?
What are the problems anticipated with the deployment of downhole tools in Cascadia and Barbados drilling?
How to put together a special logging program for SGPP?
How can fluids be sampled?
How should money be spend on Long-Range Objectives?

Highlights from this session were:

a. Mg is a key element for SGPP. The minimum Mg concentration required to wireline identification of specific minerals is that which is visible on the GLT log. KTB logs have revealed relatively poor statistics at very low Mg concentrations but it is believed that this situation can be improved. The key question is "Where is it really critical from a geological viewpoint to know whether Mg is present at, say, 0.5% or 1,5%?" Once this question has been answered, a logging programme can be designed.

b. SGPP needs a specialised gas hydrate logging suite. The discussion concluded with the observation that the existing logging suite should provide a good deal of useful information about hydrate occurrence and composition. Logging might provide more answers if the tools were recalibrated. DMP should finalist its views on the optimum logging suite for investigating gas hydrates. This suite could be tested during Leg 141 (Chile Triple Junction).

c. SGPP is most interested in sealed boreholes. The meeting concluded that the borehole seal initiative had considerable merit and should be progressed. However, there remains the possibility of scientific competition with wireline reentry.

d. Other special logging programs for SGPP's themes are comprehensive geochemical data from logs, e. g. to measure chemical changes in carbonates where core recovery is poor. The elemental data should include Na (to improve the wireline-derived mineralogy) and Mg, and therefore a high-spectral-resolution tool is desirable. The required geophysical logs include FMS, magnetometer, V_p, V_s, porosity and density, and fluid sampling, pore water pressure and permeability through a combination of LAST, Geoprops, or similar tools.

e. Fluid sampling continues to be a top SGPP priority. The meeting noted that many future ODP legs require high- or low-temperature pore-fluid samples. The technology must be developed to allow this to happen. Substantial engineering input is needed in a brainstorming session as a prelude to an engineering feasibility study of the best option(s). The JOIDES working group meeting on in-situ Pore-fluid sampling, scheduled for 23 August 1991 in Houston, would address the first stage.

f. Priorities for remedial technologies discusses during the joint session strongly echoes those developments anticipated in the SGPP White Paper. SGPP concensus, after discussion of deep drilling, is that for moderately deep drilling (1-2 km) the Somali Basin sites are typical of the sort of drilling we could support although they would not necessarily be of very high priorities. For still deeper drilling (ie 4-8 km holes), the panel is unlikely to lend any support at present to sites as those anticipated for Middleton Island or other deep subduction zone.

4. OPCOM Budget priorities.

Priority 1: Develop capability for fluid sampling and measurement of *in-situ* fluid properties:

(a) for free-flowing water in hot rock (testing system)

(b) for pore water sampling/measurement (Pressure Core Sampler - phase II)

Priority 2: Develop capability for recovering unconsolidated sand/rubble without extensive loss or damage to cores.

Priority 3: Use of alternative platforms for Sea level/Sediment Architecture objectives (eg. New Jersey transect, Coral Islands, Global Change Programs, etc).

Priority 4: Deep-Drilling for SGPP objectives (eg. Somali Basin)

Priority 5: Diamond Coring System

Priority 6: High-latitude support

Priority 7: ODP staffing costs.

5. Next meetings.

November 8 - 9, 1991 ZURICH (Judith McKenzie)

provisionally Feb/Mar, 1992 MIAMI (3 days) (Peter Swart)

September 1992, 2 - 3 days KIEL

Minutes

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- M. Coffin

Agenda

- Welcome and introductions
- Approval of agenda and past minutes
- Reports
  - Message from PCOM — R. Moberly
  - Message from the JOIDES Office — C. Fulthorpe
  - Message from the thematic panels — LITHP, OHP, TECP
- Gas Hydrate Workshop
  - Format of report
  - Proposal for a dedicated gas hydrate leg
- Review of new proposals and global ranking
- Joint session with DMP
  1. What is the accuracy of geochemical logging tools including uses of new logging tools?
  2. What are the logging characteristics and log interpretation of gas hydrates?
  3. How to make maximum use of sealed bore holes and collect samples at *in situ* temperature and pressure?
  4. What are the problems anticipated with the deployment of downhole tools in Cascadia and Barbados drilling?
  5. How to put together a special logging program for SGPP?
  6. How can fluids be sampled?
  7. How should money be spend on Long-Range Objectives?
- Status of geochemical objectives of the Barbados drilling proposal
- Formulate strategy, objectives and design for very deep drilling:
  - Somali Basin
  - Subduction zone drilling
- Old and new SGPP business
  - Next meeting
  - Membership
  - Miscellaneous

1. WELCOMING AND INTRODUCTIONS

SGPP Chair Erwin Suess opened the meeting and welcomed the attendees. The morning session of the fist day of the meeting began with a few panel members and guests missing who arrived later during the session. The minutes of the preceding meeting and the current agenda were discussed and accepted. Reports from liaisons were the first items considered on the agenda.

2. REPORTS

Report from LITHP liaison to SGPP - Robert Zierenberg reported on the last LITHP meeting held in La Jolla, CA on 14 - 16 March 1991. ODP engineer Mike Storms briefed the panel on drilling plans for upcoming Legs 137, 139 and 142 and the status of the Diamond Coring System (DCS). Storms remains optimistic about DCS. Standard rotary coring techniques will be used during Leg 139 (sedimented ridges) and sulfide recovery may be poor. The lack of and/or deficiencies with the wireline packer were likewise discussed with Storms.
LITHP, based on Leg 135 (Lau Basin) results, recommended that a second XRF-technician be staffed on JOIDES Resolution for future hard-rock legs, recommended that NARM-DPG should concentrate more on basement objectives for upcoming legs, strongly endorsed off-set drilling and proposed to reinvestigate possibilities for Red Sea drilling.
LITHP made a global ranking of all active proposals that address high priority objectives of the panel (see appendix 1 for complete ranking). The top four ranked proposals were: (1) Offset drilling layer 2/3, Hess Deep (# 375-rev.), (2) Slow ridge hydrothermal processes, TAG (# 361 A), (3) Axial crustal drilling, EPR II 9° 30' (EPRDPG) and (4) Volcanic rifted margins, N. Atlantic (# 392-396).

Following this report SGPP discussed the possibility of ODP obtaining permission for the JOIDES Resolution to drill in the Red Sea. SGPP requests that PCOM investigate this possibility in light of the changing political situation in the Middle East region.

Report from SGPP liaison to TECP - Shirley Dreiss reported on the last TECP meeting hold in Davis, CA on 21 - 23 March 1991. During the meeting three strong concerns of the panel were registered: (1) reduction of Leg 141 (CTJ) to 39 days of drilling time, (2) problems concerning the Hess Deep proposed drilling, particularly the lack of site survey information, and (3) anticipated poor recovery of shallow-water carbonate sediments during Legs 143/144 (A & G). The majority of the meeting was spent making the panels global ranking with the following top three ranking: (1) N. Atlantic (# 392-396), (2) Mediterranean Collision Zone (323 A, 330 A, 379 A, 383 A) and (3) Chile Triple Junction Leg II.

Report from PCOM liaison to SGPP - Due to the absence of a delegated PCOM liaison to SGPP, Peter Swart, who had attended the last PCOM meeting as K. Becker's alternate in Narragensett, RI on 23 - 25 April 1991, agreed to make a report but apologized for not being properly prepared. The ship track of the JOIDES Resolution was confirmed for FY 1992 and beyond to January 1993 with the ship moving into the North Atlantic and adjacent seas at that time for approximately 18 months. The preliminary mandate of the new Opportunity Committee (OPCOM) was discussed. OPCOM was established to evaluate ways to use an additional $ 2.1 M of "extra" NSF funds in new and imaginative ways to advance scientific ocean drilling. POCOM proposed the following possible uses: (1) DCS development and testing. (2) Deep drilling, (3) Alternate platforms, (4) High-latitute support vessels (FY 93 and beyond) and (5) Staff costs for the above. Other items of SGPP interest covered during the meeting included the establishment of an Offset Drilling WG and the disbanding of the Atolls & Guyots WG.

Following this report, the SGPP discussion centered on co-chief staffing of upcoming legs. The selections of co-chiefs for Leg 143 and 144 (A&G) have been announced, K. Konishi (J) & E. Winterer (USA) and L. Premoli-Silva (ESF) & J. Haggerty (USA), respectively. SGPP expressed concern about the selection of co-chiefs for Leg 146 (Cascadia) with geochemistry and hydrochemistry not being well represented. PCOM expressed a clear preference in favor of proponents serving as co-chief, whereas SGPP had specifically requested a geochemist, however, a non-proponent, as a co-chief for Leg 146 (i. e. M. Goldhaber). Staffing of shipboard scientists of Leg 146 should take this situation into consideration.

Report from ODP liaison to SGPP - A. Fisher reported on the PPSP safety review for Leg 141 (CTJ). Collision zone sites have been given broad approval with a landward drilling plan beginning first with SC3 followed by SC2 and SC1 to check for problems with gas. Post-collision sites (SC3) were not approved, but gas hydrate sites and gas hydrate drilling have been approved. G. Claypool, B. Katz and M. von Breymann are preparing a shipboard report for gas hydrate monitoring and safety procedures.

Fisher also reported on the Leg 137 (Site 504 B) results. The hole was successfully cleaned and further coring operations were completed before drilling was halted due to loss of part of the drill-string in the hole. Leg 140 will again revisit Site 504B, and, at that time, a fishing operation will be required to remove the lost equipment prior to continuing to deepen the hole. Fluids were sampled using the Los Alamos and Lawrence Livermore Berkeley sampling devises. These high temperature fluid samplers are still in a development stage. Each has its problems with contamination. They will be tested further on Leg 139 (Sedimented Ridges). J. Alt, Leg 137 shipboard scientist, reported that fluids ampled at the bottom of the hole at 160° C were apparently of bore-hole origin and not contaminated by surface sea water. The sulfate concentration were zero and anhydride apparently precipitates in the hole. With increasing temperature and depth, calcium increases and magnesium decreases. An underpressured zone was noted with renewed downward flow of water.

Currently, Leg 138 (Eastern Equatorial Pacific) is averaging 100% recovery and excellent logging conditions are producing real time data.

3. GAS HYDRATE WORKSHOP

Gas Hydrate Workshop Report - In its present form, the Gas Hydrate Workshop Report prepared by K. Kvenvolden adequately covers the content of the meeting, without being an extensive scientific report. SGPP urges K. Kvenvolden, E. Suess and J. McKenzie to see if the report could be expanded, requiring input and feed-back from the various contributors at the workshop. The report should address more strongly and adequately the safety issue in drilling gas hydrate or alternatively should refer to the gas hydrate monitoring and safety procedures, presently being prepared for Leg 136. The workshop report will be published in JOIDES Journal, with perhaps an additional article submitted to EOS. The workshop report is appended to these minutes.

Dedicated Gas Hydrate Leg - SGPP has gas hydrates as the highest ranked theme but lacks an appropriate drilling proposal. This deficiency necessitates the formulation of a dedicated gas hydrate drilling proposal, possibly by a sub-committee composed of SGPP members. Possible sites for a gas hydrate proposal in the Atlantic were discussed. C. Paull has an active gas hydrate program off North Carolina. R. Flood noted that the Argentine Basin contains gas hydrates and there is a USGS project to study gas hydrates off the Blake Outer Ridge. The USGS sponsored a meeting on gas hydrates in mid-April, 1991. Gas hydrates have been recognized in the southern area of the Barbados Accretionary Prism.

SGPP proposes that a note be published in the JOIDES Journal, as well as in other scientific publications such as EOS, requesting proposals for a dedicated gas hydrate leg, preferably in the Atlantic considering the proposed ship's track in the upcoming years. R. Hiscott will formulate the notice before the end of the current meeting.

Gas Hydrate Drilling

Gas hydrate layers, marked by prominent bottom simulating reflectors at continental margins, trap a significant proportion of global methane. The occurrence, modes of formation, stability, composition, and physical properties of clathrates are of interest to a broad spectrum of geoscientists. The Sedimentary and Geochemical Processes Panel (SGPP) of ODP considers the genesis and characteristics of gas hydrate layers to be so important that the panel has ranked the concept of a dedicated drilling leg to study hydrates at the very top of its priority list. SGPP invites scientists to submit proposals for such a dedicated leg to the JOIDES office, following procedures outlined elsewhere in JOIDES Journal. Please remember that the JOIDES Resolution will leave the Pacific for the Atlantic and adjacent seas in early 1993, where it will likely remain until at least 1995. For further details on SGPP hydrate objectives, contact:

In Europe	In North America
Judith McKenzie (SGPP chair)	Roger Flood

Joint Session with DMP - In preparation for the joint session during the following day, SGPP requests that certain items related to the study of physical and chemical properties of gas hydrates be included in the agenda topic ≠ 2. Gas hydrates properties that should be determined or investigated with drilling are lateral continuity, porosity, permeability, pore pressure, composition, amount of free gas, amount of hydrate, temperature structure, associated diagenetic products, salinity structure (freshwater hydrate), sediment fabric, growth habit (i. e. displacive, replacive disseminated), and age structure. Can these types of information be obtained from logs? Can logging be done while drilling or ahead of drilling? Are downhole seismic experiments, thermal conductivity and EMS studies possible?

4. REVIEW OF NEW PROPOSALS AND REVISED GLOBAL RANKING

Bearing in mind the proposed ship track from Feb. 1993 to Sept. 1994 in the Atlantic, ending in N Atlantic, and from Oct. 1994 to Dec. 1995 in the Atlantic and adjacent seas, six new proposals were considered.

Proposal 397. Primarily of interest to LITHP. Review could add comment on sediments and synrifting tectonics. RH to prepare response. RANK 1

Proposal 398. Main interest to SGPP is the influence of bottom currents, the glacial input of sediment and glacial/current plumes on seamounts. JM to prepare response. RANK 3

Proposal 346 - add. This is simply additional information for an earlier proposal. Proponents to be thanked for information. NO ACTION

Proposal 363 - add. Same as 363 but with amplification of paleoceanographic objectives and mention of mid-Cretaceous black shale event. NO ACTION

Proposal 361 - rev. Very high interest for SGPP, but with some problems of site survey requirements, fluid sampling techniques and representativeness of area. SGPP must emphasize the technical problem of fluid sampling that needs to be addressed. ES prepare response. RANK 5

Revised ranking. The proposed ship track and duration of stay in the Atlantic and an unsatisfactory outcome of SGPP's global ranking done at the College Station meeting in March prompted much discussion of ways and means of voting/ranking proposals, taking into account scientific themes and practical logists. Specifically the high ranking of the proposal to return to Site 801 during the March proceedings had adversely affected the ranking of Atlantic drilling proposals with SGPP interests. Therefore, the panel decided to draw up a revised ranking by eliminating non-Atlantic proposals, eliminating to Gas Hydrate "non-proposal" and adding the new Atlantic/adjacent seas proposals. The purpose and rational for this revision is to provide PCOM with input for the immediate Atlantic drilling. Another motivation by the panel to concentrate on Atlantic drilling now, was the realization that SGPP's previous high rankings of Pacific proposals did not prevent PCOM from committing the drilling vessel to the Atlantic for more than two years despite plans for highly ranked drilling objectives "in any ocean".

Voting procedure (generally agreed as good workable method for SGPP). Each member ranks each of 17 proposals from 17 (high) to 1 (low), or from 16 to 1 (etc) if he/she is proponent on one proposal. Proposal scores summed and averaged as appropriate, highest average is first rank and so on. No discussion of proposals during voting, no members need leave the room.

Final agreed ranking

			(average scores)
1	348	New Jersey Margin	13.36
2	391	Mediterranean Sapropels	12.86
3	378	Barbados accretion	12.29
4	330	Mediterranean Ridge	11.60
5	380	VICAP	11.53
6	361	TAG hydrothermalism	10.60
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5. JOINT SESSION WITH DMP

The second day of the meeting was entirely devoted to the joint session with DMP. Both chairmen had worked out an extensive agenda with each topic being introduced and the ensuing discussion lead by SGPP and DMP members having the appropriate expertise. The following questions served to introduce the topics of discussion:

1. What is the accuracy of geochemical logging tools including uses of new logging tools?
2. What are the logging characteristics and log interpretation of gas hydrates?

3. How to make maximum use of sealed bore holes and collect samples at *in situ* temperature and pressure?
4. What are the problems anticipated with the deployment of downhole tools in Cascadia and Barbados drilling?
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Accuracy of Geochemical Logs (P. Worthington)

The Geochemical Logging Tool (GLT), includes an induced gamma spectral tool (GST) which, when run in capture mode, contributes through post-cruise processing eight of the twelve elemental concentrations that the GLT provides. These elements are of primary interest to inorganic geochemists. The GST was actually introduced at the beginning of the Eighties when it was run in inelastic mode with an emphasis on organic elements in the form of the infamous carbon/oxygen ratio. The aim had been to evaluate directly the hydrocarbon content of reservoir rocks. The approach did not gain credibility, partly because of the high degree of uncertainty associated with these estimates. Emphasis shifted to capture mode applications thereafter, but carbon/oxygen logs remain a potentially useful service to the oil industry, and they are now benefiting from improved technology.

Anderson reviewed the use of the GLT in ODP. Featured scientific benefits included the recognition and interpretation of the gabbro zone on the Southwest Indian Ridge (Site 735, Leg 118) and establishing the geochemical budget of the Bonin Island Arc through subduction zone studies where core recovery was poor (Site 786, Leg 125). Anderson concluded by noting that the present state-of-the-art in geochemical log applications is to be found at the KTB programme of FRG.

Draxler reported on the geochemical logging programme at the KTB site. The pilot hole (4000 m deep) produced 98% core recovery and this has provided a unique opportunity to check log responses against core. XRD and XRF have been run routinely on core. The GLT data require processing to derive mineralogy from elemental concentrations, using the ELAN package. There are two ELAN processing chains, dry model (no water) and wet model (water). Other logs can be used in conjunction with the GLT to accommodate other minerals that are not usually included in these models. The GLT uses a sodium iodide crystal, which has limited spectral resolution. KTB have also run an advanced tool, the enhanced resolution tool (ERT), with a high-spectral-resolution germanium crystal. This is a cryogenic tool: it could be run for up to 12 hours at pilot-hole temperatures (85° C at 3000 m). Stationary readings had to be taken because of the lower counting efficiency of germanium detectors. The tool was run in delayed activation (INAA) mode and capture (prompt neutron activation analysis) mode. The downhole activation time for the capture-mode readings was about 20 minutes.

Schweitzer compared GLT and ERT spectra and demonstrated the higher spectral resolution achievable with the latter. The ERT allows other minor elements to be studied. Most of these can be inferred from delayed activation mode data. For example, Na can now be measured and procedures for Mg are currently being developed. The carbon/oxygen ratio can be measured with a precision of ±2% but the extraction of carbon remains very difficult. The key question is not " Can we measured more elements?" but rather "Which elements do we need to know and in what range of concentrations?" Then the survey can be planned accordingly. There are two survey procedures that can be used for the ERT. Continuous logging runs have less to statistically significant levels. Stationary readings are taken with a greater risk of tool sticking but there is then a need to introduce a "fake" logging speed for processing purposes. In ODP, geochemical logs have been run only in conventional capture and (occasionally) inelastic modes, in which the neutron source and gamma-ray detector are close together. In delayed activity logging the source and detector are physically separated so that a spatial change is used to create a temporal effect. Several points were raised through discussion. Mg is a key element for SGPP. The minimum Mg concentration required to wireline identification of specific minerals is that which is visible on the GLT log. KTB logs have revealed relatively poor statistics at very low Mg concentrations but it is believed that this situation can be improved. The key question is "Where is it really critical from a geological viewpoint to know whether Mg is present at, say, 0.5% or 1,5%?" Once this question has been answered, a logging programme can be designed.

Elements are apportioned between solids and fluids by trying to exclude elements that are unlikely to occur within the solid rock. Examples are hydrogen and chlorine. The opposite can apply, too, e. g. where Al is present in drilling muds. There is a balance to achieve and the key lies in the integrated use of core and log data.

The Enhanced Resolution Tool (ERT) will allow trace element concentrations to be determined, e. g. antimony, arsenic, bromine, copper, europium, indium, nickel, scandium. The accuracy will be as good for trace elements as it is for aluminium. The precision is a function of element concentration.

Shipboard geochemical logging data are in the form of relative elemental yields. Oxide data are not available on board ship. The installation of the Schlumberger MAXIS 500, intended to replace eventually the CSU, will lead to absolute elemental concentrations becoming available during the course of a leg.

Requirements for Logging and Log Interpretation in Gas Hydrates (E. Suess)

There has been a reversal in ODP's interest with regard to drilling hydrates. Previously the strategy was to avoid them; now it is to drill them. The last SGPP meeting encompassed a workshop on gas hydrates. Hydrates are present on most continental margins and on the Arctic shelf. The current interest has arisen because (i) hydrates are seen as an energy source, (ii) hydrates have an environmental impact through decomposition and thence an accentuation of the greenhouse effect, and (iii) there is scope to integration with other global programmes through an interest in methane budget.

The SGPP requirements for gas hydrates were described as follows:

- lateral continuity;
- porosity, permeability, velocity;
- composition in terms of C, H, O;
- amount of free gas vs hydrated gas;
- thermal properties, thermal conductivity;
- growth habit, sedimentary fabric, age, direction;
- salinity structure at, above and below the gas hydrate ($CH_4 . 6H_2O$ excludes sea salt during hydrate formation. Where does it go?)

The logging strategy for gas hydrates embraces the following points, some of which are discussed in Appendix II of the DMP minutes. Casing is usually set at 70 - 100 m. Most hydrates are deeper than this. The approach is therefore one of open-hole logging. Hydrates can be well characterized by logs and therefore lateral continuity between drill sites can be clearly established from the logging standpoint. The neutron tool responds to hydrogen and can be calibrated in terms of hydrogen content. This tool will provide a measure of how much hydrate is present provided that the tool response does not "saturate" due to the very high hydrogen concentrations. Conventionally, neutron logs are presented in limestone porosity units because that is the lithology of the primary calibration pits in Houston. However, they can also be presented as count-rate ratios and it might be especially useful to compare thermal (absorption) and epithermal neutron count-rate ratios because the latter will be perturbed by carbon and oxygen due to slowing-down effects. The neutron tool is run with the density tool and they are frequently interpreted as a pair. Resistivity logs will also respond strongly to high hydrate concentrations.

Permeability cannot be measured through logging. Downhole velocity measurements are straightforward.

The geochemical logging tool, run in both inelastic and capture modes, can provide information on C, H and O concentrations. The C/O ratio can be measured more precisely at high porosities. In the hydrate case, we regard the hydrates as part of the porosity within a sedimentary fabric, with a target porosity range of 35 - 50%. The separate resolution of C and O will require some laboratory measurements.

Gas zones should be identifiable through the neutron-density combination provided that the tool responses are properly calibrated.

Thermal properties might be investigated indirectly using a new tool devised by KTB. This includes a temperature sensor and a heating device; the fluid is heated up and the sensor measures the dissipation of this heat into the formation. If the hydrate layer has a low thermal conductivity, a large perturbation will be observed in the temperature profile.

Logs will only partially contribute to a knowledge of the sedimentary environment in which hydrates occur. The physical characterization of the locality is important and the key logging tool will be the FMS with its sharp spatial resolution. Again, the integration with core is essential.

Salinity structure can be investigated in several ways. One approach is to interpret the chlorine concentration log from the GLT, as done during Leg 112. Another method might be to run the GST within the GLT string in thermal-decay-time (TDT) mode to obtain a chlorine log. Both of these approaches suffer from large borehole effects. An experiment was suggested to flush seawater out of the borehole, replacing it with freshwater prior to logging. Another approach might be to use the self-potential (SP) log to identify qualitatively changes in pore-fluid salinity. The SP log could be interpreted in conjunction with data from the auxiliary measurement sonde (AMS), which is always run as part of tool strings, and which provides borehole fluid resistivity and borehole temperature logs. Yet another suggestion was to run the borehole gravimeter because of its good lateral investigation characteristics.

The drilling process itself could lead to a change in the physicochemical characteristics of gas hydrates. Logs should be run as soon as possible after drilling. An option is a hole dedicated to gas hydrate studies. Another option is measurement-while-drilling (MWD) although it will be years before an ODP-compatible MWD string is available. Yet again, a push-in tool ahead of the drill bit might avoid drilling damage: this would require knowing the depth of the hydrate layer from site-survey geophysics. For example, the WSTP tool was used in hydrates on DSDP Leg 84. This tool uses a pressure differential which might cause the hydrates to decompose. The discussion concluded with the observation that the existing logging suite should provide a good deal of useful information about hydrate occurrence and composition. Logging might provide more answers if the tools were recalibrated. DMP should finalist its views on the optimum logging suite for investigating gas hydrates. This suite could be tested during Leg 141 (Chile Triple Junction).

Sealed Boreholes (J. Boulegue)

SGPP is interested in sealed boreholes because they prevent contact between borehole waters and the infinite water reservoir above. Unsealed boreholes may collapse more easily. Sealing does not prevent convection in the hole. Sealed holes can be used in three ways:

- free-standing mode with an unequipped head;
- installation of instruments, e. g. seismometers, physical properties, chemical properties, testing of materials, temperature;
- emplacement of tracers for hydrogeological purposes, e. g. NaBr, LiBr, LiCl.

Pressure, temperature and chemistry can be addressed through packer experiments as an alternative, but these would not provide the separation of borehole fluids from the sea. A possibility is to seal different sections of the borehole.

Becker reviewed the status of the ODP instrumented borehole seal. This takes a single sample with the tubing intake near the base of the hole, and would be difficult to modify to take multiple samples at different levels. The seals are scheduled for deployment on Leg 139, Sedimented Ridges I. The objectives are to log temperatures over a long period in order to obtain a reliable downhole temperature within this active geothermal system.

The meeting concluded that the borehole seal initiative had considerable merit and should be progressed. However, there remains the possibility of scientific competition with wireline reentry.

Downhole Measurements at Accretionary Complexes (A. Fisher)

The successes and failures of downhole measurements at the Barbados (Leg 110) and Nankai (Leg 133) accretionary complexes are as follows:

WSTP	temperature measurement	generally successful, some failures of electronics, some incomplete deployments
	pressure measurements	some data collected, significance unclear
	water sampling	success less than 50%, possibly due to high clay content of sediments; fluid no different from squeeze-cake fluid
APC tool	temperature measurements	generally successful, occasional operator error, battery failure
logging	three main strings	80 m logs total for leg, borehole instability greatest problem, even with dedicated holes
packer tests	rotatable-packer (third use)	unsuccessful, poor hole conditions
ONDO	long-term temperature	result unknown, deployment very difficult due to current and poor hole conditions (actually deployed Leg 132)
VSP	seismic profile	largely unsuccessful, current, poor, hole conditions (operator error)
LAST I	*in-situ* stress	several successful deployments, failures due to operator error, battery failure
Geoprops	*in-situ* pressure, permeability, temperature	not available
wireline packer	fluid sampling	not used, failed during Leg 133

Jarrard commented on the chances of success of different types of downhole measurement in accretionary complexes, with a particular view towards the upcoming Cascadia Leg (146). The major impediment is hole instability. During Legs 110 and 131 fewer than 20% of the downhole measurement goals were met. This figure could exceed 70% at Cascadia, provided that an aggressive logging strategy is adopted, e. g. be prepared to lose a logging tool, a BHA, or maybe more than one of each. A particularly difficult issue is the determination of permeability at Cascadia. Packer measurements have only a 30% success rate in ODP, even in stable holes. Yet, Leg 146 has both packer and flowmeter permeability experiments scheduled. A further problem is downhole fluid sampling. The wireline packer will not be available and it is not clear what the status of the pressure core sampler will be. Permeability and sampling problems are, of course, compounded by hole instability.

Karig pointed out that a primary cause of hole instability is that the material drilled in accretionary complexes is close to stress failure and that the additional stress concentrations introduced by drilling are bound to induce failure. One cannot turn a blind eye to this potential situation at Cascadia. A possibility is to use the side-entry-sub (SES) aggressively and log while pullingpipe. If there is excessive hole closure, it might be desirable to washdown a hole specifically for logging: this would improve logging prospects, but it would still be necessary to use the SES in an aggressive way. The recent DMP subgroup meeting on hole stability proposed heavy muds for formation control. This approach would prove very expensive without return circulation and would degrade the geochemical logs by invalidating the photoelectric factor (Pe) curve (from the lithodensity log) and thence the magnesium correction. There exists rationale to the effect that hole conditions might be better at Cascadia than on Leg 131 (Nankai). This view is partly based on experience with a DSDP hole at Cascadia. However, it has no bearing on a future return to Barbados, where conditions can be expected to be as bad as on Leg 110.

Suess pointed out that two Cascadia sites are dedicated to gas hydrates. It would be desirable to obtain the best possible neutron logs. This would require dividing the quad-combo into two separate tool strings so that the neutron tool can be eccentred by a bow spring. A key question is whether this practice would increase the risk to the tool string. LDGO -liaison responded that if it seems at all feasible to run an eccentred neutron tool, it will be done.

Specialized Logging Programmes to Meet SGPP Needs (J. Mienert)

The SGPP priority goals are in four key areas:

(a) Fluid Flow/Gas Hydrates
The environment is one of high pore-water pressure within various lithologies. A potential problem is hole instability. Key questions are permeability, pore-water pressure, fluid conductivity, thermal gradients, gas and fluid composition, salinity structure, and amounts of hydrate and free gas.

(b) Sea Level
The environment is sand and/or coral limestone. Hole instability is again a potential problem. Key issues are the amplitude and frequency of depositional and erosional events.

(c) Palaeocean Chemistry
The environment is one of biogenic material. No specific issues for logging were identified.

(d) Sediment Architecture
The environment is primarily sand, but various lithologies are present. Hole instability is a potential problem. Key issues are physicochemical cyclicity,

structure and fracture distribution, magnitude and direction of stress, composition and chemical alteration, hydrogeology, and diagenesis.

The above goals can be distilled into five activity areas, gas, pore water, solids, structure and thermal regime, all providing input to geochronology. High-resolution geochronology requires full logs and complete sampling for interhole correlation and for tying back to seismic data. The required log inputs can be classified into two groups, geochemical and geophysical. In particular, there is sometimes a need to log shallow holes and to obtain good logs in the uppermost sediments. The only logs that can be run to the surface are the nuclear logs: there is data degradation due to casing and pipe. Shear-wave and attenuation log data might assist in relating seismic interpretations to, for example, oxygen isotope stages identified from pore fluids. Higher spatial resolution is sought from all logs, except the FMS. For example, should ODP use a thin-bed lateralog such as that used in the coal industry in Germany? The ability to sample sediments after a hole has been drilled would be an advantage. Sidewall wireline drilling tools have a 5-inch diameter and therefore cannot be used through ODP drillpipe. This technology would therefore have to be deployed through wireline re-entry.

In summary, SGPP needs comprehensive geochemical data from logs, e. g. to measure chemical changes in carbonates where core recovery is poor. The elemental data should include Na (to improve the wireline-derived mineralogy) and Mg, and therefore a high-spectral-resolution tool is desirable. The required geophysical logs include FMS, magnetometer, V_p, V_s, porosity and density, and fluid sampling, pore water pressure and permeability through a combination of LAST, Geoprops, or similar tools.

Fluid sampling (P. Worthington)

Several key issues have to be considered in planning a way forward. These include:
(a) do we wish to sample borehole or pore fluid?
(b) should we drill a smaller diameter dedicated hole for the Wireline Sampler Mark II?
(c) what commercial tools are available?
(d) are there alternative sampling strategies?

We need a minimum of four samples at a given station in order to establish the degree of mixing of pore and borehole fluids and thence to allow chemical extrapolation to the undisturbed pore-fluid state. Other basic requirements are temperature, pressure, fluid conductivity and a turbine flowmeter for permeability.

The principal scientific requirements are to obtain samples of formation fluids in basalt fracture zones, some at high temperatures, and in hard sediments such as cemented carbonate platforms. There is currently no information about pore-water characteristics in these zones. For soft sediments, the APC can be used with pore fluid being obtained by squeezing the sample. This works satisfactorily in all but high-permeability environments. For hard sediments and basement rock, in-situ pore fluid sampling is required.

Scholz reported on the status of the Wireline Sampler, built by TAM, Inc. and overseen by the subcontractor, Stanford University, The tool has an OD of 3.625 inches and the packers have to inflate to 12 - 13 inches. The temperature rating is 100° C and the tool is best suited for RCB holes because the bit is smaller. Although there were problems with packer deflation on Leg 133, the biggest problem is sample contamination because of the way the hydraulic circuit is designed. The tool needs to be redesigned to remove the compromises made during its long evolution. The cost of redesign and of developing two new tools is around $ 350.000. There is nothing in industry to compete with the Wireline Sampler.

Crocker commented on commercial formation testers which offer a doughnut seal with the formation and are therefore unsuitable for fractured rock. Furthermore, good samples are obtainable only where formation permeability exceeds 100 mD. The invading borehole fluids impart exchange ions to the formation and this effect has to be reversed before a pore-fluid sample can be regarded as uncontaminated. This reversal can take several days, an interval which would clearly be unacceptable for ODP purposes.

Draxler developed this theme by stating that even substantial pre-production may not guarantee an uncontaminated sample. The volume of fluid sampled is a critical issue. In the past 100 cc has been identified as desirable, but the geochemical community would now consider even 10 cc to be tolerable. Nevertheless, the large discrepancy between the pre-production volume of fluids (tens to hundreds and even thousands of liters) and the final volume of (hopefully pristine) pore-fluid sample remains a major issue to be resolved.

Possible alternative sampling tools are the Pressure Core Sampler and the OBCAT tool developed in the UK for use with the ODP drillstring packer. Crocker noted that there is a misperception that a low-technology sample will not satisfy high-technology needs. For example, a possible approach is to use gas lift by compressed air over, say, 1000 m. This would allow sampling with time and an estimate of formation permeability. Furthermore, by sampling a significant formation interval, we would obtain a substantial sample, especially if a zone of high permeability happens to be included. A potential problem is iron contamination from the drillpipe, but his problem might be overcome by using a go-devil with sample bottles to avoid having to pass the sample up the drillpipe. This approach would also work in hot holes. A disadvantage is the depth resolution that the method implies, but sampling could be carried out at intermediate stages of drilling. A vertical resolution of 10 m would be acceptable to the geochemical community. The whole approach needs to be subject to a cost and feasibility study by a drilling engineer.

The meeting noted that many future ODP legs require high- or low-temperature pore-fluid samples. The technology must be developed to allow this to happen. Substantial engineering input is needed in a brainstorming session as a prelude to an engineering feasibility study of the best option(s). The JOIDES working group meeting on in-situ Pore-fluid sampling, scheduled for 23 August 1991 in Houston, would address the first stage. It was anticipated that funds would be made available for the engineering feasibility study in early FY 92. It is, of course, possible that what we are trying to do cannot be done. However, the effort should be driven by the scientific goals which remain a top ODP priority.

Priorities for Remedial Technology (J. Alt)

The SGPP technology needs are:
(i) Drilling Capabilities and Core Recovery
Drilling and sampling thin sediment cover, e. g. < 50 m on upper ridge flanks.
Deep stable holes, 2.5 - 3.0 km on continental margins.
Hole stability and core recovery in alternating lithologies, sulfides, coarse rubble and loose sand.
Hot holes.

(ii) Sampling and Measurements
Recover sediments, fluids and gases at in-situ temperature and pressure (Geoprops, WSTP, Pressure Core Sampler).
Measure in-situ pore pressures, temperature, pH, dissolved constituents.
Wireline sidewall corer.
Core ahead of the bit for sampling and measurement of undisturbed material.
Sample and measure volatiles.
Borehole seals (e. g. Leg 139)

Passive tracers in sealed holes (e. g. NaBr - Leg 137)
Hot holes: upgrade tools and samplers.
Geochemical logs, leading towards enhanced resolution.
Core logs, e. g. expanded MST.
Wireline sampler.

(iii) Long-term Experiments and Monitoring
Steady-state vs. episodic fluid flow (e. g. 504 B - Leg 137).
Temperature, pressure and strain gradients.
Temperature, pressure, chemistry and strain in sealed holes.

(iv) Top Priorities
Fluid sampling capability in indurated sediments and hard rock, for a wide range of in-situ temperatures.

Pressure core sampling capability, eg PCS Phase II with multiple sampling chambers, (see SGPP recommendations March, 1991).

6. STATUS OF GEOCHEMICAL OBJECTIVES OF THE BARBADOS DRILLING PROPOSAL

Item not discussed further; but was previously considered in detail under: Downhole measurements in accretionary complexes. During the third day of the meeting SGPP and DMP resumed their separate agendas.

7. STRATEGY, OBJECTIVES AND DESIGN FOR VERY DEEP DRILLING

(a) Somali Basin, Mike Coffin made presentation of earlier proposal for deep drilling in the Somali Basin that had been considered by SOHP.

Proposal 79 - N Somali Basin, minimum 1500 m sediments through Tethyan section.

Proposal 61 - W Somali Basin, minimum 1500 m sediments in 4500 m water depth through Tethyan section.

He reviewed the tectonic and paleoenvironmental objectives.

(b) Subduction zone drilling from land, Rob Zierenberg made presentation of proposals to drill from Middleton Island in the Aleutians, approx. 10 km down to subduction zone.

He reviewed metamorphic, diagenetic and fluid evolution objectives.

SGPP concensus, after discussion of deep drilling, is that for moderately deep drilling (1-2 km) the Somali Basin sites are typical of the sort of drilling we could support although they would not necessarily be of very high priorities. For still deeper drilling (ie 4-8 km holes), the panel is unlikely to lend any support at present to sites as those anticipated for Middleton Island or other deep subduction zone.

8. OPCOM BUDGET PRIORITIES

After extensive discussion of items, developments and potential purchases to spend the extra 2.1 M $, SGPP arrived at the following prioritization:

Priority 1: Develop capability for fluid sampling and measurement of *in-situ* fluid properties:

(a) for free-flowing water in hot rock (testing system)

(b) for pore water sampling/measurement (Pressure Core Sampler - phase II)

Priority 2: Develop capability for recovering unconsolidated sand/rubble without extensive loss or damage to cores.

And, of the TAMU list:

Priority 3: Use of alternative platforms for Sea level/Sediment Architecture objectives (eg. New Jersey transect, Coral Islands, Global Change Programs, etc).

Priority 4: Deep-Drilling for SGPP objectives (eg. Somali Basin)

Priority 5: Diamond Coring System

Priority 6: High-latitude support

Priority 7: ODP staffing costs

9. MISCELLANEOUS ITEMS

(a) Liaisons:

NARM-DGP (Aug. 11-12) Nickolas Christie-Blick

OHP (Oct 1-3) Dorrik Stow/Makoto Ito

TEDCOM (Sept 11-13) Jeffrey Alt

FLUID SAMPLING WG (Aug) (suggestions)

- P. Swart
- P. Froelich
- H. Elderfield
- S. Dreiss
- M. Kastner
- J. Kharaka

(b) Further report back from PCOM (Mark Langseth)

Strong competition for Cascadia co-chiefs, including SGPP proposal for M. Goldhaber. Review to be carried out of ODP operations by panels. Further extension of ODP by NSF looks promising. PCOM priorities for engineering developments given.

(c) Next Meetings

November 8 - 9, 1991 ZURICH (Judith McKenzie)

provisionally Feb/Mar, 1992 MIAMI (3 days) (Peter Swart)

September 1992, 2 or 3 days KIEL

(d) Membership

USSR member- SGPP suggestion of GALIMOV

USA rotation (replacements for Shirly Dreiss and Frederick Prahl)

- Judy McKenzie will sound out our suggestions before formally proposing.

(e) ICP-IV

International Conference on Paleoceanography (IV) in Kiel in September 21 - 25, 1992, could have joint meeting with OHP in Kiel then - idea received favorably.

Meeting closed at 12:55.

"Gas Hydrates and Ocean Drilling"

Organized and chaired by Keith Kvenvolden and Erwin Suess

INTRODUCTION

This workshop "Gas Hydrates and Ocean Drilling" was held in conjunction with the meeting of the Sedimentary and Geochemical Processes Panel (SGPP) at College Station, Texas, on March 5 - 6, 1991. In attendance were panel members and invited participants (Appendix A), totaling about 35 individuals. The purpose of the Workshop was to review the geological, physical-chemical, and geophysical aspects of gas hydrates in oceanic sediments in order to provide guidance to ODP for drilling, coring, and testing the gas hydrates that will be encountered on future ODP legs.

DISCUSSION TOPICS

The discussion centered around six main topics with selected speakers addressing each of the topics and goals as follows:

1. **Gas hydrates and the global methane budget.**
Purpose: discuss the role of gas hydrates in global change and define the place of ODP in the Global Change program.
Focus: stability and reservoir size of gas hydrates in sediments of the Arctic shelf and of outer continental margins.

2. **Physical-chemical characteristics of gas hydrates.**
Purpose: examine the fundamental properties of gas hydrates and consider the conditions leading to hydrogen sulfide hydrates occurring separately or syngenetically with methane hydrates in continental margins and/or sedimented ridge crests.
Focus: physical chemistry of gas hydrates; evidence for hydrogen sulfide gas hydrates on the Cascadia margin: safety measures needed by ODP to cope with hydrogen sulfide hydrates.

3. **Geophysical characteristics of gas hydrates.**
Purpose: consider the arguments of free gas vs. no free gas at the base of the gas hydrate zone and examine the assumptions for the system: sediment-water-free gas-gas hydrate in seismic models of bottom simulating reflectors.
Focus: percentages of pore space filled with gas hydrate; gas hydrate formation from "undersaturated" methane solutions; ODP safety standards with regard to drilling of gas hydrates.

4. **ODP Pressure Core Sampler.**
Purpose: examine the status of the PCS and particularly of the development for phase II to achieve scientific goals formulated by SGPP.
Focus: discuss capabilities for recovering sediment at *in situ* temperatures and pressures for analysis of gas hydrates, pore fluids and gases, and microbial activity; for preserving sediment structures, through-wall imaging of internal structures, fabric analyses, and physical properties measurements; for transfer of gases, fluids, and solids through pressure ports; and for calibration of well logs.

5. **Safety procedures for ocean drilling.**
Purpose: revise safety procedures for drilling gas hydrates
Focus: formulate recommendations for PPSP.

6. **Gas hydrate objectives of ODP for FY 1992.**
Purpose: re-examine objectives and sites of Leg 141 (Chile Triple Junction) and Leg 146 (Cascadia Margin) to emphasize gas hydrate objectives after elimination by PCOM of proposed gas hydrate leg offshore Peru.

Focus: discuss thermogenic vs. biogenic sources of methane and the role of fluid movement in active margin settings; consider other possible gas hydrate objectives for future drilling legs.

AGENDA AND SUMMARY OF PRESENTATIONS

March 5

8:30-9:00	Introductions (Suess, Kvenvolden)
9:00-10:00	Gas hydrates, carbon cycle (Kvenvolden, Brooks, Paul)
10:00-10:15	Break
10:15-12:15	Chemistry and physics of gas hydrates (Miller, Sloan, Boulegue, Claypool)
12:15-13:00	Lunch (ODP)
13:00-15:00	Geophysics, gas/no gas (von Huene, Hyndman)
15:00-15:15	Break
15:15-16:15	Pressure Core Sampler (Kvenvolden, Pettigrew, Dunlap)
16:15-17:30	Safety Considerations (Ball, Claypool, Katz)
17:30-20:00	Dinner
20:00-22:00	Informal discussions, Manor House Inn

March 6

8:30-10:30	Gas hyrate objectives of ODP (von Breymann, Lewis)
10:30-10:45	Break
10:45-12:30	Conclusions and Recommendations

A brief summary of each of the remarks follows:

Kvenvolden set the stage for considerations of the global importance of gas hydrates by pointing out that a lack of knowledge leads to the wide ranging speculation concerning the role of gas hydrates and the size of the methane hydrate reservoir. Decomposing gas hydrates may currently contribute 2 - 4 Mt/yr of methane carbon to the atmosphere. This contribution is minor compared to other known sources of atmospheric methane. However, increasing temperatures may increase the flux of methane from gas hydrates.

Brooks described gas hydrate which occur at subbottom depths of less than 6 m at water depths ranging from 400 to 2,400 m in the Gulf of Mexico. The methane in these gas hydrates was either from biogenic or thermogenic sources based on molecular and isotopic compositions. Seismic wipe-out zones, hummocky, and pockmarked surfaces are associated with the gas hydrate occurrences. Shallow biogenic gas hydrates were also observed in the Eel River Basin offshore northern California.

Paull discussed the methane record in ice cores for the past 20,000 years during which atmospheric methane concentrations changed from 320 ppbv to 600 ppbv at about 18,000 years ago. He suggested that this change might be related to gas hydrate decomposition caused by sea level lowering of 100 m at that time. The gas hydrates would destabilized from the bottom up with an estimated release of 1.8×10^{-4} Gt/km^2. Thus 1 Gt of methane would be released by each 5,600 km^2. Because the gas hydrate reservoir is so large, this released methane (a greenhouse gas) could affect global climate; the methane release could also cause sediment instability and submarine slumps.

Sloan presented an historical review of gas hydrates which were first discovered in the laboratory in the early 1800s. In gas hydrates, water molecules form a structural framework of cages that contain gas molecules. The size of the cages is fixed and can include only gas of specific molecular diameters. Two crystalline structures are possible. In Structure I the vertices of the cages are joined whereas in Structure II the faces of the cages are joined. Methane hydrates are Structure I, but with about 1% propane the geometry of the cages will shift to Structure II. Eight heuristics of gas hydrates led to nine applications: (1) Biogenic methane, carbon dioxide, and hydrogen sulfide form Structure I, but with propane form Structure II; (2) Structure II has greater stability field than Structure I; (3) Hydrogen sulfide hydrates are uniquely stable; (4) 1 m^3 hydrate contains 160-180 m^3 gas; (5) Thermogenic gas hydrates should have similar heat transfer properties; (6) Gas hydrates can exist with only one other phase; (7) In deep water drilling, hydrates can occur when water-based drilling fluids are used; (8) Hydrate crystal morphology dictates strength of structure; and (9) Metastability will exist only over short time scales (days).

Boulegue considered hydrogen sulfide and its role in the formation of hydrate. He had observed hydrogen sulfide on platinum and noticed that the ratio was similar to that found in fully saturated hydrogen sulfide hydrates. There was a concern that hydrogen sulfide hydrates would pose a problem for ODP. Discussion led to the conclusion that hydrogen sulfide hydrate formation or decomposition should not be a major problem but that hydrogen sulfide should be monitored during the drilling operation.

Claypool posed five questions of importance to gas hydrate drilling: (1) What are pressure-temperature conditions that control methane hydrate stability; (2) How much methane is necessary to stabilize the hydrates; (3) Is free gas present; (4) Can gas hydrate act as a seal to high pressure gas; and (5) What procedure should be used to estimates the drilling depth to the base of zone of gas hydrate stability. To answer these questions he proposed that a new equation ($P = \exp [46.74 - 10{,}748/T]$, where P is in kPa, and T is in K) be used to define the methane-water-hydrate system and that hydrostatic, not lithostatic, pressure be used. He concluded that gas hydrate formation requires 80 - 150 mM methane and that free gas at the base of gas hydrate cannot be at high pressure, i. e., cannot exceed hydrostatic pressure if water is present.

von Huene reviewed the geophysical results of gas hydrate occurrences observed on DSDP Leg 76 and 84 and on ODP Leg 112. He noted that a BSR is not always observed where gas hydrates are present. Reprocessing seismic records shows that what may first appear as a continuous seismic reflector may in fact be patchy in occurrence. Low amplitude BSRs may indicate absence of free gas. An increase of gas hydrates with depth will give rise to stronger reflections. Some gas is needed to get reflectivity. Synthetic seismograms showed 60% porosity and 10% gas hydrates. A three hole experiment, proposed for offshore Peru and rejected by PCOM, was suggested for offshore Chile in order to evaluate the relationship between the BSR and the occurrence of gas hydrate.

Hyndman discussed a model for gas hydrate formation in subduction zones where accreting sediments are expelling fluids upward. Upward fluid flow also occurs where there is rapid sediment loading. In this model the BSR represents a layer of gas hydrate formed through the sweeping upward of biogenic methane. The hydrate builds upward in the stability field, and the BSR occurs where fluid expulsion is high. This model contrasts with the conventional view of in situ gas hydrate formation. Both models have problems which were discussed. The new model was applied to the Cascadia Margin. Analyses of seismic data suggest that the gas hydrate occupies about 1/3 of the pore space and that the gas hydrate base is 5 to 50 m thick. There is little gas below the BSR. Conclusions reached were (1) no increase in BSR reflector strength over structural highs; (2) no flat spots at base of hydrate; (3) no reflections at base of gas layer; (4) no attenuation of underlying reflectors by gas; (5) velocity-depth shows increase through BSR; (6) AVO best fit indicates no free gas; and (7) gas hydrate permeability more like snow than ice.

Worthington reviewed the logging characteristics of gas hydrates. Logs used conjunctively can yield quantitative assessment of gas hydrates. A comparison was presented between various logging devices and the theoretical and measured responses to gas hydrates and gas and water. Results were shown for gas hydrates recovered from the NW Eileen State No. 2 well in Alaska and DSDP Site 570 offshore Guatemala. Information about gas hydrates from cross plots was demonstrated: (1) Density vs. Neutron porosity; (2) Sonic velocity vs. Neutron porosity; and (3) Density vs. Sonic velocity. A recommended logging program included the following: Temperature and pressure, Density and neutron activation; Sonic wave form, Gamma ray, Dual lateralog, Carbon and oxygen (geochemical log), Caliper log, and Spherically focussed log.

Pettigrew After an historical review of the Pressure Core Barrel by Kvenvolden and a review of guidelines for the Pressure Core Sampler, Pettigrew described the current status of the Pressure Core Sampler, which is 42 ft. long, has a 6 ft. pressurized section, and 2 fluid sampling ports. The core is recovered at near *in situ* pressure and bottom hole pressure is trapped. the Pressure Core Sampler has been tested five times, three times on Leg 124 and twice on Leg 131 with various degrees of success. Questions were raised concerning temperature control, fluid transfer, and contamination by drilling fluid. A calculation was made showing that the maximum pressure that could result from a trapped gas hydrate would be about 3,000 psi which is well within the 5,000 psi design range of the tool.

Dunlap described the Texas A & M pressure sampling system that was designed and used several years ago. This device was deployed in shallow water and was opened in a hyperbaric chamber where engineering properties of the sediment were measured, and samples were taken for gas analyses. There is a concern about gas hydrates affecting the foundations for oil-well platforms in deep water. A system is being designed to push a probe ahead of the drill to measure properties related to gas hydrates, such as shear strength, pore pressure, resisitivity, thermal conductivity, sediment density, and temperature. A core penetrometer is being considered to determine type of sediment and pore-water pressure. A device is also being constructed to make gas hydrates in the laboratory to measure physical properties.

Ball reiterated the concerns of the PPSP and indicated that this panel would consider proposals, on a site by site basis, that request to drill through the BSR. Guidance from this workshop will be useful.

von Breymann reviewed ODP objectives in gas hydrate drilling. The next ODP legs with gas hydrates are 141 (Chile Triple Junction) and 146 (Cascadia Margin). It is important to look at question of gas hydrates when designing a leg proposal. Legs may be readjusted to answer gas hydrate questions. The possibility of thermogenic hydrocarbons must be considered. Phase I development of Pressure Core Sampler requires an operational tool that at a minimum can recover gases and liquids. A gas manifold needs a lead person to interface with ODP. Logging of gas hydrate occurrences is essential Model testing of gas hydrates needs at least shorebased interest. The following measurements are important for gas hydrate research: (1) composition and quantity of gas, (2) presence and absence of free gas, (3) porosity/velocity calibrations, (4) amount of gas hydrate as percent of porosity, (5) permeability of gas hydrate layer, (6) concentration of methane above and below BSR, and (7) source of methane and other gases - local source vs. migration.

Lewis discussed the scientific rational and objectives of ODP Leg 141 (offshore Chile). This leg involves a ridge crest environment with a complex migrating triple junction and ridge crest subduction. Of interest in gas hydrate research is Line 745 where three holes will be drilled. Along this line the BSR is quasi-continuous and two holes will penetrate the BSR if approved. In addition, one hole will be drilled near the toe of the slope on Line 750, and one hole will penetrate the region of the triple junction on Line 751.

Hyndman review briefly the Cascadia Margin drilling for Leg 146 to define fluid expulsion and physical properties. Sites will be drilled offshore Vancouver to test diffuse fluid flow and offshore Oregon to test focused fluid flow. One fourth of the leg will be devoted to gas hydrates. The gas hydrate objectives are: (1) calibration of BSR pressure-temperature conditions; (2) measurement of velocity, porosity, permeability and estimates of heat flow; (3) calibrate seismic data interpretation; (4) test gas hydrate formation model; and (5) evaluate diagenetic associations of gas hydrates.

RECOMMENDATIONS

From the above presentations and the accompanying discussion, the following conclusions and recommendations were made. There was a general consensus that gas hydrates are an important research topic in ocean drilling. Even though more than 20 years has passed since gas hydrates were first recognized as naturally occurring substance, much remains to be learned about these intriguing materials. ODP provides an important platform for the study of gas hydrates occurring in oceanic sediments. Current drilling practices of ODP are capable of recovering partially decomposed samples of gas hydrate. To make the study of gas hydrates quantitative, there is an immediate need for use of a functional Pressure Core Sampler which is capable of recovering gas and liquids at *in situ* pressures. Such a device will provide not only information about gas hydrates but also about the composition and concentration of fluids within and below the zone of gas hydrate stability. In order to gain new knowledge about gas hydrates, the following specific recommendations are made by SGPP:

Predictive equation for depth of gas hydrate stability field.
The temperature and pressure regime below the seafloor determines the stability field of pure methane and mixed gas hydrates. The SGPP concurs with the recommendations by the workshop participants that an analytical equation be tested and substituted for the graphic method, used unchanged since the days of DSDP, and that a software package, allowing numerical solutions for any environment of gas hydrate stabilities, be developed for use aboard the JODES Resolution to improve safety measures.

Pressure Core Sampler:

1. **Manifold for extracting free and hydrated gases**

A gas sampling manifold is required to obtain the contents and composition of free and hydrate gases. The existing manifold assembly of the PCS tool appears to be inadequate, due to large internal dead volumes, to conduct the necessary experiments with gas hydrate contained inside the pressure chamber. The SGPP concurs with the recommendation of the workshop participants that a previous successful gas sampling manifold (Kvenvolden, USGS Menlo Park) and a new but untested design (Whelan, Woods Hole Oceanographic Institution) be perfected by ODP with input from both of these scientists as well as future shipboard geochemists.

2. **"Harpoon" for extracting pore waters.**

For shipboard analyses of the pressurized samples obtained by the PCS system, the "harpoon" is presently the most suitable attachment for subsampling fluids. It utilizes the internal pressure of the sample chamber to self-squeeze pore waters from the center of the core thereby eliminating possible contamination by drilling fluid. SGPP concurs with the recommendations of the workshop participants that design, construction, and operation of the harpoon be completed with input from the shipboard geochemists of Legs 141 and 146.

3. **Exchangeable pressure chamber.**

The pressure core sampler under development by ODP is a coring system capable of retrieving samples at bottom hole pressure, and hence is the key tool for pursuing several major objectives of SGPP, notably the behavior of fluids, gases, and gas hydrates in accretionary prisms. The SGPP considers that successful completion of these objectives requires three exchangeable pressure core subassemblies and recommends that these be available for the upcoming Legs 141 and 146. These assemblies should be used on a rotating basis with one chamber attached to the PCS system during sampling, while the contents of the second one are subsampled and analyzed aboard ship and the third one is being readied for a new deployment. This approach allows a complete downhole profile, as opposed to a single measurement per hole. It provides adequate turn-around time for close sample spacing downhole, eliminates the costly construction of an as-yet unavailable transfer chamber, and ensures back-up in case of damage. If trace metal concentrations are of high priority, the multiple subassemblies should be made of titanium; if gases, dissolved metabolites, or major sea water ions are to be measured, the less costly stainless steel version is adequate.

Gas hydrate leg.
Understanding the interaction of natural gas hydrates with the thermal and fluid regime of continental margins and in particular accretionary complexes, is the highest scientific priority of the SGPP. Likewise, the presence of gas hydrates has uniquely influenced safety deliberations by the PPSP in drilling deep margin holes. Hence, the participants of this workshop recommend that a dedicated gas hydrate leg be planned and drilled similar to the one previously proposed for the Peru Margin (355A). The SGPP and the PPSP, outside proponents and investigators should design such a leg with drilling opportunities in the Atlantic or the Pacific Oceans.