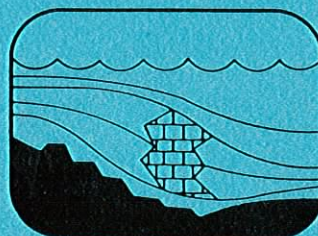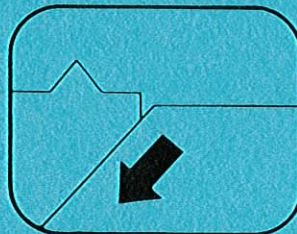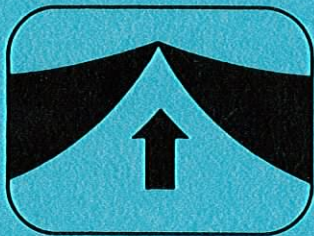# GEOCHEMISTRY
PROGRESS AND OPPORTUNITIES

PROCEEDING OF A JOI-USSAC WORKSHOP

LAKE ARROWHEAD
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GEOCHEMISTRY PROGRESS AND OPPORTUNITIES
WORKSHOP

EXECUTIVE SUMMARY

Miriam Kastner and Garrett W. Brass

This is the report of the Geochemistry Progress and Opportunities Workshop. During the workshop we indicated that we would attempt to write a comprehensive report of the workshop recommendations by condensing the reports of the five working groups. Once the final versions of these reports began to arrive, however, it became clear to us that condensing them into a single narrative would sacrifice valuable ideas and recommendations and would weaken both the emphasis placed on particular problems by the individual working groups or the relationships between topics which were very different for different working groups. As a consequence, we are pleased to present here the reports as presented to us after revision by the working group participants.

There are several common themes in the reports of the working groups which we wish to call to the reader's attention in order to make their importance more apparent. Some of these themes are common to nearly all the working groups, some to only a few. Nevertheless, they appear to us to be the topics of central importance for planning the future of geochemical studies in the Ocean Drilling Program. It is these topical recommendations which we wish to present to the hard working multitude planning the future of the Ocean Drilling Program and to those vital and often unsung scientists who write the proposals which provide the essential creative drive for the program.

I.   ALTERATION OF THE CRUST AT HIGH TEMPERATURES

The alteration of the oceanic crust at high temperatures was an important focus for most of the working groups. The processes by which seawater enters the crust, alters and is altered by reaction with hot crustal rocks and returns to the sea is known from surface studies and by analogy with hydrothermal systems in continental settings which can be studied in outcrop, but we still know very little about the actual process going on at ridge crests below the surface. The depth to which fluids penetrate is unknown as are the exchange reactions between seawater and upper oceanic crust. This process is clearly important both for its ability to control the composition of many elements and isotopes in sea water and for its ability to transfer material into the crust where it is eventually involved in the subduction process and in equilibration with the upper mantle.

Not all of these hydrothermal systems are exposed on naked crust, many are buried by substantial bodies of sediment. These environments present different paths for alteration products and bring new materials and physical-chemical environments into the process. The formation of sediment hosted mineral deposits and transformations of organic matter in these

systems suggest an importance in studies of resource development. As these systems reach their high temperature limits they enter the realm of metamorphic reactions and provide an opportunity to bridge the gap between laboratory experiments and field studies on outcrops long since returned to room temperature and surface pressures.

II. ALTERATION OF THE CRUST AT LOW TEMPERATURES

In parallel with high temperature alteration, there is a continuing process of alteration of the oceanic crust at low temperatures by reaction with seawater and sediment pore waters. This process is slower but continues over vast regions of the ocean floor, long after the initial heat of intrusion has been dissipated by the crust. In addition, slow alteration generally goes on through an intermediate layer of sediment of variable composition and generally increasing thickness with age which may also interact with the migrating fluids. The effects of this process particularly the magnitude of mass transfers to and from the crust over time are unknown. Our only opportunity to look deep in the oceanic crust is in ophiolites and there is no way to know whether these rocks were young or old when they were uplifted onto the continents or even the degree to which the uplift process itself has altered them. Since the same subduction processes discussed above promote the equilibration of these alteration products with the mantle, the mass transports are, once again, of vital importance.

III. PROCESSES AT CONVERGENT MARGINS

As the previous discussion has demonstrated, understanding the subduction process is important in view of its critical role in supplying material to the mantle. Other aspects of the subduction process are similarly important. The continuing supply of materials to the subduction zone and their partitioning between subducted, accreted and subcreted material leads to the formation of tectonically and geochemically important and poorly understood accretionary complexes. Fracture systems channel fluid flow. Compactive de watering and dehydration reactions expel fluids into the sea. Rising temperature and pressure lead to reactions between fluids and their surroundings. Energy sources are exploited by organisms both on the sea floor and, perhaps, at depth in the sediment. Deep in the accumulating sedimentary complex, reactions reach metamorphic conditions. Fluid movements and chemical reactions lead to changes in physical properties which, in turn, affect deformation. All of these processes transfer material between crust, sediment and seawater with attendant implications for marine and atmospheric chemistry and benthic biology.

IV. PASSIVE MARGIN PROCESSES

Many of the geochemical processes operating in the subduction zone environment are also important in passive margins. In particular, fluids continue to move in passive margin systems with their accompanying mass transports and reactions with sediments and crust. Material within passive margins is heated and compressed by continuing sediment loading and subsidence without the dynamic, compressive processes of the subduction zone. But we expect that in the long run, passive margins are in danger of becoming active either directly through the formation

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of subduction zones beneath them or through collision with other, active, margins. The material stored in passive margins may remain out of active geochemical cycling for many millions of years only to be released in a very rapid pulse during activation of the margin. These inventories and the processes of collisional rejuvenation are still poorly known but are vital to our understanding of the continuing operation of the geochemical cycles of the oceanic system.

V.   CARBON FLUXES RESERVOIRS AND PROCESSES

The preceding connecting themes have focussed on general geological processes; processes which transport and alter materials in ways significant to the chemistry of the ocean. This theme, common to much of the discussion which follows, focusses on a single element, carbon. Carbon plays a unique role in the discussions of the working groups. Chemically, carbon occupies two oxidation states in the geochemical scheme of things and the proportions of and transfers between these forms are sensitive indicators of chemical states and are tied to similar changes in the oxygen, iron and sulfur systems. In addition, the marine geochemistry of carbon is inextricably linked to the chemistry of the atmosphere through the abundances of both oxygen and carbon dioxide and through them to the thermal state of the Earth's surficial environment.

Carbon is, in addition, the fundamental element of living systems. Both the isotopic and molecular composition of carbon contain information on the conditions of living systems in the past which are unobtainable from any other source. The production and consumption of fixed carbon is not limited to the hydrosphere; bacterial activity in sediments and in hydrothermal systems may carry on in conditions not yet explored. Finally, fixed carbon, stored in the earth, is the source of fossil fuels.

The inventory of carbon in its various forms and environments remains incomplete. Our understanding of the processes by which carbon is transformed in the geological environment is still partial and we know very little about important fluxes of carbon between the surface environments in which we live and the geochemical reservoirs in which most of the worlds carbon is stored.

These five themes represent only those common interests of the working groups which form the most significant links among them. Many other important questions are raised here, questions as important as the major themes but more specific in their focus.

The identification of important geochemical themes and questions was not the only goal of the workshop. In the report you will find a wealth of specific recommendations for drilling strategies, downhole measurements, exploitation of holes after drilling and new sample collection and analysis techniques. While these are too abundant to list, some of the highlights include the following:

I.   DEEP DRILLING INTO THE OCEANIC CRUST

Deep penetration into the oceanic crust and even into the top of the mantle is essential for the understanding of the depth of penetration and the magnitude of the mass transfers in crustal alteration processes. In particular the problem of exploring the depth of high temperature alteration of young crust might be addressed by the exploitation of offset sections where tectonic activity has exposed deep sections of the crust and even upper mantle to the drill. The extent of alteration of old crust by continued, slow, low-temperature alteration will eventually require a deep (ca. 5 km) hole into old crust; a hole which may be beyond our present capabilities.

II. DEEP DRILLING INTO SUBDUCTION ZONES AND PASSIVE MARGINS

Deep penetration in these regions requires drilling into regions where sediment accumulations are thick and well control problems may be encountered. Nevertheless, in the future we must explore these important regions by drilling in order to sample sediments and fluids and to make measurements in situ, measurements which can not be made in any other way.

III. INSTRUMENTATION OF HOLES AND INSTRUMENT DEVELOPMENT

The exploitation of drill holes depends upon both the development of drilling capabilities and the continued improvement of our ability to make measurements and collect samples in drillholes. The wireline logging capabilities of the current program produce an outstanding data set. Improvements continue in these tools as new developments arise and new tools are brought on line. Independently developed "third party" tools have made substantial contributions and new developments in downhole measurements of such parameters as physical properties, gravity and magnetism, and state of stress will expand our horizons. Specific recommendations to improve our abilities to sample formation fluids and to bring sample back to the ship at in situ pressures are in the working group recommendations.

There are many other recommendations in the working group reports which follow. All represent collective consideration by the working groups and are thus made by an experienced and highly capable group of experts. All appear practical. Most only await the necessary support of a successful proposal.

The conveners of the Opportunities in Geochemistry workshop have enjoyed the energetic and helpful collaboration of our colleagues. Everyone at Lake Arrowhead made a special effort to forward the goals of the workshop. New and exciting ideas swarmed through the meeting rooms and into the dining rooms and dorms. We wish to thank all of the participants for their contributions. We are especially grateful to the working group leaders: Mike Arthur, Flip Froelich, Bill Hay, Barry Katz, Jim Natland and Paul Worthington who worked on, long after the meetings were over, to see that the reports of the working groups were the true expression of the creative energy of their colleagues. Our most grateful thanks go to Allison Burns who carried much of the administrative burden of the workshop and made sure that all of us got there and then got home again. Finally we wish to express our gratitude to JOI and USSAC for supporting this effort. Their money has been well spent and the Ocean Drilling Program will be strongly affected by the new ideas in these reports.

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BASEMENT CRUSTAL ALTERATION

I.   INTRODUCTION

Charge to Working Group: The working group viewed the problem of basement alteration as reflecting all compositional change imparted by fluids. This encompasses two main themes: 1) high-temperature processes associated with magma injection at ridge crests, and 2) subsequent lower-temperature interactions in older crust. Alteration may occur until final consumption of the crust at convergent margins. We consequently catalogued our consideration of alteration effects under two environments: high-temperature ridge-crests, and lower-temperature ridge-flanks.

We took high-temperature alteration processes to include injection of magma into ocean crust and the subsequent - or even simultaneous - circulation of hydrothermal fluids. Early interaction of hydrothermal fluids and rock at temperatures $\geq$ 500°C may influence substantially the material which is subsequently altered by low-temperature fluids during the remainder of the active period of crust/fluid interaction. In addition, there may be a feedback of alteration on magma composition by the introduction of altered crust and/or aqueous fluids into magma chambers. Depending on the volumetric extent of high-temperature alteration and its possible isolation from low-temperature interactions, deep hydrothermal processes may dictate the composition of the crust which is eventually subducted into the upper mantle.

In part, our perception that low-temperature alteration may be crucial in crustal and oceanic mass balances is based on thermal considerations. These data document that perhaps 80% of basement heat flow occurs distal to the ridge crest (e.g., Sclater et al., 1971). This observation raises major questions regarding potential coupling of the heat loss with crustal fluid-rock reaction and alteration.

The need to document the extent of low-temperature crustal alteration is in turn driven by its potentially critical importance in controlling sea-water chemistry. For example, potassium is known to be enriched in some basement rocks as a result of low-temperature alteration processes (e.g. Hart, 1976; Donnelly et al., 1980), and thus present basement alteration represents a potential potassium sink from the ocean reservoir. This, however, contrasts with the observed potassium source related to high-temperature export from active ridges (Von Damm et al., 1985). We lack adequate estimates for the magnitude of the low-temperature flux for potassium and a suite of other elements which are affected to a greater or lesser degree.

Viewed from the perspective of the altering crust, the imparted chemical modification can affect overall crustal composition to an unknown but once again potentially significant degree. Because altered ocean crust is an important component of volcanism at convergent margins, understanding the extent of this crustal alteration is a first-order problem in crustal cycling.

II.   HIGH-TEMPERATURE INTERACTIONS

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We considered two types of interactions at high temperature in the ocean crust: those processes occurring in the vicinity of magma bodies at spreading ridges, and those associated with high-temperature sub-solidus recrystallization of gabbroic rock.

A. Governing Processes. Venting of hydrothermal fluids which precipitate sulfides, iron-rich clay minerals, or Fe-Mn oxyhydroxides upon cooling and mixing with sea water in every case implies interactions between heated sea water drawn into the crust, and rock materials or magmas somewhere at depth. Sampling of the deep reaction zones and other portions of the fluid flow regime in the crust is the obvious complement to sampling the venting fluids and hydrothermal precipitates on the sea floor.

Following from these processes, cooling of the crust is accomplished by drawing heat from the hot but now consolidated rock making up the gabbroic layer - first by convection, then by conductive processes. Hydrous fluids may be introduced into the rocks immediately surrounding magma bodies (possibly into the magmas themselves), and into the eventual solid body of gabbro crystallized from those magmas at various stages in this sequence. This may be abetted by structural modification of the ocean crust.

An important consideration is the strong contrast in intensity and spatial/temporal continuity of hydrothermal venting between normal segments of slow- and fast-spreading ridges. The systems so far examined at the East Pacific Rise are clearly far more vigorous and pervasive than those along the Mid-Atlantic Ridge; the few examples we have of cored basalt from Mesozoic Pacific crust suggest that this vigor persists to the point of final addition of extrusives at the top of the crust. This produces a characteristic style of alteration and mineral veining only feebly manifested in drilled basalts form the flank of the Mid-Atlantic Ridge (Duennebier, Gettrust et al, 1986; Menard, Natland, Jordan, Orcutt et al., 1986). But we have no long sections of altered rock from fast-spread crust that are at all comparable to penetrations at several sites in the North Atlantic.

A very real possibility is that very shallow fractured rock becomes impregnated with magmas at levels well above what is perceived seismically as the magma-chamber reflector at the East Pacific Rise (e.g.Detrick et al., 1987). Not all of these magmas will recede back down to such depths, but they will remain at shallow levels in the crust until they crystallize, are forced to the sea floor by later injection of magmas, or mix with those magmas. The isolated magmas thus have an opportunity to interact directly with circulating fluids or altered crustal rocks in the very shallow crustal lid over the magma chamber.

The role of circulating fluids in the cooling and chemical modification of the bulk of the ocean crust - the gabbroic layer - is virtually unknown, and is likely to be quite different at fast and slowly-spreading ridges. Evidence from Hole 735B on the slowly-spreading Southwest Indian Ridge indicates that fluids entered deforming gabbroic rocks either during or just following their final crystallization, while a complex tectonic process of unroofing and initial uplift from a rift-valley setting to a shallow location on a transverse ridge was taking place (Robinson, Von Herzen et al, 1989; Dick et al, in press). The fluids were taken up primarily by amphiboles at

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water flow at topographic highs, or outcrops generally, but it also has a primary influence on the duration of exchange between the crust and the oceans. For much of the ocean basin, the exchange of mass and heat by flow continues so long as outcrops persist. When sedimentary cover becomes complete, burying even basement highs, direct exchange between the oceans and the crust becomes greatly restricted or halts completely. Control of the advective transfer of mass and heat is thus largely a function of topographic relief and sedimentation rate.

Flow in the crust moves through fractures. Consequently, the depth and density of fracturing is a third fundamental parameter in the control of the extent of crustal alteration as well as the temperature regimes of circulating cells. While there is relatively little detailed information on factors controlling fracturing, a general belief is that spreading rate does exert a crude influence on this critical parameter. As a result, there may be large differences between fast and slow-spreading ridges in regards to extent of exchange and alteration, depth of reaction, and potentially temperature regime.

Quantifying exchange of crustal material with the oceans and the mantle as a result of alteration must include an assessment of the influence of these parameters on the exchange of material occurring in the interval between formation and subduction of the crust. The selection of drill sites through which we seek to define an integrated value of crustal alteration is predicated upon evaluating the roles of topography, sediment cover, and spreading rate.

B.   Drilling Strategy. Our drilling strategy is predicated on the first-order differences in structure observed in the two most typical types of ocean crust, namely, rifted slowly spreading ridges, and non-rifted fast-spreading ridges (MAR-type and EPR-type). On the flanks of slowly-spreading ridges, the principal structural entities are ridges and basins of fairly large lateral dimensions (kilometers to tens of kilometers). On the flanks of the East Pacific Rise, the principal structural unit is the abyssal hill, considered from deep-tow studies to be fault bounded (Larson, 1971; Luyendyk, 1968). Abyssal hills are rarely more than a kilometer in width, and have relief of 100 m, usually less. At comparable sedimentation rates, topography on the flank of the East Pacific Rise will become completely buried much more quickly than on the Mid-Atlantic Ridge, thus sealing the crust sooner from the influence of sea water. Obviously, important differences in sedimentation rate within both the Atlantic and Pacific basins need to be considered.

The rationale for a drilling program which takes into account differences in the two types of ridges (defined by contrasts in topography and fracture density induced by structure), must be designed by utilizing the three input parameters than can be derived from survey information to define hydrologic regimes. These are: 1) sedimentation rate (fast or slow); 2) crustal age (young or old); and 3) heat flow (variably high and low, confirming that convective processes are active, or uniform and low, establishing that conductive processes in the sediment and uppermost crust, are in force).

In general, we wish to determine the consequences of alteration in the several settings, and under the various conditions, indicated by arrows in the upper part of the diagram. The consequences

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include the integrated extent of alteration, and its thermal history as determined from mineral stabilities and sequences of veining/alteration observed in the rocks. To approximate either local or global mass balances, it is important to establish alteration profiles in basement at various settings, and their relationship to porosity structure and crustal chemistry. Overall, we imagine that holes of 300-500 m depth are a minimum requirement to document alteration-induced changes in porosity structure at any location.

Drilling transects for MAR-type and EPR-type crust run from comparatively young, poorly sedimented regions, to buried topography on older crust. For the MAR-type, the real proportion of exposed basement diminishes to the west, on a transect between Sites 395 and 417/418, already drilled. Sedimented areas range from small sediment ponds to smoothly sedimented, almost buried crustal ridges. We suggest clusters of holes at four generic locations, to sample the crust at thickly and thinly sedimented targets, and at a bare-rock location on an exposed ridge. We anticipate that the specific hydrologic regime will be documented at each location by pre-drilling surveys which include seismic reflection profiling, heat-flow measurements, and sediment sampling, to determine the surface expression of pore-fluid gradients.

For fast-spread crust, formally on the flank of the East Pacific Rise, we have selected the equatorial sediment prism as one place likely to provide information about the influence of sediment distribution on the hydrologic regime and alteration. An important observation is that even accumulations of sediment several hundred meters thick over large areas have not completely sealed the crust hydrologically (Baker and Kastner, ms). Whether this is the case for the entire equatorial region has not yet been established. However, marine pelagic sedimentation rates north and south of the equatorial sediment prism are much lower still, such that sediment accumulations even on Paleogene crust are very thin. Certainly there must be important contrasts in the hydrological regime both east-to-west, and north-to-south, across the equatorial sediment prism. This is the principal, very large-scale, hydrological regime in the eastern Pacific, and it may one that dominates exchanges between seawater and the ocean crust within the ocean basins.

Therefore we propose three transects: 1) a series of holes on a crustal isochron from a thinly sedimented region on the south to the thickest part of the sediments; 2) a series of holes on successively older crust, but on an isopach of significant sediment thickness (200 m?); and 3) a series of holes parallel to the latter, but in a thinly-sedimented region of the crust, where there are significant basement exposures on the abyssal-hill scale at all locations.

To parallel the North Atlantic transect, a contrast between hydrologically sealed and unsealed crust should also be established for the East Pacific Rise. Since sealed crust evidently is not present in the eastern equatorial Pacific, this may require establishing the hydrological contrasts between Mesozoic and much younger crust in the Pacific.

We emphasize that this is a generic program only, one designed to control as many input parameters as possible in defining the differences between hydrologic regimes of MAR and EPR types of crust. The specific drilling program eventually proposed will have to consider detailed

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information in input parameters before sites are selected.

IV. PRIORITIES

We prioritize the programs outlined for high-temperature and low-temperature processes separately, not having the wherewithal to compare apples and oranges. Priorities are given in descending order alphabetically. Programs given equal weight have the same alphabetical designation, but are separately numbered.

1. High-temperature Processes
   a. Fluid interactions with gabbroic crust (Layer 2 - Layer 3 transition).
   b. Drilling of the reaction-zone region of the ocean crust at a   spreading-ridge axis.
   c. Drilling of the vertical fluid-transfer region beneath an active or fossil vent field.

2. Low-temperature Processes.
   a-1. The north-trending isochron transect across the equatorial sediment bulge, eastern Pacific.
   a-2. Contrasts between Mesozoic (sealed) and younger (unsealed) crust produced at fast-spreading ridges.
   b-1. The isopach transect on the equatorial sediment bulge.
   b-2. The entire transect of MAR-type crust.
   c. The northerly transect on the thinly-sedimented EPR (here shown as linked to scheduled zero-age drilling at the EPR crest).

V. MEASUREMENTS

A. Chemical and Isotopic Measurements. We have known for some time that altered basement basalt is strikingly different in chemical, mineralogic, and isotopic characteristics from fresh rock. The major focus of the drilling recommended here is to understand the origin of these differences and to show how these differences contribute to large problems.

Previous studies have concentrated on bulk chemistry (both major and trace elements), mineralogy, and - to a lesser extent - on the oxygen and strontium isotopic characteristics of altered crust. Clearly, these studies must be continued and extended. As knowledge of alteration increases, some new measurements and new applications of existing measurements will be called for. Existing measurements which will have a high priority thus include bulk chemistry (to define lithic contrast) and mineral compositions.

Probably the substance of greatest single interest is bound water. Carbon dioxide and the oxidation state are of high and parallel interest. Elements of special interest which are thought to be added during low-temperature alteration include K, Rb, Cs, Li, and Ba. Although in general bulk additions of these elements are indisputable, there are documented local depletions

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and the total budgets of all of these elements need to be evaluated carefully. Most of these last-named elements are of interest to igneous petrologists attempting to evaluate their significance in the generation of island-arc calc-alkalic magmas above subducted slabs of ocean crust, and the results of these investigations will be of interest to this audience.

There are several other elements of interest. Sr is of uncertain distribution in altered crust and should be carefully evaluated. There are documented instances of supposedly refractory elements which have apparently been mobilized during very low-temperature alteration, and these need to be evaluated. Of these, Y and the rare-earths are of special interest, and Zr and Ti have been noted. The element Mg is of special interest both because of its large original abundance and because there are instances both of loss and of gain in altered crust. It is fair to say that our knowledge of the total behavior of all the elements during alteration and mass exchange with the oceans is inadequate.

Many of the above elements and some others can be logged by the GLT, thus accurate measurements on rock and sediment samples will be needed for the calibration of this tool. Furthermore, fairly precise mineralogical information will be needed to model the logging data.

The time-sequence and duration of alteration are of central interest. Presently, our consensus is that alteration is dominantly a very young phenomenon (occurring mainly at or near ridge crests), and that it slows drastically when sediment cover impedes free access to sea water. However, oxygen isotopic studies suggest that alteration may continue for a much longer time. There are potential isotopic studies which have the potential capability of providing needed information on the timing of alteration. Because alteration generally involves the fixation of potassium, an effort should be made to extend the present Argon 39-40 techniques to find the relative, and possibly absolute, ages of formation of several of these minerals, including K-feldspar, celadonite, and several zeolite minerals.

The sequence of alteration and its implications for chemical evolution of altering fluids needs to be investigated. Sequences of discrete veins, as well as zonation in single veins, and even in single vein minerals, needs to be undertaken. The cathodoluminiscence method on calcites might provide an important microstratigraphy of changing fluid compositions.

An approach of high priority is the study of strontium isotopes, concentrating on the sequential formation of minerals. This isotopic ratio promises to yield information of the relative contributions of crustal and seawater strontium, and also potentially on the age of the seawater.

Oxygen isotopic measurements that have proven useful in previous studies need to be extended and expanded. Mineral pairs might be especially useful, if they can be shown petrographically to be coeval. The combination of the ubiquitous calcite with quartz or other oxides might yield more firmly established temperatures of alteration.

The fluids themselves remain enigmatic, and are a major goal of this project. Fluid inclusion studies, both of quartz in veins and possibly other minerals, may place constraints on filling

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temperatures and fluid compositions.

There are additional isotopic ratios that have not yet been applied to ocean-crust alteration but which should be attempted. Sulfur isotopic studies are well established, although in different geological environments. There are very minor sulfates in altered crust, but pyrite is widespread and might yield useful information. Relatively newly-developed isotopes of interest include boron and lithium, both of which are important in the low-temperature alteration process. The alteration of crust should be a challenge of prime interest to those developing these techniques.

All of these measurements will require careful sampling strategies, which will vary according to the particular study. Because many of these studies require carefully selected materials, shipboard XRF and XRD capabilities will be heavily used during the description and sampling of the core. Attention should be given to the potential use of a plasma analytical device on board ship to analyze very small samples during this process.

B.   Physical Measurements. The standard logging package (especially porosity and velocity, but also caliper and gamma) will be an essential part of this project. Because the physical properties of altered are of such importance, consideration should be given to post-drilling surveys, such as the oblique seismic experiment, to characterize the velocity-structure of the upper part of the crust. Additionally, we need to know the large-scale extent of lateral heterogeneity of alteration, and will have to develop geophysical (probably seismic) methods to determine this.

VI.   SITE SELECTION GEOPHYSICS

The selection of sites will require a good knowledge of basement topography prior to drilling (high-resolution bathymetry - SeaBeam, SeaMarc, Hydrosweep). This, combined with high-grade profiling, will be the single most important survey requirement. Especially in the Atlantic, the buried topography may be single most important criterion for siting holes.

In several areas, especially in Neogene crust, the knowledge of local heat flow should be obtained, and the hydrological regime modeled. Drilling should be attempted with reference to well-defined topographic highs and lows in an area. Unless the distribution of heat-flow is ephemeral, these highs and lows should correspond to differing regimes of flow within the crust beneath the sediment; thus contrasts in alteration may be found.

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GEOCHEMICAL IMPACT OF FLUID CIRCULATION

I.   STATEMENT OF THE SCIENTIFIC PROBLEM

Large-scale fluid circulation through the earth's crust is now recognized as a pervasive chemical transport process whose length- and time-scales dwarf those of chemical diffusion (Figure 1). The rates of fluid migration, compositions of the fluids themselves, and chemical-rock reactions along flow paths control many important geological and geochemical processes (Torgersen, 1990). However, the long-term cumulative impact of fluid flow through the oceanic crust and its sediments are poorly understood form observations of only the integrated geochemistry of solid phases remaining after flow ceases. Only Ocean Drilling into areas of active fluid migration on the seafloor can discover the scales and magnitude of fluid transport and provide samples of the *in situ* fluids to address fundamental geochemical problems. The as-yet unquantified geochemical fluxes associated with these fluid transports are thought to be important factors in global processes which control crustal, atmospheric, and oceanic chemistry (COSOD II).

We summarize here important scientific questions, illustrate where drilling into the sea-floor is likely to encounter active fluid interactions, and identify technological problems that must be overcome to better understand the global impact of fluid transport.

A.   What are the sources, flow rates, pathways, and mechanisms of fluid circulation through the upper crust and overlying sediments? This knowledge is critical to obtain an understanding of the global impact of fluid migration on diagenetic processes, the time and space scales on which interactions between fluids and their host rocks/sediments occur, and the ultimate fate of fluids and their solutes -- whether expelled to the overlying ocean, recirculated wholly within closed cells below the seafloor, or subducted and ultimately recycled into the upper mantle.

B.   What are the compositions of circulating fluids under *in situ* conditions? Fluids recovered from formations not at earth surface conditions of pressure, temperature, or oxidation state, are commonly contaminated or disturbed upon recovery. To reconstruct the reaction pathways and their thermodynamic and kinetic controls, it is necessary to measure or recover fluids with their *in situ* characteristics intact, or at the very least, to be able to reconstruct these primary compositions from empirical knowledge of changes occurring during recovery.

C.   By what processes (and reactions) is fluid flow responsible for (1) metal deposits (metallogenesis); (2) hydrocarbon migration (transport from source rocks to reservoir traps); (3) carbonate cementation (lithification) and dolomitization; (4) metamorphic reactions (deep burial of sediments); and (5) tectonic behavior of the rocks (fracturing, faulting)?

D.   How significant for global geochemical balances are the fluxes associated with fluid flow, and what is the impact on processes at the earth's surface that are linked to cycling of elements through the earth's atmosphere-biosphere-geosphere system, to hydration of the oceanic crust, and ultimately to the cycling of volatiles between the lithosphere and asthenosphere?

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II. NEW FRONTIERS

A. Overview. In the last decade, geochemical assessments of regional-scale rock metamorphism, ore emplacement, and heat loss form the oceanic crust have reinforced the view that large scale fluid mass transport through the crust is required to explain the large inferred water/rock ratios required for chemical-rock reactions (Taylor, 1988; Norton and Taylor, 1979; Etheridge et al., 1983; Walther and Wood, 1986; Wolery and Sleep, 1976; Mottl, 1983). Other studies have implied the existence of pervasive "open-system" fluid flow (Bethke, 1988; Kesler, 1988; Nesbitt and Meulenbachs, 1989;; Anderson and Hobart, 1976; Kastner, et al., 1986; Torgersen et al., 1988; Stute, 1989; ODP Leg-110 and Leg-112; Gieskes et al., 1989; Moore et al., 1988). Mechanisms of fluid sourcing and models of fluid migration have been proposed to accommodate these observations (Etheridge et al., 1984; Nur and Walder, 1988; Bethke, 1986, 1988; Lasaga, 1989). Biological, geological and chemical manifestations of fluid flow at the seafloor are now widely recognized (Corliss et al., 1979; C.A.S.E., 1985; Boulegue et al., 1986; Kulm et al., Suess et al., 1985; Westbrook and Smith, 1983; ODP-504B; Bender et al., 1985/86; Maris et al., 1984; Sayles and Jenkins, 1982; Paull et al., 1984; Kuenfolden and von Huene, 1985).

Fluid migration occurs in many different tectonic setting. Active continental margins, where compression and stacking of sediment wedges ahead of subduction zones causes forced dewatering of sediments, are now known to be areas of expulsion of fluids with exotic chemistries (Langseth and Moore, 1990). Passive and active continental margins exhibit gravitational circulation due to (fresh) groundwater penetration or to dissolution of evaporite deposits, both of which create salinity-induced density differences and gravitational flow (ODP leg-112). Sedimented ridge axes contain high temperature forced-convection circulation cells induced by heat loss from the cooling of newly formed oceanic crust. Free convection through ridge flanks may also drive large volumes of fluids at low temperatures, but almost nothing is known about the areal distribution, flow rates, or compositions of these fluids because of their very slow velocities, even though this transport may dominate fluxes of several constituents to/from the ocean. In addition, there is now increasing suspicion that seawater circulates through stable carbonate platforms. However, in only a few of these cases is there sufficient information to permit estimates of geochemical fluxes to or from the ocean (Table 1).

B. Type Cases. The following geological settings are suggested as potentially exciting areas for fruitful investigation:

1. Gas Hydrates: Gas hydrates are solid water plus methane clathrates (probably containing additional volatile hydrocarbons and other gases) that form relatively shallow in marine sediments saturated with methane. Gas hydrates can contain up to about 170 times more methane per cm^3 than can exist in free space at one atmosphere. They represent one of the earth's major remaining reservoirs of potentially-recoverable natural gas (Kvenvolden, 1988), yet were are almost totally ignorant of the mechanisms producing and destroying these hydrate zones and the processes controlling the storage and release of hydrate gases in the environment. Gas hydrates are typically identified in marine sediments by seismic reflection data which detects

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the density contrast between hydrate-filled and gas-filled pore spaces. producing a bottom simulating reflector (BSR). Despite the well-understood physically chemistry of these substances and the recovery of gas hydrates during several lets of Ocean Drilling, the zone where they form and where they dissociate as sediment thickens and water depth increases known only general terms.

Specifically, we do not understand the details of a number of the basic properties of marine gas hydrates:

(1)   If gas hydrates form a methane migrates through sediments, then their formation must impede the flow of fluids by sealing sediment permeability. The fluid over-pressure below the hydrate zone in turn may induce fracture permeability and stochastic flows.

(2)   Heat flow can be deduced form an estimate of the thermal gradient between the depth of the BSR and the sediment surface by assuming that the pressure and temperature conditions at the BSR coincide with the known PT stability field of methane hydrates. This is a powerful means of mapping heat flow over accretionary complexes, but the technique has not been accurately calibrated form *in situ* gas hydrate compositions or measurements of temperature gradients and thermal conductivities through hydrate zones. Gas hydrates presumably affect the thermal conductivity of sediment which may alter both heat flow and thermal structure of the upper few hundred meters of the sediment column.

(3)   The total amount of methane locked up in gas hydrates is poorly known. Methane is an important greenhouse gas. Small climatic changes in the stability conditions affecting this enormous reservoir could result in net release (on warming of bottom waters) or storage (on cooling of bottom waters) of enough gas to affect global climate.

(4)   The presence of gas hydrates in sediment constitutes and unknown quantity in conventional estimates of acoustic velocity. Drilling gas hydrate zones is necessary to obtain *in situ* measurements of acoustic velocity.

(5)   Small scale changes in the depth to the BSR are caused by temperature and compositional anomalies. Such changes in the depth distribution might prove to be invaluable for imaging subsurface regions with preferred fluid pathways.

(6)   Gas hydrate formation, which solidities water, leaves the remaining pore fluids greatly enriched in sea salts whereas gas hydrate decomposition adds salt-free water to the pore fluids. Dramatic changes in the compositions of the pore fluids must have and enormous impact on diagenetic reactions, and the density changes imparted to fluids must induce large-scale gravitationally-driven fluid circulation.

(7)   Methane released from hydrate dissociation can migrate upwards toward the sediment-water interface and be oxidized to carbon dioxide, promoting *in situ* precipitation of authigenic calcium carbonate caprocks or veins that seal sediment permeability. The isotopic signature of these carbonates is both an important clue to detect this mode of carbonate cementation and also a recorder of the methane source (biogenic or thermogenic) after the gas hydrate zone and methane sources

have disappeared.

The nature of these effects and their impact on the environment, thermal regime, fluid flow, and diagenesis remain unresolved without direct sampling of the entire system to collect the dissolved gas, free gas, hydrated gas, water, and solutes, and to measure the physical characteristics of the sediment. Only Ocean Drilling through hydrate zones can provide the depth penetration and sampling required to fully understand the impact of gas hydrates on the global environment.

2. Ridge Flanks: Low temperature ($\sim 150°C$) convection is thought to occur over about one-third of the ocean floor (COSOD II). By far the greatest part of this convection occurs on the flanks of young, mostly sediment-depleted, spreading ridges. These ridges usually evolve form bare rock surfaces at zero age to carbonate-covered ridges with increasing age. The very sluggish nature of the free convection in ridge flanks will have to be revealed chemically rather than thermally because of the ten-fold greater sensitivity of ionic diffusivities compared to thermal conductivities in detecting advective transport. Despite the slow convection rates anticipated, rates of chemical exchange with the ocean may be ten-fold greater than that associated with the $350°C$ hydrothermal discharge at ridge axes because of the enormous areas of the seafloor involved (Table 1).

There are essentially two types of convective systems on ridge flanks: (1) those with thin, permeable sediment cover in which vertical recharge and discharge of basement fluids takes place through sediment cover. These systems are characterized by concave-upward heat or chemical depth gradients (recharge) or convex-upward gradients (discharge). (2) Those systems with thicker, impermeable sediment cover in which recharge and discharge of basement convecting fluids occurs through basement outcrops or along fractured or faulted surfaces within the sediment. these areas are characterized by uniform and low heat flows (relative to theoretical values) and linear thermal and chemical depth-gradients.

In general, Type-1 system occur on younger ridge flanks and Type-2 systems occur off ridge. Type-1 systems might be manifested by variable basement fluid chemistry observed in adjacent holes. Conversely, type-2 holes would be expected to have uniform basement fluid chemistry over large lateral distances.

A number of unanswered questions about ridge flank convective systems require drilling into basement:

(1) What is the lateral scale of convective systems and of individual circulation cells? Is the convection steady state or transient? What is the depth of convection in the crust?

(2) What is the permeability of the sediments? What is the permeability of the basement? When, where, and how does the basement "seal"? Is there retrograde dissolution of the initial vein-pore "sealing" phases ?

(3) What are the sites of discharge and recharge? What are the flow rates at these sites and throughout the system as a whole?

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(4)   What is the chemical composition of the convecting fluids? What chemical reactions and their rates control this composition? How much heat is carried by the convecting fluids? How do these systems affect the thermal and chemical budgets of the ocean? What is the age of basement fluids: the time since these fluids left ocean water?

3.   Sedimented Ridges: Newly-created seafloor near mid-ocean ridges that is buried beneath rapidly accumulating sediments provides setting where thermally driven fluid migration is controlled by the sediment package. The sediment characteristics and the tectonic nature of the ridge determines flow rates, pathways, processes, and thus fluid composition. Localized thermal sources and fluid conduits result in focused flow through the sediments. This flow modifies the characteristics of the fluid, which controls both the extent of the elemental exchange with the crust and provides a source of metals for ore deposits. In addition, hydrothermal processes generate petroleum from sedimentary organic matter. These processes are controlled by the nature of the underlying crust, sediment cover and heat flow. On this basis, a matrix of "type locality attributes" can be summarized as follows:

TECTONIC CONTROLS	SEDIMENT CONTROLS
spreading rates	sediment compositions
maturity (age of the system)	sedimentary structures
rifting processes	bedding and faulting
oceanic vs. continental crust	

Fast versus slow spreading rates, as well as young versus old systems. will lead to significantly different heat regimes. This difference in turn affects the size of the circulation cells and thus the depth of crustal alteration. The dimensions of the fluid flow field will also influence metal, sulfur and hydrocarbon concentrations which can lead to the formation of ore deposits and petroleum deposits. Older systems (Escanaba) are characterized by a cooler cell and large sulfide deposits and associated petroleum whereas younger systems (Middle Valley, Juan de Fuca) are generally more active (hotter) system which have had less time to develop extensive sulfide deposits.

The plumbing of these systems is driven by tectonic and sedimentary controls. The tectonic regime controls fracture distributions, fluid flow rates, and cooling patterns. In addition, the sediment structure influences fluid pathways by concentrating flow along coarse, highly permeable layers. The periodic deposition of turbidites (as observed in Middle Valley) provides horizontal zones for fluid flow. Highly focused flow along these pathways generates localized veins of ore genesis. The formation of sills during the rifting process (Guaymas Basin) also modifies fluid pathways by establishing physical barriers to fluid flow.

Sediment composition exerts an important control on the source materials for metalliferous and petroleum deposits and crustal alteration. For example, flow through the organic-rich sediments of the Guaymas basin results in significantly different fluid composition compared to Red Sea

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(evaporite) types of environment. This not only alters the fluid composition in terms of elemental concentrations and speciation, but also determines the physical properties of the fluid.

Drilling sedimented ridges should thus aim to define temperature gradients, physical and chemical characteristics of the fluids, permeability and structure of porous pathways, and the locations and extent of recharge and discharge areas in a three dimensional framework.

    4.   Convergent Margins: There are many types of accretionary prisms and convergent margins characterized by distinct attributes. In order to understand the global impact of fluid circulation, drilling must include synoptic assessment of such factors as:

(1)   The nature of the convergent margin: subduction, tectonic erosion, obduction and accretion rates;

(2)   The ;morphology of the subducted crust: seismic ridges, seismic ridges, seamounts, abyssal plains;

(3)   The type of plate collision: ocean-ocean, continent-ocean, continent-continent, ridge-continent;

(4)   The geometry of the collision: subducting slab angle and convergence angle;

(5)   The sediment volume involved in the collision: (a) the volume of sediment draped over the accretionary wedge;

(6)   the physical properties of the sediment which influence fluid flow pathways and diagenetic reactions: compaction, lithification, fracturing and mud diapirism and chemical properties as related to sediment type (pelagic versus terrigenous, evaporites and organic carbon content);

(7)   High and low heat flow margins. Heat flow is affected by fluid migration and may also serve as a tracer for fluid transport. Heat flow also provides an important control for diagenetic reaction kinetics.

Because active margins are also important areas for crust-mantle exchange, the measurement of selective tracers will help evaluate not only the extent of this interaction but also provide unique clues of fluid sources and pathways. For example, the ridge-trench collision at the Chile Triple Junction provides a unique geological setting where injection of mantle volatiles into the basal portion of the subcreting slab provides a potential tracer of fluid sources and flow patterns within the trench wall.

Although the emphasis for drilling in active margins has focused on accretionary wedges, detrital slope and shelf sediments are also important for fluid migration and mixing of fluid types. Such fluid types can include those expelled from the wedge, trapped in the sediment interstices, and fluid derived form deep sources and through mineral dehydration reactions in the sediment and basement rocks. In order to sample fluids form deep sources, boreholes should penetrate the decollement zone and into basement. This type of sampling will require technological advances in drilling and in fluid sampling tools.

    5.   Carbonate Platforms: carbonate platforms are thick accumulations of calcium

carbonate-rich sediments produced by benthic organisms in relatively shallow waters, e.g. the Bahamas and coral atolls. Although dominantly composed of calcium carbonate, they differ from pelagic carbonate-rich sediments because they are an assemblage of metastable carbonate minerals (aragonite and high magnesian calcites) and consequently tend to be susceptible to diagenetic alteration. Although carbonate platform occurrences are limited in the modern ocean, analogous sedimentary carbonates comprise a major portion of the Paleozoic record. In addition, they form a significant proportion of petroleum reservoir rocks (~60%) and host important ore minerals.

Most studies of shallow-water carbonate diagenesis have been confined to Pleistocene to Recent sediments, the results of which are often extended to ancient carbonate rocks. As a result, interpretations of these carbonates are heavily biased by diagenetic conditions associated with Pleistocene sea level fluctuations. There is a growing concern that diagenesis under these conditions differs dramatically from Pre-Neogene conditions (with no rapid sea level changes). For example, we know from previous drilling studies that much of the diagenesis takes place under marine phreatic conditions rather than in the freshwater realm encountered during low sea level stands. However, few geochemical studies of formation fluids at any depth in carbonate platforms have been undertaken, and, therefore, we know little about the rates at which these diagenetic reactions take place and/or the role of fluids in mass transport processes.

Attempts to made major diagenetic processes, such as the dolomitization, cementation, and formation of secondary porosity and permeability, indicate the necessity for extensive fluid flow (thousands of pore volumes of fluids), especially along the flanks of platforms. Several possible mechanisms for generating such flow have been proposed. Among these are geothermal convection, fluid density differences, and hydrostatic pressure differentials. These hypotheses point to the importance of quantifying fluid flow within sediments, identifying driving mechanisms for generating this flow, and assessing compositional changes associated with chemical and microbial diagenesis.

The absence of data on fluid compositions and fluxes in carbonate platforms reflects not only the small number of carbonate platforms actually drilled but also the fluid sampling technology currently available. Future studies and new techniques provide opportunities to quantify these processes. Future drilling of carbonate platforms for other purposes (e.g., sea level information) must also include detailed studies of fluid flow and diagenesis, particularly along the flanks of platforms where circulation is likely to be most active.

6.   Passive Continental Margins: Passive margins contain the vast majority of the sediment volume in the oceans as well as a major portion of the world's petroleum resources. As a result, the proportional volume of fluids in passive margins is greater than in the rest of the marine sedimentary environment. Therefore, diagenetic processes in passive margins represent important contributions to the global geochemical inventory and potentially large fluxes that are critical to our understanding of global geochemical balances.

We must establish the dominant processes and the compositions of fluids in a suite of end-

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member regions. The first two decades of DSDP and ODP have shown the importance of advective processes on material transport to the continuing evolution of these enormous volumes of sediment.

We now need to establish the variability of processes in different end members as they relate to:

(1)   The sediment type in terms of the relative contributions from terrigenous and both shallow and deep water marine sediments;

(2)   The ages, thermal evolution, and maturity of the margin;

(3)   The pore fluids that have evolved from *in situ* processes, advection of water form continental sources (both meteoric and evaporitic) and metamorphic processes;

(4)   The sources, volumes, and flow rates of fluids that may be controlled by the climate of the adjacent continent;

(5)   The influence of the physical properties of the sediments on fluid transport, and the ability of the fluids to alter sediment porosity and permeability structure. It is important to distinguish porosity flow characteristics between fracture and porous flow conditions;

(6)   The relationship between depositional setting and conduit plumbing.

7.   Metamorphism: Metamorphism represents a continuation of the chemical alteration of sediments under temperature and pressure conditions that are generally much deeper than those associated with diagenesis. Metamorphic processes accelerate chemical and physical changes within sediments and drive the system toward thermodynamic equilibrium. Major phase transitions, dewatering reactions, and release of volatile components result not only insignificant modifications of the sediments undergoing metamorphism, but also generate a major flow of fluids with exotic chemistries. Deep burial diagenesis has been hypothesized to be of importance to the chemistry of most of the sedimentary column in areas such as the Texas Gulf Coast and may be of first order importance for generating chemical fluxes in many sediments. Therefore, understanding the total diagenetic history including metamorphism of rocks in heir evolution form ocean sediments to mountains, and thus the global geochemical fluxes associated with these transformations, requires an assessment of the processes that occur during deep-burial diagenesis at elevated temperatures and pressures.

The importance of metamorphism in generating fluid flow and chemical fluxes within sediments, and probably between sediments and overlying waters, is gaining increasing acceptance a concept. However, there is scant observational data to support the idea. The hypothesized importance of this process points to an urgent need to study fluid flow and composition at depth in areas where this process is likely to be of importance. The following considerations will guide drilling to select sites where metamorphism can be studied:

(1)   there is a gradual depth transition from diagenetic to metamorphic alteration conditions;

(2)   There are wide ranges of pressure-temperature regimes in which metamorphism can occur;

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(3) The fluid and solid phase products depend on several major variables, including the composition of the initial sediment, the "openness" of the system to fluid flow, injection of hydrothermal fluids, rates of change in pressure-temperature conditions, and the tectonic setting in which metamorphic processes take place.

Drilling into the oceanic lithosphere where metamorphism is active will provide a quantum leap forward in our understanding of geochemical alteration on a global scale. We can start to assess the significance of metamorphic processes as a driving force for fluid flow, chemical fluxes, deep burial diagenesis of sediments, and chemical exchange between the ocean and sea floor. In selecting sites to study metamorphism and its related influences, active margins are preferable to passive margins because metamorphism is more likely to occur more rapidly and at shallower depths there than at passive margins.

8. Deep Microbial Activity: Diagenesis, fueled by microbially-mediated transformation of organic matter, is a fundamental process in the marine sedimentary environment. It affects the transfer of carbon between organic and inorganic reservoirs over time, the formation and degradation of hydrocarbons, the precipitation of authigenic phases, the cementation and lithification of strata, and the degradation of organic biomarkers.

There is a growing awareness that microbially-mediated diagenetic reactions extend from the earth's surface to considerable depth into the crust. Geochemists have for some time postulated deep-seated microbial activity from the distribution of metabolic products dissolved in the pore fluids (NH_4^+, H_2S, CH_4, CO_2) and the continued transformation of sedimentary organic matter observed downhole. However, this claim was not without controversy because conventional techniques for microbial rate measurements failed to show deep activity. Microbial cultures recently obtained from ODP material (Leg 112) have now provided direct evidence that the depth of active microbial processes extends much deeper than conventional wisdom (tens of meters) to at least 100 m if not kilometers below the sea floor.

This realization raises a number of high priority objectives to be addresses by drilling. the ultimate environmental conditions that limit the extent of the active biosphere are of fundamental interest. Determination of reaction rates at which diagenetic products and isotope fractionation proceed within the sediment column is required. Limiting temperatures and pressures for microbial life in the crust need to be ascertained as well as potentially-stimulating conditions for bacterial growth. Fluid convection and availability of substrates must play a major role here. Ocean drilling provides the only capability for reaching and sampling the environment that constitutes the lower boundary of the earth's biosphere.

III. TECHNOLOGICAL PROBLEMS

A. Overview. Before we can successfully drill and capture fluids from these geological setting, measure their fluid compositions, and begin the process of establishing flow paths, rates, and chemical reaction processes, a number of fundamental technological problems must to be overcome. For example, we must recover fluids (gases and solutions) under *in situ* conditions

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without sampling artifacts. We must recover fluids from deep, high-temperature, acidic environments containing high sulfide levels. We must recover fluids from deep, high-temperature, acidic environments containing high sulfide levels. We must recover gas hydrates in their initial solid form with the sediment, gas, and solutions characteristics intact. We must eventually be able to both measure and successfully model and verify the first-order flow directions and rates. We have prioritized the five most important technological recommendations, which are discussed in more detail below.

Priority Number 1: Complete the modifications (Phase Ib) of the Pressure Core Sampler (PCS) to obtain gas and solution compositions under *in situ* pressure, and immediately begin routine use of this device aboard ship t establish its reliability.(Short Term Objective).

Priority Number 2: Begin research and development by inviting proposals from the scientific community to design, build and test Chemical Sensors and Chemical Sampling Devices for wire-line borehole fluid profiling and for long-term deployment on instrumented strings in borehole observatories. (Short-term Objective).

Priority Number 3: Begin the process of redesigning Packers that have the capability to pump and capture clean formation fluids from intervals in the borehole. (Short-term Objective).

Priority Number 4: Continue implementing and testing Re-entry Wire-Line Chemical-Physical Sensor Packages (down-hole tool). It is critical to develop the capability to profile conductivity, temperature, pressure, oxygen, iron and manganese, sulfide and methane both in instrumented holes prior to instrumentation and in other re-visited holes where flows are likely to be rapid. (Long-term Objective).

Priority Number 5: We strongly endorse all efforts to establish the Hydrogeochemistry of geological setting with fluid circulation by cross-hole experimentation and by development and testing of coupled geochemical and hydrological models.

B.   This working group offers the following specific recommended modifications for fluid sampling to implemented immediately aboard *JOIDES RESOLUTION.*

1.   Existing Routine procedures for "Normal" Sediments (low-temperature). The current procedures for sampling whole round intervals has the advantage that it permits high resolution vertical profiles of pore fluid chemistry. Although we endorse the current policy for routine sampling and analyses on legs where geochemical objectives are not high priority, we strongly recommend that flexibility be implemented in the sampling scheme in order to permit as much sampling as required to fulfill both the pre-stated objective as well as any others which may arise during the course of the leg.

In order to fulfill the major objectives of the geochemical program as defined above we must

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collect samples that establish *in situ* fluid compositions without artifacts due to contamination, and temperature, pressure and oxidation changes on recovery. To achieve these aims were recommend that whole round sections of cores from which fluids will be obtained be handled within portable glove boxes under inert gas atmosphere to minimize exposure of core samples to oxygen. this procedure would include the cutting of whole round core sections as well as the actual squeezing for pore water recovery. Additionally, it is advantageous to extract pore fluids with squeezers that have been pre-equilibrated to the formation temperature.

Sample contamination was thoroughly discussed by the working group. A consensus was reach that routine use of Ti squeezer (or some other non-ferrous, inert material) be implemented immediately as routine procedure to obtain pore fluid samples uncontaminated with metals. Trace metal characterization of the fluids is critical to certain geochemical objectives Therefore capability to collect, process and store contamination-free samples should be available aboard ship. This capability includes facilities for pre-cleaning sample vessels, a portable collapsible laminar flow bench for cleaning and sample transfers, and the availability of Ultrex or comparable grade clean acids for cleaning equipment. these capabilities are not of a routine nature, but should be available to shipboard scientists as the need arises.

Another form of contamination is that derived form the surface seawater used to circulate the borehole. Quite often, spurious pore fluid data are attributed to dilution (contaminating) by the drilling fluid. In some cases, the formation waters are not dramatically different from seawater composition, and in other cases where seawater circulation into the crust is anticipated, such contamination can not be distinguished form primary circulation. This distinction is of critical importance for distinguishing actual fluid circulation in the formation from spurious introduction of seawater into the formation or into fluid samples by the drilling or recovery process. Surface seawater contains a number of constituents not present in bottom waters or in formation water. Several of these constituents for example, dissolved freons, have been introduced to the atmosphere and surface ocean anthropogenically over the last 40 years. Deep ocean waters (and sediment and crustal fluids that have not contacted the surface ocean since the advent of refrigeration) contain no freons. Thus drilling fluids contain a "natural" tracer that can be employed to detect contamination. The measurement of freon is quick, reliable, inexpensive, and has a dynamic range of analysis that would permit shipboard detection of very small degrees of contamination. We recommend that the Project investigate the feasibility of routinely measuring the freon content of all fluid samples recovered *in situ* under gas tight conditions, particularly in formations where the circulation of bottom seawater into or through the formations is anticipated.

Changes from *in situ* temperature and pressure are inherent in the standard core retrieval procedures. The physical and chemical characteristics of pore fluids obtained with *in situ* (WSTP) samplers and pressure core barrels (PCS) are less likely to deviate from those existing in the formation. In order to evaluate the effect of changes in the properties of whole round samples and the associated pore fluids, an systematic program of cross comparison between the samples obtained by various methods must be implemented immediately. We recommend the use of contingency time during available legs to carry out such a comparison on core samples

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from a wide range of sedimentary environments (see *in situ* methods below).

2.   Phases I-b and II of Pressure Core Barrel development (Pressure Core Sampler, PCS) should be brought to fruition as rapidly as possible to provide the capability of recovering fluids and gases at *in situ* pressures, and to re-establish *in situ* temperature (if feasible in the very short term). The PCS will provide for the first time the ability to quantify the amount of gas that is present *in situ* in a volume of sediment. This information is essential to understanding fluid migration in, for example, accretionary prisms. with a controlled temperature chamber, the PCS can be used to identify gas hydrates and to determine their chemical and physical properties. This information is critical to understanding the processes of gas hydrate formation and association, and for estimating the volume of the world-wide gas-hydrate reservoir. Although our first-order mandate for the PCS is the recovery of gases and fluids, the PCS design must be sufficiently flexible to permit evolutionary design changes with time which will allow (1) the measurement of sediment properties such as acoustic velocity and thermal conductivity, (2) the imaging of internal structures, (3) the injection and withdrawal f labeled tracers, (4) the determination of engineering properties of sediments, and (5) ultimate transfer of samples under pressure to lock-on transfer chambers for shorebased analyses.

The *in situ* Barnes tool (harpoon) has proven unsatisfactory in recovering formation fluids suitable for establishing their *in situ* characteristics, especially for gases. At present (or at least as soon as our fist priority recommendation is implemented), there will be three methods to recover fluids. We recommend that (1) the PCS be immediately adapted to contain a harpoon so that pore fluid samples can be withdrawn from inside the pressure core barrel at *in situ* pressures once the PCS is on deck; (2) the PCS (fluid capable (be used routinely aboard ship as soon as possible, at least three-times per hole (widely spaced) in any hole deeper that 300 m; (3) comparison tests be performed between samples obtained from squeezers (as modified), the Barnes tool, and the PCS (as modified) in the same holes at near-by intervals during the contingency time on all available legs; and (4) a procedure to archive the PCS core sample be established parallel to the pore water squeeze cake samples.

3.   Sample Storage: We concluded that the current shipboard sample storage procedure is inadequate for the preservation of samples for subsequent shore-based analyses of gases and their isotopes. Were recommend that the Project consider storing a sub-sample of gas tight pore waters in Jenkins-type Cu-seal tubes. These subsamples would be in addition to the current storage in glass ampoules and plastic seal tubes, a procedure which should be continued. Furthermore, we endorse the routine collection and storage of frozen core samples (currently designated as the Organic Geochemical Sample) for posterity. There are at least two potential uses (biomarkers and bulk organic ^{13}C) that will be best utilized form these samples. However, were recommend that these samples be flash frozen (either in liquid nitrogen or in a dry ice and alcohol bath) before transfer to the deep freezer.

4.   High Temperature Sampling of Fluids: Sedimented ridges and deep crustal drilling will almost certainly encounter fluids with temperatures up to the critical point os water and beyond. For most purposes, and upper limit of approximately 400°C can be expected to

become routine. These hot fluids will also be highly corrosive and acidic. Recoveries of the fluids is critically important to solve the scientific problems to be addresses at these sites. In addition to the fluids, it will also be important to develop the technologies which will be able to recover the surrounding solid phases, both sedimentary and igneous rocks. An immediate assessment of the critical temperature-sensitive elements al all downhole components likely to encounter hot fluids should be addressed immediately, and plans formulated to replace or modify these components.

C.   Long-term goals.

1.   Passive Tracer Experiments (Instrumented Holes and Wire-Line Profiling). It is important to detect perturbations in the borehole fluid chemistry at horizons where lateral flow is rapid in order to establish the stratigraphic details of fluid flows. Such experiments can be performed in open or sealed holes or between packer elements. These experiments must be designed with the capability to recover and/or remotely sense the chemical compositions of the borehole fluid at times of weeks to months to years after drilling. It is critically important now to start the process of designing, building and testing the chemical sensor (probes and electrodes) and fluid sampling devices (active water catchers and passive borehole "peeper " chambers) that will ultimately be needed to obtain chemical composition profiles in boreholes to identify zones of rapid later flow.

Advecting fluids frequently transport non-seasalt concentrations of chloride, hydrogen sulfide, soluble metal sulfides, methane, and carbon dioxide. In some cases, salinities (conductivities) are dramatically different at flow horizons. These fluids can also be very acidic Electrodes that sense chloride, sulfide, Ph and pCO_2 are commercially available and could be lowered into drilled holes by wireline techniques (or hung on instrumented strings containing thermistors, conductivity and pressure sensors) to record profiles *in situ*. These sensors have been used in low temperature sedimentary environments and at high pressures, but they need testing under extreme pressure and temperature conditions. Development work for this application would include durability and stability testing, engineering a flow-through cell to periodically pump downhole fluids past the electrodes, and *in situ* calibration techniques. Probes for sensing *in situ* trace concentrations of manganese and iron are being developed for deep ocean work and can be adapted for use with wire linen profiling.

2.   Packers. Two types of packers are available which can be used for obtaining water samples. The standard drill string straddle packer which has been previously used for measuring permeability, can potentially be adapted to take water samples. This device is presently under development. Water samples form each interval are retrieved using a wireline retrieval system.

The second packer device which is currently ready for deployment is a straddle packer operated using a wireline. specific intervals previously identified can be isolated and the interval pumped until constant chemical composition is attained. The internal plumbing contains Ph, conductivity, and calcium probes. Water samples are then stored in chambers and later retrieved

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after recovery. Up to four samples can be stored per wire line trip. One of the principal advantages of both types of packers is that they can take fluid samples from cemented and/or lithified rocks. The principal disadvantage is the potential for contamination of fluids by the packers themselves or by the materials of which the straddle is constructed.

D.   Very Long-Term Technological Advancements. A number of new approaches will be required to obtain a three-dimensional view of fluid circulation in complex stratigraphic and tectonic settings. The effort to understand even the first-order hydrogeology of these structures will demand Multiple, Closely-spaced Holes in which both active an passive tracers and pumping experiments can be performed to obtain information about the spatial scale of permeability and flow. Multiple Visits to the Same Sites and Holes will be required to obtain information on the relaxation time of the borehole fluid and the temporal scales of flow. Very Long-Term Instrumented Holes will be needed to detect episodic or sporadic flow induced by natural perturbations such a gravitational convection, seismic pumping, or magma injection. some of these holes will be Sealed at a Number of Depths (Permanent Packers) to re-establish the stratigraphic intervals of primary fluid pathways while monitoring fluid compositions with either *in situ* chemical sensor or peeper chambers.

Table 1. Estimates of Fluxes to the Ocean (after COSOD II).

|	Water Flux (km^3/yr)	Chemical Flux to Oceans (10^{12}mole/yr)
Ocean Ridge Crests (Hydrothermal Forced Convection)	24	Ca = +0.2 Mg = -1.3
Ocean Ridge Flanks (Free Convection)	560	Ca = +1.0 Mg = -1.0
Convergent Margins (Porosity reduction on Compaction)	1	Ca = ? Mg = ?
Passive Margins (Hydrologic Groundwater Flow)	100	Ca = +5 to +3 Mg = -5 to +3
Carbonate Platforms (Hydrologic Groundwater Flow)	?	Ca = ? Mg = ?
Gas Hydrates (Complete Dissociation)	?	Ca = ? Mg = ?
Deep Metamorphism (Tectonic Displacement)	?	Ca = ? Mg = ?
Rivers (Continental Runoff)	37 x 10^3	Ca = + 12 Mg = + 5

FLUID CIRCULATION
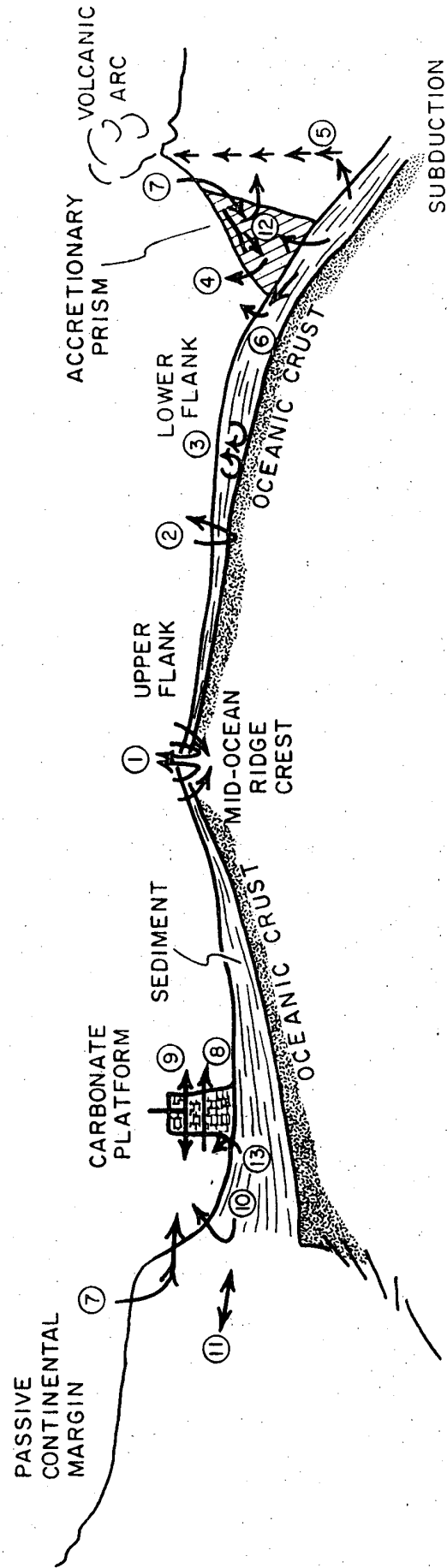
Figure 1. (Legend overleaf)

FIGURE LEGEND

Examples of Fluid Circulation:

(1) Forced (high temperature, hydrothermal) circulation at mid-ocean ridge crests, both sedimented and unsedimented.

(2) Free (low temperature) convection through mid-ocean ridge flanks permeating sediment with expression into the ocean.

(3) Free convection wholly-contained within mid-ocean ridge flanks and their sediments.

(4) Expulsion of fluids from compacting wedges of sediments in accretionary prisms.

(5) Expulsion of fluids and volatiles from the subducting slab and incorporation into (or expulsion through) volcanic arcs.

(6) Expulsion of fluids from the subducting slab, migration along the decollement, and expulsion into the ocean ahead of the toe of the accretionary prism.

(7) Penetration of meteoric water into marginal sediments of passive and active margins.

(8) Circulation of seawater through carbonate platforms due to differences in elevation head across the platform.

(9) Circulation of fresh water and/or saline water through carbonate platforms due to local precipitation-evaporation balance.

(10) Expulsion of pore fluids from deeply buried passive margin sediments due to compaction and deep metamorphic dewatering reactions.

(11) Migration of deeply buried continental waters.

(12) Migration of fluids due to formation and/or destruction of methane hydrates.

(13) Migration of pore fluids from deeply buried sediments along edges of carbonate platforms.

From: COSOD II; Whitaker and Smart, 1990; Langseth and Moore, 1990; Torgersen, 1990; Moore, Mascle, Taylor et al., 1988; and many others.

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I. INTRODUCTION

Organic geochemistry has matured as a science to a point where it can now be applied confidently to a wide variety of earth science problems in the context of scientific ocean drilling. We have identified six global themes that are of major importance and of equal scientific merit: 1) Organic Carbon Inventory, 2) Paleoclimatology, Paleoceanography and Paleobiology, 3) Gas Hydrates, 4) Biogeochemical Diagenetic Processes and Pathways, 5) Role of Dissolved Organic Carbon in Diagenesis and Carbon Cycling, and 6) Thermogenic Processes at Active Spreading Centers. Two of these themes, the gas hydrates and thermogenic processes (3 and 6), require site-dependent studies. The others are not geographically constrained.

II. THEMES

A.   Organic Carbon Inventory. The type of sedimentary organic matter and its spatial and temporal distribution are important elements when examining global change and geochemical cycling and fluxes. Although over 26,000 total organic carbon (TOC) analyses have been performed as part of the DSDP/ODP programs (Emeis and Brown, 1989), the assembled database is not considered satisfactory for the purposes stated above. The largely DSDP-based database has largely been biased toward intervals with anomalous quantities of organic matter (i.e., "black" shales), contains a disproportionate amount of data from the Atlantic Ocean, generally lacks information associating the available organic carbon values with lithologic and biostratigraphic data, and usually lacks any information on the origins of the organic matter (i.e., marine versus terrestrial). Previous attempts to associate TOC values with lithology and organic source or provenance have largely been the result of individual investigators examining specific problems usually of only regional significance.

Identifying how much organic matter is buried, where it is buried, the type of organic matter, and the associated lithology is important because these variables are a direct response to such factors as productivity (both marine and terrestrial), organic preservation, and climate. For example, an increase in aridity will result in a decrease in the net transport of terrestrial material, both organic and inorganic, into the marine system. Spatial variations in the type and quantity of organic matter over short distances provide information on transport and depositional processes, while variations over large distances may provide information on oceanic circulation and water mass properties. Global increases in productivity may reflect increases in CO_2 partial pressure in both the atmosphere and in the ocean surface waters.

The development of a satisfactory TOC database will require a more intense routine shipboard sampling program in association with other on-board activities (i.e., carbonate carbon or IOC, lithologic description, physical properties, etc.) and the acquisition of additional organic geochemical data on all samples where reliable results may be obtained, in addition to those samples which bear on safety questions (see routine shipboard sampling and analysis section).

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B.   Paleoclimatology-Paleoceanography-Paleobiology.   The organic matter contained in marine sediments retains histories of the oceanic environments and biological populations of former times. Molecular, isotopic, and elemental compositions provide indications of seawater temperature and oxygenation, continental climates, and biotic assemblages. These records complement and refine microfossil data and can provide proxy data in locales where mineral preservation is poor.

Studies of marine sediments have identified a variety of biomarker compounds which yield information about sources of organic matter, transport routes, and depositional conditions (cf., Simoneit, 1986). A gas chromatogram of biomarkers extracted from a representative ODP sediment sample is shown in Figure 2. Some of these compounds evidently derive from specific types of marine organisms. For example, long-chain polyunsaturated alkenones are diagnostic of a few species of the class Prymnesiophyceae, notably coccolithophorids of the family Gephyrocapsaceae (Brassell et al., 1986a and b; Prahl et al., 1988), and 4-methylsterols are indicators of dinoflagellates (Robinson et al., 1984). The existence of diagenetic derivatives of these biologic precursors in sediments as old as Cretaceous gives evidence for the presence of these organisms among former marine algal assemblages.

Detailed molecular studies have shown that some biomarker compounds, most notably the long-chain alkenones, retain information about the photic zone temperatures of former times (Brassell et al., 1986 a and b; Prahl et al., 1988). During times of lower temperatures, the number of carbon-carbon double bonds increases. The long-term stability of alkenones in marine sediments preserves this record to at least the early Pleistocene. These detailed molecular studies also can yield histories of biotic evolution and radiations.

Glacial-interglacial sea level changes and variations in continental aridity/humidity appear to affect the relative proportions of land-derived and marine organic matter. The total organic matter parameter of the C/N ratio is higher during times of predominance of continental input in sediments from DSDP Leg 75 (Meyers, unpublished data), DSDP Leg 96 (Jasper and Gagosian, 1989), and ODP Leg 108 (Stein et al., 1989). Molecular indicators are likely to follow this pattern, even though the preservation-production challenges have obscured correlations to date. The variety of available compounds provides many opportunities to evaluate ratios of specific compounds and of lipid types which can serve as proxy indicators of marine and continental production.

Applications of organic geochemical determinations of past oceanic conditions generally have been limited to relatively broadly defined problems such as characteristics of organic-carbon-rich Cretaceous black shales and Neogene upwelling deposits. Finer-time-scale, higher-resolution studies have been few. Advances in knowledge and particularly in analytical refinements of the past decade now allow more small-sized, organic-carbon-lean samples to be investigated. These advances provide important, new opportunities.

Organic geochemical investigations of marine sediments have identified techniques that can be applied to assess paleoclimatologic and paleoceanographic conditions and to paleobiology. An

important example, illustrated in Figure 3, is the possibility of determining sea surface temperatures independent of the ice-volume effects that influence δ18O measurements. Modern advances in this field expand the potential contributions. More paleo-indicators remain to be discovered.

High-resolution organic geochemical analyses should be incorporated into studies of paleoceanography. Coordination of biostratigraphy, isotope stratigraphy, and molecular stratigraphy should be commonplace. Proven biomarker compounds should be studied, while the existence of new compounds needs to be investigated. Such investigations, however, should not be the basis for routine collection of frozen samples.

Good locations for future studies include areas under present and former zones of enhanced marine production and areas that have received alternations in marine and continental inputs.

C.   Gas Hydrates. Gas hydrates are crystalline substances composed of solid cages of water molecules which include molecules of gas. In nature, gas hydrates are composed mainly of water and methane and occur under specific temperature and pressure conditions that are found in sediment in high latitude regions associated with permafrost and in outer continental margin sediment at water depths exceeding about 300 meters. In ocean drilling, it is the gas hydrates of outer continental margins that are of particular scientific interest, because the amount of methane that is apparently sequestered in these gas hydrates is enormous, perhaps exceeding 10,000 gigatons (Gt) of carbon, where Gt = 1015 g carbon (Kvenvolden, 1988; Figure 4). This carbon reservoir is one of the largest in the global cycle of organic carbon.

Although naturally occurring gas hydrates were recognized about 20 years ago, only general information is available about their global distribution and composition, and virtually nothing is known about the dynamics of their formation and destruction. Estimates of the amount of methane associated with gas hydrates are preliminary, based on minimum data and broad extrapolations. Of immediate technical interest to the Ocean Drilling Program (ODP) are safety questions resulting from penetration of the gas hydrate zone during drilling of outer continental margin sites. Of interest to the petroleum industry are the resource potential and production hazards of gas hydrates. Finally, because the gas-hydrate reservoir is so shallow, it is subject to global changes in atmospheric temperature and pressure, and therefore the methane,
a greenhouse gas, from gas hydrates may be important in consideration of changing global climate. For all of the above reasons, a global and detailed study of gas hydrates is essential.

Through marine seismic surveys and drilling by DSDP and ODP, it is now recognized that gas hydrates occur in most continental margins. About 30 localities worldwide have been described (Kvenvolden, 1988; Figure 5). Most of the localities have been identified through the presence on marine seismic records of an anomalous reflector, called a bottom-simulating-reflector (BSR), which is thought to define the base of the zone of gas hydrates. Hydrates have been recovered by coring in the Atlantic Ocean (Blake Outer Ridge), in the Gulf of Mexico, in the Pacific Ocean offshore Mexico, Guatemala, Peru, and California, and in the Sea of Okhotsk. A study of the controlled decomposition of gas hydrate recovered offshore Guatemala revealed the details

of the molecular and isotopic composition of gas-hydrate gas and water (Kvenvolden et al., 1984). In general, methane in marine gas hydrates is of a microbial origin with the exception of some gas hydrates in the Gulf of Mexico. Currently, there is no concerted research study of marine gas hydrates in a global context, but the ODP program offers the potential for such investigations.

Although it is known that marine gas hydrates are globally distributed in outer continental margins, the details of this geographic distribution are not understood. The seismic signatures are not unequivocal, and gas hydrates are known to occur where there is no obvious seismic indicator. The stratigraphic
distribution within the gas hydrate zone is also not known. Evidence to date suggests that gas hydrates are usually associated with the coarser-grained stratigraphic units, but other evidence suggests that gas hydrates can occur in other forms, from finely dispersed in sediment to massive occurrences. Where gas hydrates have been recovered, the composition has been measured, but the number of measurements is small and does not necessarily reflect the compositions on a global scale. No measurements are available of the amount of methane that is present in gas hydrates, other than in an individual sample, or of the amount of gas that may be trapped beneath gas hydrates. The quantitative measure of the volume of methane in sediment and sediment gas hydrates is one of the most important points to be investigated in order to understand the global methane balance, and in turn the global carbon balance. Although a model for gas hydrate formation by in situ microbial methane generation has been formulated (Claypool and Kaplan, 1974), many questions remain concerning the details of deep methanogenesis in a region of active sediment accumulation. Other aspects and consequences of gas hydrate formation such as the effects on carbonate diagenesis and the pore water salt balance are generally not understood. In addition, the natural disassociation of gas hydrates has not been investigated in detail and may have important
implications relative to global climate.

D. Recommendations.

The following are specific recommendations:

(1) Improve seismic analysis techniques to augment the ability to map marine gas hydrates regionally as well as stratigraphically.
(2) Improve well log techniques to augment methods of identification and quantification of gas hydrates.
(3) Develop and deploy a working pressure core sampler in order, for the first time, to measure the absolute volume of methane in and associated with gas hydrates.
(4) Using all available techniques, core and analyze the gas hydrates in settings where thermogenic and microbial processes dominate methane generation and migration in gas hydrate formation.
(5) Determine the dynamics of gas hydrate formation and destruction by detailed biogeochemical and isotopic studies.
(6) Integrate data on a worldwide basis to determine the methane gas content of the

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marine gas hydrate reservoir.

E.   Biogeochemical Diagenetic Processes and Pathways.   Despite nearly two decades of organic geochemical research, we still do not have a complete understanding of the complex biogeochemical pathways by which organic matter is cycled on and within the Earth. Elucidating general diagenetic pathways and, more specifically, rates and mechanisms of the cycling processes, is critical to our eventual understanding of the couplings between spatial and temporal inventory changes within global elemental budgets.   Only with a grasp of the mechanisms of these diagenetic transformations will a better understanding of the connection between global budgets and global climates be achieved.

A quantitative understanding of organic matter cycling is a problem which is much larger than the scope of the Ocean Drilling Program alone.   However, because the ocean sediments represent a repository of the best (and often only) clues to past interactions between element cycling and global climate changes, they must be considered a critical source of information. Components of the organic matter cycling problem are currently being addressed by various organic geochemical studies. These include: 1) the evaluation of the effects of in situ organic matter diagenesis (subsequent to organic matter production but prior to transport) (e.g., Benner et al., 1987; Benner et al., 1984; Ember et al., 1987; Newell et al., 1989; Wilson et al., 1985), 2) the effects of diagenesis occurring during both vertical and horizontal transport (e.g., Cifuentes et al., 1989; Hedges et al., 1988; Hedges et al., 1986; Lee and Cronin 1982; Wakeham et al., 1984), and 3) post-depositional microbially-mediated diagenesis occurring within surface sediments (e.g., Berner 1985; Damste et al., 1989; Martens and Klump 1984). A common objective throughout most of these studies is to differentiate the measured, integrated sedimentary signals into individual components describing both the original source input and the diagenetic overprint. Achievement of this goal will allow us to filter out diagenetically induced signals and reliably relate the original source input signals preserved in the sediments to changes in global inventories (Dean et al., 1986; Hayes et al., 1987; Rau et al., 1989).

Specific, long-term, organic matter diagenetic questions of interest to the general geochemical community and consistent with the ODP mission include: 1) what are the pathways by which organic matter undergoes diagenesis (e.g., are specific diagenetic reactions, such as reduction, microbially driven or are they abiotically induced)? and 2) how important are microbially-mediated processes in deep, subsurface diagenesis?

The first question is important to our ability to effectively "see through" the effects of diagenesis and characterize sedimentary organic matter in terms of its original source input. It is also important in understanding the interaction between the physicochemical environment of the depositional system and organic matter cycling. Several inconclusive studies have been undertaken in nearshore environments and in laboratory simulation experiments to evaluate the mechanisms and kinetics of specific diagenetic processes (e.g., Ertel and Hedges 1983; Hatcher et al., 1982; Quirk et al., 1980; Wolff et al., 1986). It is unclear whether the reaction rates derived from these simulations can be compared to the rates of organic diagenetic processes occurring under much different time/temperature regimes experienced by organic matter under

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natural burial conditions.

The second problem noted above is of great concern to organic and inorganic geochemists alike. Previous investigators have suggested that microbially-mediated diagenetic processes (e.g. sulfate-reduction and/or methanogenesis) may extend downward to great depths within a given sediment (Whelan et al., 1986). If so, the implications for continued organic geochemical changes, such as the production of dissolved organic carbon, might be very significant in terms of organic ligand/metal complexation and flux (see below).

Also important would be the possibility that organic matter produced at these depths would bear the organic geochemical signals of these microbial organisms. At present, these signals (i.e., biomarkers) are often used as indicators of the paleo-depositional environment, with the assumption of little or no microbial activity below approximately 1 meter subsurface depth. However, continued addition of microbial biomass during burial and/or microbial-mediated alteration of the "environmental signals" (Moldowan et al., 1986) would force us to re-evaluate the use of certain biomarkers as paleo-depositional environmental indicators.

These problems can be addressed using holes of opportunity. The major constraint would be a site containing a long, continuous, sedimentary section. High resolution down-core sampling for organic geochemistry in a core with good stratigraphic control would allow us to better evaluate specific diagenetic reactions (i.e., precursor/product relationships) and possibly obtain estimates of pseudoreaction rates. By analyzing for specific biochemicals known to have very short half-lives outside of living organisms (e.g., phospholipids, ATP), one might be able to make significant statements regarding the down-core distribution of viable/active microbial populations. Using this method for assessing microbial activity, in addition to more classical microbiological techniques (e.g., radiocarbon labeling, culturing and staining techniques, etc.), might provide insight into the distribution of active vs. viable microbes.

F.   Role of Dissolved Organic Matter in Diagenesis and Carbon Cycling.   New measurements of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in the water column by techniques pioneered by Suzuki et al. (1985) and Sugimura and Suzuki (1988) indicate that this pool of largely undescribed compounds may be extremely important in determining ocean nutrient and redox chemistry (Jackson, 1988). Understanding how dissolved organic matter (DOM) is cycled into and out of the ocean from the earth's crust is an objective we have identified for future study as part of ocean drilling.

To date no scientist has attempted to study dissolved organic matter (DOM) in any form in drilled fluids. Studies of sediments at the sediment-water interface indicate DOM fluxes out from some marine sediments (Heggie et al., 1987). Many of these dissolved materials are certainly produced by microbial reactions within the uppermost sediments. Other dissolved compounds may be produced by biological or chemical reactions at depth. These compounds may migrate slowly to the surface by diffusion or be transported to the sea floor by advective processes. Much of the DOM in the deep ocean has been shown by 14C dating to be relatively old (Williams and Druffel, 1987). How DOM can be old and also reactive is a puzzlement.

Production of labile DOM from old carbon source buried deep in the sedimentary column, followed by migration, may explain this apparent inconsistency.

DOM within the sedimentary column may also have important but as yet unrecognized roles in diagenesis. For example, many trace elements form organocomplexes which may change their availability for inorganic reaction. Organic acids can affect carbonate and other acid-base equilibria.

DOM measurements need not be made at sea but are presently feasible. Pore water sample aliquots should be properly stored to prevent oxidation and returned to a laboratory with a high-temperature catalytic combustion analyzer. Initially, we recommend an effort to generate depth-concentration profiles of DOC and DON that could be related to the changes in inorganic pore water constituents, especially those indicative of redox transitions (e.g., the onset of sulfate reduction). Assays for microbial viability (e.g., DAPI staining and fluorescence) at the same depth horizons would be desirable. Later, larger pore water samples could be devoted to studies of the isotopic and chemical characterization of the DOM fraction. Measurements should be attempted in fluids from a wide variety of environments in order to identify the most important source (or sink) regions.

G.   Thermogenic Processes at Active Spreading Centers. Hydrothermal activity occurring in actively spreading ridges and back-arc basins buried under a sedimentary cover is of interest for organic geochemistry. This theme addresses the effects of high-temperature fluid interactions with sedimentary organic matter over the active spreading centers to determine the fate of the products and altered residues and to quantify sources and fluxes of carbonaceous species. Two such areas have been studied, namely Guaymas Basin, Gulf of California, by both deep sea drilling and submersible, and the Escanaba Trough, northeastern Pacific, by dredging and submersible (Curray et al., 1982; Kawka and Simoneit, 1987; Kvenvolden et al., 1986, 1990; Simoneit, 1985, 1990a).

Igneous processes there have pronounced effects on the chemistry of the hydrothermal fluids reacting with the basalts and sediments. The hydrothermal activity permeates the sedimentary column and can breach the seafloor, building up mounds and chimneys, many of which actively vent fluids at temperatures measured from warm to greater than 350^oC (Lonsdale and Becker, 1985). These fluids may carry large amounts of gases and petroleum (e.g, H_2S, CH_4 to high molecular weight organic compounds) derived from the thermal alteration of sedimentary organic matter (in these cases geologically immature) during hydrothermal circulation in the subsurface (Simoneit and Lonsdale, 1982; Simoneit, 1985, 1990a; Simoneit et al., 1988).

The generation, expulsion and migration of hydrothermal petroleum are extremely efficient and rapid (Simoneit, 1983; Didyk and Simoneit, 1989), occurring over a wider temperature window than conventional petroleum formation in slowly subsiding sedimentary basins (Hunt, 1979; Tissot and Welte, 1984). However, the products that have formed at different temperatures are admixed in the mounds at the seafloor (Didyk and Simoneit, 1990; Simoneit, 1990b), and thus the processes in such "field laboratories" must be studied versus subbottom depth where the

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products and residues are separated according to their origin (e.g., aliphatic hydrocarbons from low-temperature generation versus aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons [PAH], from high temperature generation). The compositions of these hydrothermal petroleums vary from volatile (condensate-type) to tarry oils consisting of methane to greater than C40 hydrocarbons and a myriad of biomarkers, hetero and polar compounds (Didyk and Simoneit, 1990; Kawka and Simoneit, 1990; Simoneit, 1985). Migration of products occurs in solution, suspension (emulsion) and bulk phase (Didyk and Simoneit, 1989; Peter et al., 1990). The role of organic complexing in metal sequestering and transport is not known. Organic matter alteration leaves a residue of carbon (spent kerogen after expulsion of petroleum) behind in the sediment (Simoneit et al., 1984), but its fate at greater subbottom depths is not known. Previous drilling (Leg 64 of DSDP) did not penetrate to basement and barely reached the greenschist alteration zone with poor core recovery.

Thus, drilling can address the following subtopics:

(1)   Depth trends of organic matter alteration in terms of   product, precursor and residue compositions and concentrations,

(2)   Migration and fluxes of all carbonaceous species,

(3)   Dissolved organic carbon (DOC), speciation and importance to inorganic processes,

(4)   Catalytic and complexing interactions,

(5)   Reactions or migration of residual carbon,

(6)   Interactions in the basalt "basement"/sediment zone and introduction of deep-sourced carbonaceous species,

(7)   Chemistry and stability of organic compounds at ultrahigh temperatures and pressures (organic metamorphism), and

(8)   Comparisons and intercalibrations with laboratory   simulations. These subtopics can only be accomplished by drilling and will benefit from close collaboration with other chemical, geological and geophysical expertise.

It is recommended to transect drill a minimum of three sedimented regions with active spreading centers, including one hole each in the recharge zone. These regions are the Guaymas basin where the source organic matter is of primarily a marine origin, to be contrasted with an area in the northeastern Pacific
(e.g., Escanaba Trough or Middle Valley) where the source organic matter is mainly terrestrial in origin. A third area for future consideration would be a sedimented back-arc system (e.g. Bransfield Strait). The drilling sites proposed at the present time are as given in Proposal 275E Revision to ODP for the Gulf of California and sites of opportunity with the scheduled ridge drilling program in the northeastern Pacific.

New methods for sample acquisition and onboard analyses need to be modified, developed and applied. The pressure core sampler (PCS) must be available for routine operation in a corrosive medium at high temperatures (maximum 350-400oC) and to hold the gas and fluid pressures expected. A manifold to quantify and remove gas, liquid and solid samples from the PCS needs to be designed, built and deployed. Analytical capabilities of the gas chromatographic (GC)

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system need to be upgraded to determine ephemeral gases, for example H2, CO2, CO, H2S, CH3SH, COS, CS2, N2, NH3, as well as the hydrocarbons (CH4 - C6H14 and benzene). Their analysis can be done by providing a GC with thermal conductivity, nitrogen/phosphorus, and sulfur (FPD) detectors. A temperature probe for downhole measurements is essential and hole logging is mandatory.

III. SAMPLING STRATEGY

The sampling strategy for organic geochemistry depends on the specific research problems being undertaken. Within the organic geochemical themes that we have proposed, however, there is a need for implementation of a shipboard organic geochemistry program in addition to the selected programs that meet the specific needs of the research themes. For the shipboard program, we recommend the following routine as well as non-routine procedures.

A.   Routine Shipboard Sampling Procedures. At present there is no clearly defined, routine program of analysis of organic geochemical parameters in ODP. This situation contrasts with that of the ODP inorganic geochemistry program which has its roots extending as far back as DSDP Leg 35 (Gieskes and Lawrence, 1976). In the inorganic program the following parameters are measured routinely in pore waters squeezed from sediment samples: alkalinity, salinity, Ph, cations of calcium, magnesium, and potassium and anions of sulfate and chloride. These parameters are generally ephemeral and must be determined immediately onboard or else the information will be lost forever. The wisdom of collecting these data has been verified by the increased knowledge that has been gained concerning the chemical processes taking place in oceanic sediments (e.g., Gieskes, 1981).

Organic geochemists have been remiss in not insisting that important organic geochemical measurements be routinely made as part of DSDP and now ODP. In order to move forward toward a routine shipboard organic geochemical program, we propose the following:

(1)   Routine sampling should include total organic carbon analysis (TOC) and headspace gas analysis for hydrocarbons (C1-C6) should be made once per section.

(2)   · These measurements should be performed in association with interstitial water, physical properties and lithologic descriptions.

(3)   Rock-Eval pyrolysis and pyrolysis-gas chromatography should be done on all samples with TOC values > 0.5 weight%.

Organic geochemical aspects of scientific ocean drilling have now matured sufficiently to adopt the use of sampling schemes designed for specific objectives and to forego the present practice of routine collection of frozen full-round sections. We recommend that the extant collection of archived frozen samples continue to be preserved, either frozen or freeze-dried, and that the lithology of the frozen samples be described and made known to the general scientific

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community. Further collection of a 25 cm full-round interval every third core should be curtailed. However, the opportunity to obtain a collection of complete frozen cores from holes dedicated to geochemical study should be retained for special circumstances (e.g., Holes 532B, 658C).

B.   Nonroutine Shipboard Sampling Procedures. Shipboard sampling facilities need to be available for the collection of samples for dissolved organic carbon and isotopic analyses of both gases and solids. Facilities should also be available to extract samples with organic solvents and perform gas chromatography of the extract.

IV.   NEW TOOLS/TECHNIQUES

In order to conduct the studies stated above on gas hydrates, a pressure core sampler (PCS) is required. This sampler will need a manifold for gas collection, a means to quantify the gas, and a temperature bath. In the future, a smaller volume sampler will be required and another that can withstand higher temperatures and acidic environments, for the thermogenic processes investigations on active spreading centers.

Future capabilities onboard ship should include the ability to measure fixed gases including CO and CO_2 and sulfur and nitrogen compounds. There is also interest in more routine use of the carbon logging tool.

V.   LONG-TERM MONITORING

There is an interest in the long-term monitoring of the formation and degradation of gas hydrates and the flow rates and composition of low molecular weight organic compounds in both high-and low-temperature convective systems.

VI.   LOCATIONS OF INVESTIGATIONS

A.   Convergent margins for the monitoring of petroleum source-rock potential and for studying fluid migration in accretionary prisms and subduction complexes.

B.   Complete stratigraphic sections (associated with geochemical reference holes, paleoceanographic holes, etc.) for global carbon inventory, organic diagenetic investigations, and paleoclimatologic, paleoceanographic, and paleobiologic studies.

C.   Gulf of Mexico and/or Gulf of California for the sampling of possible thermogenic and biogenic gas hydrates.

D.   Continental margins off of Peru and/or Guatemala and under upwelling areas off Mauritania and Namibia for the detailed investigations of the dynamics of formation of biogenic gas hydrates.

E.   Ridges in the northeast Pacific and Gulf of California, young marginal basins in the Mediterranean Sea, and back-arc spreading centers for the investigation of thermogenic processes.
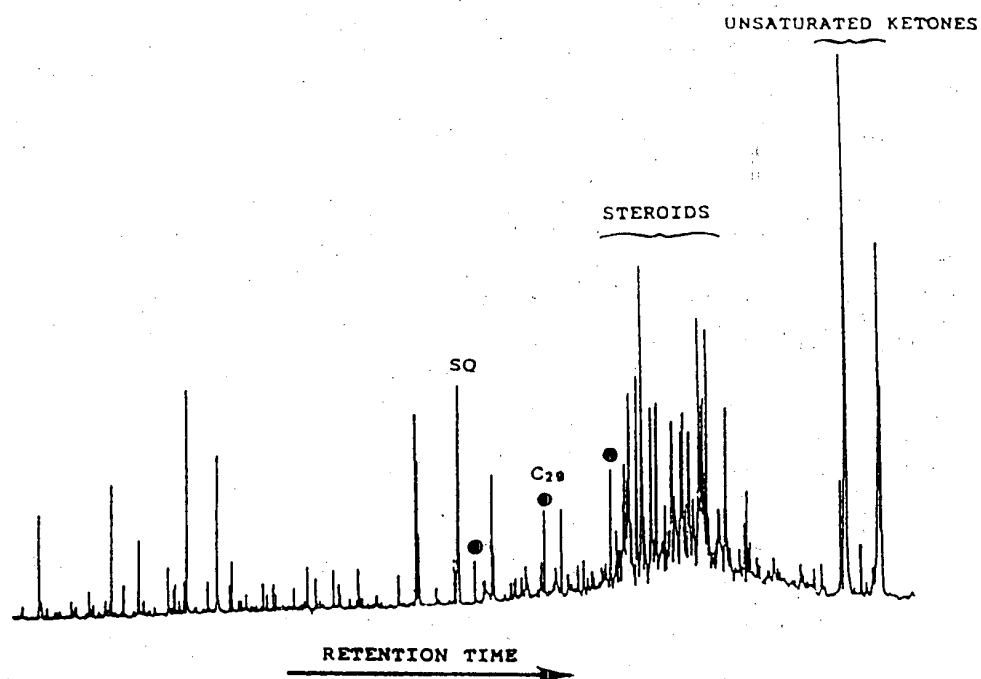
Figure 2. Gas chromatogram of total extractable lipid material from ODP sample 108-658A-21-6, 7-14 cm (late Pliocene). C27, C29, and C31 n-alkanes are identified by dots; SQ indicates squalane. (From Poynter et al., 1989)
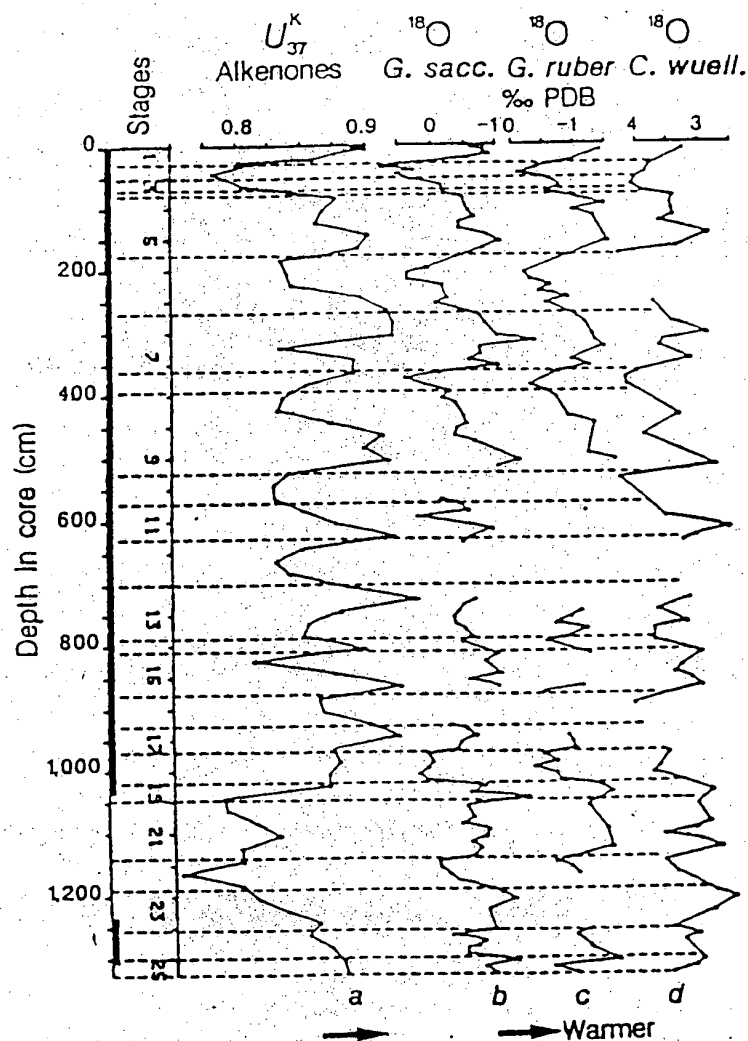
Figure 3. Comparison of downhole measurements of the UK37 ratio and δ18 values of foraminifera in Meteor core 1641502 from the Kane Gap offshore northwest Africa. G. sacculifer and G. ruber are planktonic, and C. wuellerstorfi is benthic. (From Brassell et al., 1986)

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ATMOSPHERE
3.6

MARINE BIOTA
3

SEA

SURFACE
30

INTERMEDIATE
250

DEEP
700

DISSOLVED
ORGANICS
IN WATER

GAS
HYDRATES
10,000

LAND

LAND BIOTA
830

DETRITUS
60

PEAT
500

SOIL
1400

FOSSIL
FUEL
5000

DISPERSED CARBON
20,000,000

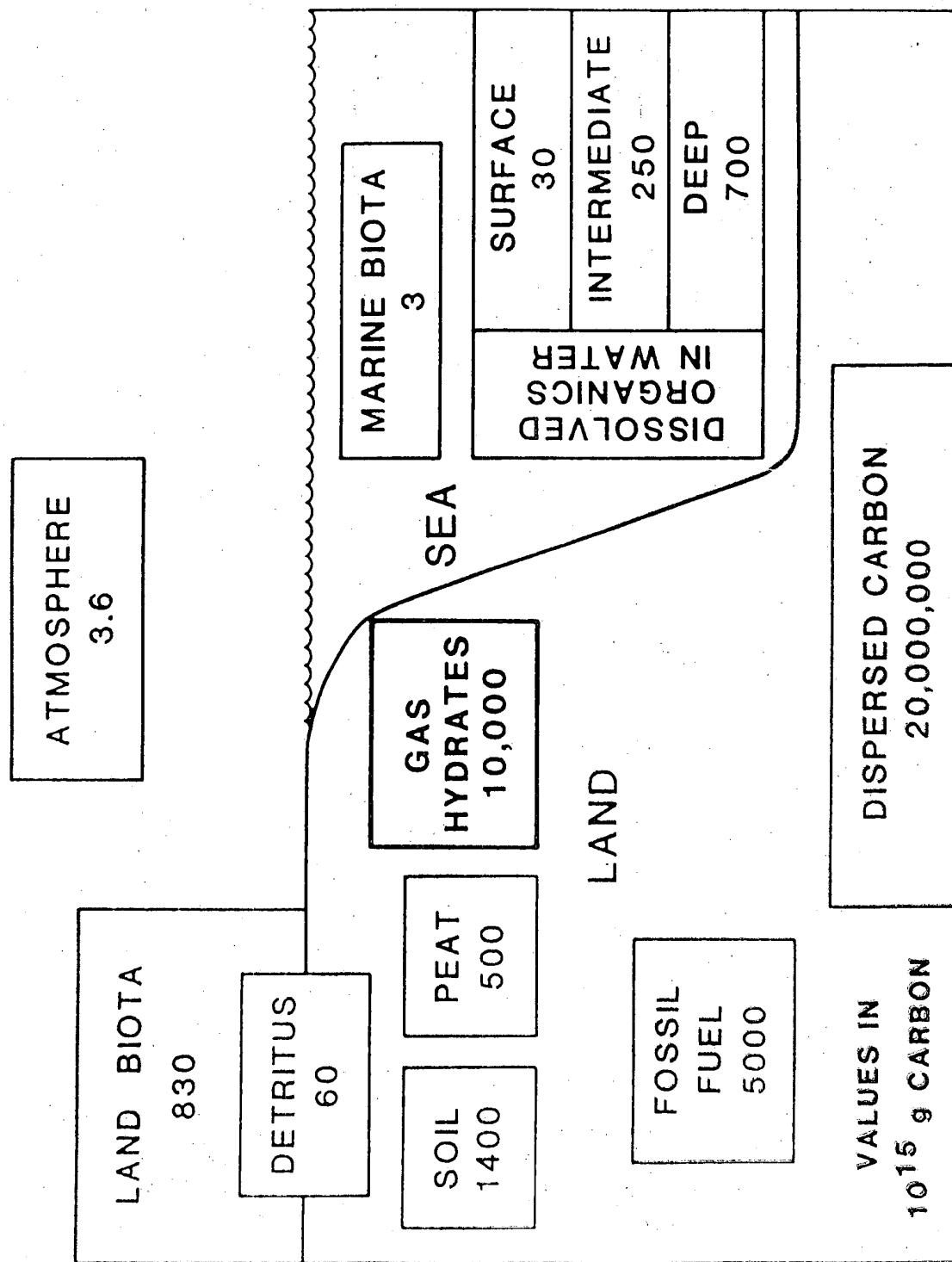VALUES IN
10^{15} g CARBON

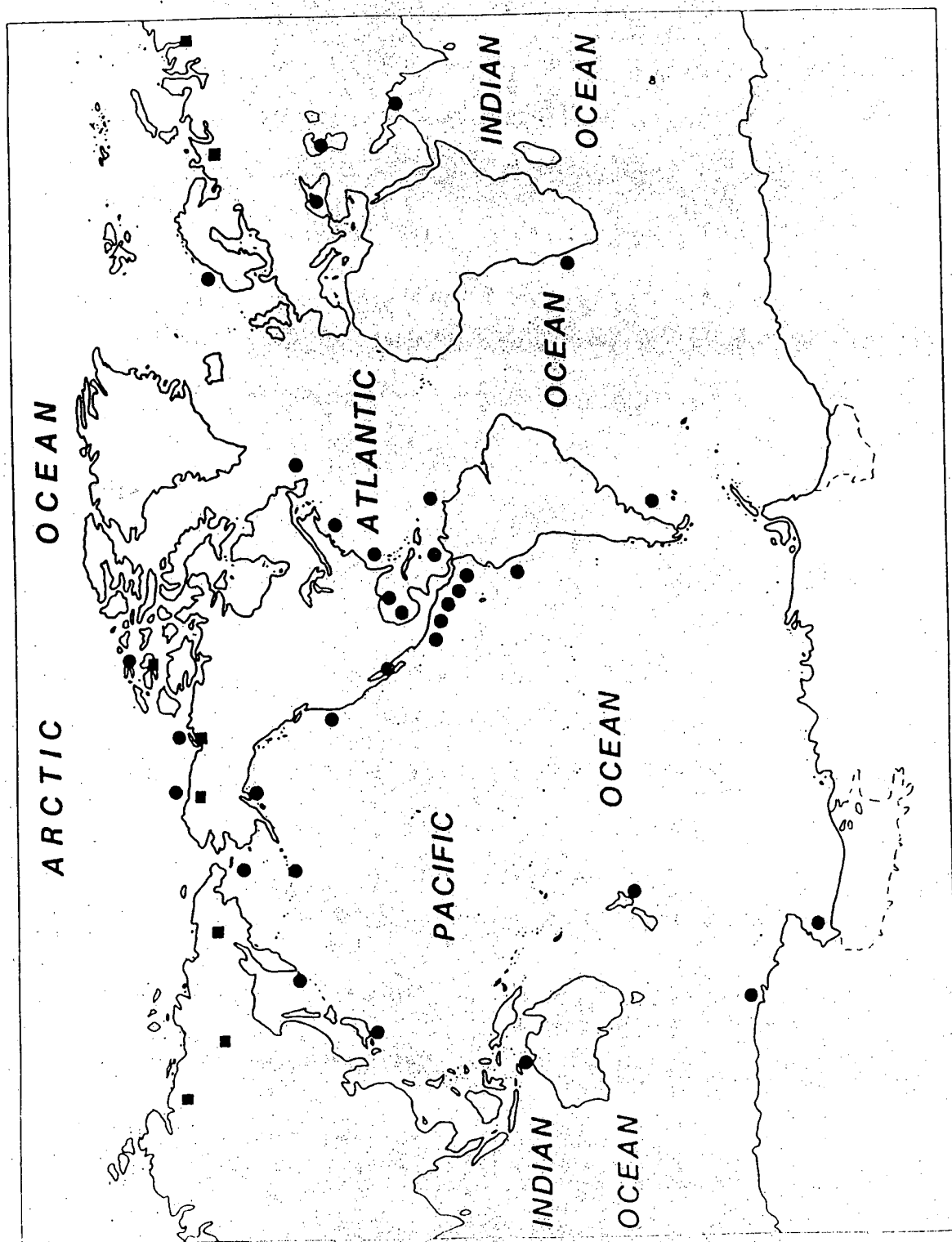Figure 4. Organic carbon in some reservoirs of the carbon cycle (adapted from Moore and Bolin, 1986/1987).

Figure 5.   Distribution of known gas hydrate occurrences.

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PALEOCEANOGRAPHY

I. INTRODUCTION

The goal of the paleoceanography group is to understand the physical and chemical behavior of the ocean as a component of the ocean-atmosphere-cryosphere-lithosphere system. Paleoceanography is concerned with the circulation of the ocean in the past and with the processing of particulate and dissolved inputs to become sediments and weather oceanic crustal rocks. Fluxes at the surface of the earth are driven by exogenic forcing, principally solar radiation, and by endogene forcing related mostly to the flow of heat from the deep interior of the planet. Variations in the exogene and endogene forcing have resulted in changes in climate on the surface of the Earth and in changes in the fluxes of materials delivered to and output from the ocean.

Investigations of the past decade have suggested that in the past there may have been modes of circulation of the ocean and atmosphere radically different from that observed today (Brass et al., 1982a; Brass et al., 1982b). It has also become apparent that the global fluxes of surficial materials on the planet have changed significantly on time scales from tens of thousands to hundreds of millions of years (Delany and Boyle, 1988). During the late Phanerozoic the output of sedimentary materials in the ocean has been about 30 to 50 of the global total; although the sedimentary record in the ocean basins only includes the later Mesozoic and Cenozoic, it shows significant temporal and spatial variations, recording global environmental change from an era with warm polar temperatures and low meridional temperature gradients to the ice age conditions of the Pleistocene with extreme meridional gradients (Savin Hay et al., 1987; Hay, 1988).

II. NEW OPPORTUNITIES

What is new that allows us to progress beyond what was possible before? We can make progress because:

(1) We can now, in some instances, make correlations to +/- 10 Ky (eg. Yu et al.,1990).

(2) We have some new proxy indicators, and other prospective indicators are being developed (Boyle, 1986; Boyle, 1988; Murname and Stallard, 1988; Shemesh et al., 1989).

(3) We are beginning to accumulate a reference set of climate models, both atmospheric GCM's and coupled ocean/atmosphere models (Barron, 1984; Barron, 1986; Parrish and Barron, 1986).

III. THE INFORMATION BASE

The information base on which interpretation of paleoceanographic conditions rests decreases

with increasing age, so that we know less and less about the conditions on Earth when the atmospheric and oceanic circulation were increasingly unlike those of the present and recent geologic past. The decrease of information with age reflects a number of factors:

(1)   destruction of the record with age as a result of erosion, diagenesis, subduction and metamorphism, reducing the size of the database (Moore et al., 1978).

(2)   loss of the record from regions where ocean floor has been subducted (Sclater et al., 1980).

(3)   uncertainty of the paleogeography of the Earth, especially the location of suspect terranes at times in the past (Sengor, 1987, Wilson et al., 1989)

(4)   decline of the precision of stratigraphic correlations due to the less complete record and, throughout much of geologic time, to less frequent and less extreme changes in environmental conditions than during the immediate geologic past (Riedel, 1981; Moore and Romine, 1981).

(5)   less certainty of the interpretation of proxy indicators for environmental parameters (discussions in Savin, 1981, Barron, 1987 and Woodruff and Savin, 1989).

It follows that the most significant paleoceanographic problems that can be solved during the 1990's are differ both qualitatively and quantitatively for increasingly ancient periods.

IV.   THE PROGRAM

We propose a comparative study of paleoceanography conditions prevailing during the six most different states of conditions on the Earth's surface during the past 100 m.y.:

(1)   The Modern Earth

(2)   The Bipolar Glacial Earth - The last glacial maximum

(3)   The Monopolar Glacial Earth - The Late Miocene

(4)   The Warm Earth with Minimal Meridional Temperature Gradient - The Early Eocene

(5)   The Warm Earth with Moderate Meridional Temperature Gradient and Oxic Oceans - The Maastrichtian

(6)   The Warm Earth with Maximal Ocean Anoxia - The Cenomanian-Turonian Boundary

The modern earth serves as a reference standard; we do not plan research into modern conditions, but recognize that it is important to compare the nature and rates of processes in the past with those of today, as well as to recognize the implications of the studies of ancient environmental conditions for predictions of future global change. It is important to remember that the interglacial conditions that prevail at present are an extreme and have been short-lived in the past. Climates comparable to the Holocene have occurred only during 10% of Quaternary time.

The timing and extent of the major climatic fluctuations from glacial to interglacial conditions during the Quaternary are quite well known, but the ultimate cause of the ice age remains elusive (Ruddiman et al., 1986; Molnar, 1990). For the Earth's recent past, the Late Pliocene and Quaternary, when the south pole has remained glaciated and the northern hemisphere continents have alternated between extensive glaciation and restriction of the ice to a few large islands, the most important problems to be tackled involve investigating the interrelations between changes in solar insolation, atmospheric circulation, oceanic circulation, changes in the composition of the atmosphere, growth and decline of ice sheets, sea level change, isostatic response of the earth's crust, and apparent uplift of many regions of the Earth. deal with the mechanisms controlling Quaternary climate and the relationship between ocean climate, atmospheric chemistry and atmospheric climate. Most of these questions can be examined adequately by study of piston cores, and sampling by drilling is required only on the continental margins.

During the Late Miocene, the Earth had an extreme asymmetrical distribution of ice resulting in asymmetric atmospheric circulation (Flohn, 1981). Antarctica was extensively glaciated whereas the northern hemisphere continents were ice-free. The upwelling systems on the western margins of the continents were more intense than before or since. Sediment flux to the ocean was typical of the earlier Miocene and Oligocene, only half that prevailing during the Pliocene and Quaternary. Within the Late Miocene stratigraphic correlations can, in many instances, be made with a precision of 10 to 50 ky. Although hiatuses are abundant in the Late Miocene, much of the global record is preserved, and the paleogeography is well known.

Paleoceanographic reconstructions will permit us to examine the differences between the horizontal and vertical circulation of the oceans on a monopolar glacial Earth with the bipolar glacial Earth of the Quaternary. It was a time of changed boundary conditions: a restricted Central American seaway and Tethys; tectonically and climatically induced desiccation of the Mediterranean; beginning of uplift of large highland areas and mountain ranges (Kennett, 1985; Woodruff and Savin, 1989).

The existing geochemical and fossil data indicate that the Early Eocene may have been the warmest interval in the Earth's history; it was the only warm period to leave a record at all latitudes in every ocean basin (Shackleton and Boersma, 1981). Both geochemical and paleontologic evidence suggests that the polar and equatorial temperatures were very nearly equal, a condition that is both intriguing and difficult to understand (Cirbus Sloan and Barron, 1990). Constraints imposed by more restricted Paleogene sedimentary record, by diagenesis, and

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by greater uncertainties in the interpretation of proxy indicators will prevent paleoceanographic analysis at the same resolution possible in the Neogene. The major excursion of the 13C/12C ratio of dissolved inorganic carbon in the middle Eocene ocean may represent the beginning of climate instability and deterioration, but the major cooling episode that initiated the trend of high latitude and deep water cooling did not begin until the latest Eocene (Miller and Fairbanks, 1983; Miller and Fairbanks, 1985; Miller et al. 1988). Although time stratigraphic correlations might not be as precise as those of the Late Miocene or Quaternary, the potential uncertainties of temporal correlation are offset by the fact that the climatic fluctuations were evidently much less, and during the Early Eocene the state of atmospheric and oceanic circulation did not change over millions of years. The present distribution of DSDP and ODP sites with Paleogene sediments is such that large areas of the ocean, particularly the Pacific, are underrepresented. This has limited the resolution of Paleogene paleoceanographic reconstructions. In addition, in several regions the available Paleogene records are of poor quality as a result of low rates of recovery, due to our past inability to recover soft sediments interbedded with cherts.

The drastic transient environmental changes that occurred at the Cretaceous-Tertiary boundary have been discussed at length elsewhere, and will undoubtedly continue to be studied as the best known example of global catastrophe.

The Maastrichtian was a time during which there was a moderately strong equator to pole temperature gradient, but the polar regions were still temperate. The oceans received large quantities of calcium carbonate but little detrital sediment, a condition of supply opposite to that of today (Southam and Hay, 1981) The spatial record is restricted because more than half of the Pacific basin floor that existed during the Late Cretaceous has subsequently been subducted. Changes in biota during the Maastrichtian suggest gradual climatic deterioration, but paleomagnetic reversals and pronounced cyclic changes in sedimentation should permit a precision of correlation comparable to that of the Late Neogene.

During the Cretaceous there were several episodes during which the deep waters of the ocean became anoxic or suboxic (Hallam, 1987; Summerhayes, 1987). The best documented and most widespread of these was the transient episode of ocean anoxia that occurred at the boundary between the Cenomanian and Turonian Stages (Schlanger et al., 1987; Arthur et al., 1987). Stratigraphic correlation of this interval can be quite precise and recognized on a global scale even in the absence of carbon rich facies by a very sharp, well-defined, large excursion of the 13C/12C ratio. This episode is especially well documented in the Atlantic Ocean, the Tethys and in marginal seas, but most of the Pacific Basin that existed at the time has subsequently been subducted. The states of atmospheric and oceanic circulation under which extensive areas of the ocean can become anoxic are surely very different from those of other times, and may be especially significant in representing an extreme of environmental changes without extraterrestrial forcing.

V.   SOURCES OF INFORMATION

Our source of information about the ocean in the past has come mostly from materials preserved

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on the sea floor and in the weathered ocean crust. The Ocean Drilling Programs have produced the largest organized and homogenous data base on sedimentary materials for any part of the earth, and despite the problems of uneven coverage, represents 70% of the surface of the globe. The recent wide distribution of the Deep Sea Drilling Project data base in the form of CD-ROM's to be used with personal computers revolutionizes access to the large body of analyses (National Geophysical Data Center, 1989).

One potential source of new data is the cores which have already been taken and reside in the core repositories; but many of the goals proposed here will require acquisition of new materials. The existing material provides the indispensable background information to allow us to select sites where there is a high probability of obtaining the samples required for new analyses.

The existing core collection is overwhelmingly sediment and sedimentary rock.However, an important sink for materials entering the ocean may be the minerals formed by weathering of the oceanic crust and causing alteration. Attempts at quantification of these fluxes are meager and wholly inadequate to give any idea of the possible variations over geologic time. Further analysis of existing material may provide some new information, but recovery of additional materials is essential.

Another potential data source is the collection of log information which have been obtained later in the Deep Sea Drilling Project, but much more significantly during the recent years of Ocean Drilling Program operations.

Auxiliary sources of samples may be core materials in the repositories of the U.S. Geological Survey and of industry. In most instances the cores taken by industry were taken for specific objectives related to hydrocarbon exploration, and represent a selection of data different from that which the scientific community may require, but efforts should be made to develop closer contacts and evaluate the usefulness of this source.

The primary source of new data will be samples taken at critical locations for the specific purpose of providing the information necessary to decide between alternative hypotheses.

It is important to continue the efforts to integrate information and ideas about the paleoceanography of the ocean basins proper with studies of shelf and marginal seas, where shallow water depths or restricted connection to the open ocean result in positive or negative fresh water balances and result in differentiation of water masses.

Integration of the information gleaned from study of deposits found on land with that from materials recovered from beneath the sea must be developed. Land areas offer important clues to ancient climates and atmospheric circulation.

VI.   CLIMATE MODELS

Numerical climate models are experiments attempting to reproduce physical conditions in the

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atmosphere and ocean by calculations from first principles (Barron, 1984; Barron, 1985). Climate models for ancient times are hindcasts of the physical conditions that should have existed. They are useful in determining whether the assumptions regarding boundary conditions (the specified distribution of land and sea, composition of the atmosphere,etc.) are reasonable; if the conditions hindcast by the model do not resemble the paleoenvironmental conditions interpreted from proxies, it is likely that the model boundary conditions were incorrect. Climate models are also useful in identifying regions that are particularly sensitive to changes in external forcing. At present, the resolution of global climate models available for paleoclimate studies is coarse, usually a grid of 4 x 7 degrees. However, as computing capabilities increase during the next decade, the resolution will become finer and the results more readily related to real world data (Simmons et al., 1988). The results of experiments with global or regional atmospheric climate models and with coupled ocean-atmosphere climate models base on ancient boundary conditions should be incorporated into future paleoceanographic problem definition (eg. Luther et al., 1990).

VII.   THE OCEAN SYSTEM

The ocean can be regarded as a major component of the complex of interacting fluids and solids forming the Earth's surface layers. The ocean is the largest fluid reservoir in terms of both the mass of water and of dissolved materials. Seen as the central component of the earth's surface system, the ocean receives inputs from land and the atmosphere as well as from fluids circulating through the underlying ocean crustal rocks and expelled from the sediments deposited on the ocean floor and margins. Material entering the ocean in either particulate or dissolved form is processed and removed from the water as either sediment or weathering products of crustal rocks. Ultimately, material deposited on the ocean floor is subducted to return to the mantle or become volcanic, or is obducted onto the continental blocks.

A.   Inputs. We need to know more about the spatial and temporal variations of material inputs to the system:

> River
> Ice
> Eolian
> Volcanic
> Hydrothermal
> Groundwater
> Dewatering of sediment wedges
> Compaction of sediments

Rivers are the most important agents delivering material to the sea (Garrels and Mackenzie, 1971). Pinet and Souriau (1988) have evaluated factors affecting the sediment supply to the sea at present. Garner, 1959 noted that humid and arid climates produced coarse and fine grained sediments respectively from the same mountain range. Raymo et al. (1988) have suggested that mountain building processes may markedly affect sediment the supply both in terms of quantity

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and type of material. Perlmutter and Matthews (1989) have shown how changing climate must affect sediment supply on a regional and global scales. How have these responded to changes in rates of tectonic activity (ie. rates of sea floor spreading, subduction, vertical uplift, and mountain building), climate change, sea level change, changing groundwater flow and changing rates of sediment delivery and loading? Under what conditions are materials left stored on land; what conditions result in delivery to the ocean? We must devise methods for deconvoluting the mixed signal from all these sources represented by sedimentation in the global ocean, and enough is known that the problem may not be as complex as it might at first seem.

Changes in the groundwater flux directly into the oceans through continental margin sediments must surely have occurred as a result of sea level rise and fall, and may also have occurred in response to changes in the hydrologic cycle on land (Hay and Leslie, 1990). Changes in the groundwater flux cause diagenetic changes within the margin sediments.
The rate of expulsion and composition of water driven out of compacting sediments is a function of their accumulation rate and composition. The solutes contained in the expelled waters constitute a major flux into the ocean (Sayles, 1979; Kastner, 1981; Sayles, 1981). The composition of waters being expelled from different oceanic sediments is being determined by projects currently underway, such as the Global Ocean Flux Study (GOFS).

The dewatering of sediment wedges is especially large where subduction is occurring. Preliminary estimates suggest that the flux of solutes out of these wedges may, for some elements, be of the same order of magnitude as the dissolved load of rivers (Han and Suess, 1989). It is critical to predictions of global environmental change that this source be quantified.

Delivery of eolian materials reflects atmospheric transport paths and also offers clues to the climatology of the source regions (Prospero, 1981; Sarnthein et al., 1982; Leinen et al., 1986; Clemens and Prell, 1990).

The delivery of volcanic materials to the surface of the earth has varied greatly through time (Kennett, 1981); what effects does the subsequent weathering of massive outpourings of ash or basalt have on inputs to the ocean system?

B.   Interior Processing.   Distribution of river and ice-borne terrigenous materials depends on surface and deep currents at the sites of delivery to the ocean. Deposits of terrigenous materials can be used to estimate the size of drainage basins and location of divides directing water to different ocean basins (Hay et al., 1989; Shaw, 1989). Information on the provenance of material can be sued to learn about the delivery of fresh water to the ocean, as well as to learn about climatic conditions within the drainage basins.

The processing of dissolved material by the ocean is largely moderated by organisms (Broecker, 1971; Lisitzin, 1972; Broecker, 1974; Berger, 1981; Berger et al., 1981; Barron and Whitman, 1981; Kennett, 1982; Broecker and Peng, 1982). The outputs of calcium carbonate and opaline silica, the two major mineral components fixed by planktonic organisms and accounting for most of the rain of pelagic sediment, have very different distributions. This presently relates to the

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peculiarities of their production and dissolution. At present the silica secreting diatoms are most effective at utilizing nutrient-rich water, and the carbonate-secreting organisms utilize less nutrient-rich areas.

The ocean system responds to vertical motions of the water; within the surface layer, convergences form fronts along which surficial downwelling occurs; divergences induce upwelling of near surface waters. Downwelling of water to intermediate and greater depths occurs in relatively isolated regions where the water can be become greatly differentiated from normal seawater. Downwelling of water to form intermediate and deep water masses of the ocean presently supplies oxygen to the interior whilst diffuse abyssal upwelling water gradually returns nutrients to the near surface whence more localized mixing or upwelling can introduce it to the photic zone. How have the processes and specific sites of downwelling and upwelling changed through time? What mechanisms of dense water production have prevailed in the past? At present dense water is thought to be formed by four mechanisms: 1) increasing salinity by expulsion of salt during the formation of sea ice, 2) chilling of water by the atmosphere, 3) increasing salinity by evaporation, and 4) mixing of waters of equal density but different temperature and salinity (Apel, 1987). At present the first two mechanisms appear to dominate the global system, but any of these may have been the most important mechanism at different times in the past. Fronts on the ocean surface mark regions of oceanic convergence and downwelling; they mark the boundaries between different climatic regimes. They often leave a distinctive record in the sediments (eg. Morley, 1989).

The vertical motions of the water can be grossly interpreted from the distribution of pelagic sediments and organic carbon. However, paleoceanographic interpretation needs identification of major water masses. In the ocean today the major water masses of the ocean interior are distinguished by knowledge of a combination of the following properties:

Temperature
Salinity
Nutrient Content
Oxygen Content
Silica Content
Alkalinity

VIII. PROXIES FOR ENVIRONMENTAL PARAMETERS

In order to test the hindcasts of models of the climate at times in the past, some of the physical conditions existing at times in the past, such as surface temperature, salinity, and patterns of oceanic circulation, must be known. The recent studies by Woodruff and Savin (1989) provide a model of the kinds of paleo-ocean transects that are needed. The record of these physical conditions in ancient ocean is contained in deep sea sediments in form of micropaleontological, geochemical and sedimentological proxies. However, some of the proxies

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used to interpret paleoclimate may be affected by subsequent alteration processes, limiting their effectiveness. For example, the oxygen isotopic composition of calcareous microfossils, which is a paleotemperature proxy, can change during diagenesis, overprinting or removing the original isotopic signature. Other proxies can be affected in similar way as well. If we are to extend the usefulness of such valuable proxies back in time, better criteria for identifying sediments that have undergone diagenesis must be established. This may involve integrated multiple isotope and trace element geochemical studies of specific sequences with contrasting lithologies. Independent proxies for the same parameters should be developed as well.

A.   Proxies for Oceanic Circulation. Ancient patterns of surface ocean circulation have traditionally been reconstructed by documenting the distribution of shallow water and planktic fossils. The deep water circulation can be traced by measuring and comparing the carbon isotopic composition of benthic foraminifers (Curry et al., 1988). This method is based on the observation that as deep waters migrate along the ocean floor they collect isotopically light carbon from the decay of raining particulate organic matter. Thus the relative age of a deep water mass can be estimated by the carbon isotopic composition of its dissolved inorganic carbon, a value that is recorded by benthic foraminifer residing within the water mass. By comparing the compositions of foraminifers from within and between basins, one can estimate the rate and patterns of deep ocean circulation. Similar information can also be attained from the distribution of sediments that are carried by currents (e.g. clays). Proxies that hold potential but have not yet been tested, include neodymium isotopes. Nd which has two isotopes, one that is daughter product of radioactive decay, shows systematic variation in the modern ocean. This is due primarily to the fact that the major input of the radioactive daughter isotope is in the north Atlantic through runoff and because of the short residence time of Nd. Since Nd is incorporated into foraminifer shells without fractionation, analysis of fossil foraminifers from different basins may provide clues to ancient circulation patterns.

B.   Proxies for Atmospheric circulation. At present there are a number of proxies that reflect atmospheric circulation (Rea et al., 1985). Dust grains transported by the winds form eolian sediments, and can often be traced to specific sources. The distribution of these grains in the ocean have been tied to zonal winds. In addition, there are less direct indicators of wind patterns. Upwelling zones occur under regions where wind patterns cause divergence of surface waters. This occurs predominantly along the equator and in the polar convergence zone. The upwelling of deep nutrient rich waters usually increases the level of productivity. Sediments underlying these zones become rich in the products that are characteristic of high productivity regions, primarily silica and organic matter. Mapping the distribution of such deposits in ancient oceans also provides vital information about atmospheric circulation.

C.   Proxy indicators for watermass properties. Proxy indicators for some of these watermass properties are already known and there are prospective proxy indicators for some of the others:

   Temperature: Oxygen Isotopes, Degree of saturation in ketones

   Salinity: Oxygen isotopes, Ba ?, Interstitial water chlorinity ?

Nutrient Content: Carbon isotopes, Cd

Oxygen Content: Carbon isotopes, Benthic foraminifers

Silica Content: Ba ?

Alkalinity: Carbonate dissolution rates?

IX.   STRATIGRAPHIC CORRELATION

The global description of paleoceanographic conditions from proxy indicators of water mass properties depends on high-resolution stratigraphic correlations between widely separated locations. The paleontologic, paleomagnetic, isotopic and chemical criteria used in stratigraphic correlation and their calibration to the numerical time scale are being continually reviewed and reevaluated (eg. Aubry et al., 1988). The interpretation of process rates is dependent upon the numerical ages assigned to stratigraphic intervals and horizons. However, assignments to the numerical time scale based solely on biostratigraphic and magnetostratigraphic data has limited application. Complete preservation of the original magnetic reversal signal throughout an entire cored sequence is rare; in the worst case, the paleomagnetic signal has been totally overprinted. Without adequate paleomagnetic control, stratigraphic correlations must be made using fossil bio-assemblage zonation schemes which have uncertainties in the order of one million years. In addition to the uncertainties of precision, biostratigraphic correlation is also limited because the distribution of most species is not global; high latitude regions and marginal seas often have restricted assemblages.

Significant enhancement of stratigraphic correlation has come from the use of stable isotopes. Oxygen and carbon isotope stratigraphy has become standard for those parts of the time scale in which significant variations occur. However, fluctuations of the relative abundances of isotopes of these elements are small throughout much of geologic time.

Recently, the addition of strontium-isotope stratigraphy to the inventory of stratigraphic correlation tools has offered great hope for significant progress (Koepnick et al., 1988). The residence time of Sr in the oceans is long relative to the residence time of water, hence the Sr-isotopic composition of the oceans is homogeneous, with the exception of some restricted environments. The Sr-isotopic ratio of sea water is incorporated into the calcareous shells of living organisms. Thus, a record of the paleo-Sr isotope ratio of sea water can be recovered from calcareous fossils in the sedimentary sequence. This record indicates that the ratio in sea water has not remained constant with time. Detailed knowledge of the structure of the Sr-isotope sea-water curve through time provides an excellent potential to date a sediment for which the Sr-isotopic ratio is known. The production of this age curve is dependent upon the quality of the paleomagnetic and biostratigraphic data with which it was calibrated. High-resolution Sr-isotopic studies of specific Neogene time slices have demonstrated that there are periods when the curve is steep (ideal for high-resolution age dating) and when it is flat (poor

for age dating). In order to benefit fully from this potentially powerful stratigraphic tool and better define the detailed structure of the sea water curve, a concentrated effort should be made to secure routine Sr isotope measurements of cored marine pelagic sequences. The more Sr-isotopic data in conjunction with high-quality paleomagnetic and biostratigraphic control, the better the resolution of age dating using the Sr-isotope sea-water curve will become.

In addition to its stratigraphic potential, Sr isotopes are an ideal tracer for studying changes in the rate of fluxes to the ocean. The Sr isotopic ratio of sea water is thought to be controlled by a combination of fluxes with varying isotopic compositions, i.e. river and hydrothermal inputs plus dissolution of marine carbonates. Changes in the rates of these fluxes (and perhaps others) would result in changes in the Sr isotopic ratio of sea water. Thus, the compiled Sr-isotope sea water curve is a record of changes in influx rates. Knowing the temporal distribution and magnitude of these changes could give valuable information for understanding material mass balances to and from the oceans and thus be indirectly related to mantle processes (hydrothermal activity) and the terrestrial climate record. Strontium isotope studies of marine sediments offer new potential for advancing paleoceanography, both as a stratigraphic tool and as a tracer for mass balance estimates.

X.   DIAGENESIS

Diagenesis is important both as a source of and sink for solutes from the ocean, and as a source of false signal or noise in the interpretation of paleoceanographic conditions.

A large part of the paleoceanographic information obtained from the study of deep sea materials relies on sediment chemistry. In most cases it is necessary that the sediment components that are studied have retained the chemical (or isotopic) compositions acquired at the time of their formation or sedimentation.   Much work in recent years, based both on pore water composition and on sediment petrography and chemistry, has indicated that diagenetic alteration, especially of carbonate components of ocean sediments is widespread, even in some Neogene sediments. Much early paleoclimatic work, especially that based on stable isotope ratios, did not pay adequate attention to the possibility of diagenetic alteration. It is important that in future work, the degree of diagenetic alteration of proxy oceanographic indicators be carefully monitored, and that new approaches be developed to monitor the state of preservation of the paleoclimatic signal.

XI.   SPECIFIC REGIONS

A.   The Polar Regions. The regions of the Earth most sensitive to environmental change, the polar regions, are also the regions where the least amount of scientific ocean drilling has taken place (Thiede and Vorren, 1988). Several Legs have explored parts of the Southern Ocean and Antarctic margin, but the Arctic has remained essentially inaccessible.

The role of the Antarctic continent in influencing ocean chemistry is largely unknown. The area of Antarctica is 13.2×10^6 km^2 (approximately half the size of North America), and during the

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Mesozoic and early Cenozoic the continent was not glaciated and probably had a humid climate. Erosional processes during that interval must have delivered large amounts of sediment to the continental margins and weathering products would have influenced the chemistry of the world oceans. There is also evidence that at certain times during the late Paleogene and in the Neogene there were warmer intervals during which the volume of Antarctic continental ice was greatly diminished. Erosion by water and ice streams must have been important during those intervals.

The influence of Antarctica on global climate has been most commonly viewed in the light of its modern configuration - a large, glaciated landmass approximately bisected by a large mountain range. This results in the oceans surrounding the continent being important sites of intermediate and deep water formation. It affects meridional heat transport at high latitudes. This view of Antarctica is not appropriate for the Mesozoic and early Cenozoic. Then, ice cover on Antarctica was greatly reduced or absent. There is evidence that during that time a seaway traversed the Antarctic continent from the Ross Sea to the Weddell Sea, and it is likely that a number of other marine basins existed at that time. Furthermore, the continent was not well centered over the South Pole as it is today. These may have greatly altered the role the Antarctic continent played in global climate.

Drilling in Antarctic waters has so far been limited to the area of the Ross Sea, the Weddell Sea, and Prydz Bay. The influence of Antarctica on both climate and sediment budget could be greatly clarified by a major drilling program in this region. In spite of difficulties of drilling on the Antarctic continental margin, this is of high priority for paleoceanographic interpretations.

There is virtually no paleoceanographic information from the Arctic Basin. Knowledge of ancient conditions in the Arctic is absolutely essential to gain insight into how the Earth has responded to environmental change in the past. It is recognized the JOIDES Resolution cannot operate in the Arctic ice pack, and alternative methods for the recovery of core materials must be pursued.

B.   Depth Transects. To facilitate the reconstruction of paleocirculation patterns, it will be necessary to provide depth transects of submarine plateaus in critical regions. These depth transects allow for the reconstruction of the vertical distribution of deep water masses in ancient oceans. Such transects should be conducted for times representing each of the Earth's major states in all three major ocean basins. Potential locations include the Shatsky Rise in the Pacific, the Kerguelen Plateau in the Indian Ocean, Walvis Ridge in the South Atlantic, and Maud Rise in the Southern Ocean.

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GLOBAL CRUSTAL MASS BALANCE

I.   PREAMBLE

It will be possible to examine global mass balances in large part by the study of material obtained from globally distributed sites drilled for other objectives. However, it is possible to define many specific site objectives relative to globally integrated signals. Some very important aspects of global balances can be approached by extrapolation from one or more key sites in particularly sensitive or important regions; others may be approached primarily by using data from sites drilled for other objectives. Obviously, adequate global mass balances will depend on the existence of a global distribution of sites spanning at least 180 my, with continuous records and complete sampling. There is no doubt that this objective will not drive the drillship, yet this is one of the most fundamental aspects of earth history. Success in this endeavor requires imaginative development and application of geochemical/ isotopic tools that help to constrain or extrapolate to mass fluxes and their changes through time.

As a general objective, an understanding of the importance of transfer among various crustal reservoirs and processes involved requires 2 fundamental types of data: 1) component accumulation rates (carbonate- and organic C, terrigenous detritus, volcanic components, hydrothermal components) in sedimentary reservoirs as a function of time, which provide the historical context of crust/mantle mass exchange, and 2) secular records of isotopic ratios and other geochemical indicators for elements of key importance in geochemical cycling-- O, C, S, Sr, Nd, Li, B, Ge/Si, Sr/Ca and Mg/Ca in biogenic calcites, etc. The latter provide clues to the directions of mass transfer and, to some extent, the processes involved, including low and high-temperature alteration of oceanic crust and its effects on seawater chemistry (O, S, Sr, Nd, Li, B isotopes, Mg/Ca), variations in weathering of continental crustal rocks and fluvial transport of solutes to the oceans as a function of tectonic and/or climatic change (C, S, and Sr isotopes, Ge/Si, Sr/Ca), etc. No single secular trend can constrain all possible processes, and, therefore, the judicious use of a combination of indicators as well as accumulation-rate data will be necessary.

II.   OBJECTIVE 1: ALTERATION HISTORY AND CHEMICAL SIGNATURES OF OLD OCEANIC CRUST

At present there are no sites that penetrate a significant depth into older oceanic crust, far from ridge hydrothermal systems (>30 Ma) that would allow quantification of the nature and extent of deeper parts of the crust and the geochemical exchanges that occur during extended low-temperature alteration (Donnelly et al., 1979). The duration and downward penetration of this alteration are unknown. Significant exchange of K, Sr, Mg Ca and oxygen isotopes are implied by pore water geochemical changes in overlying sediment sequences (e.g., Gieskes and Lawrence, 1981; Bender et al., 1986). An understanding and quantification of this exchange will be very important to global geochemical cycles of selected elements. In addition, there may be other important signals (Li, B and their isotopes) that will provide a means of tracing temporal changes in crustal alteration, both in terms of effects on seawater chemistry and in

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fluxes to volcanic arcs and ultimately to the mantle (Hart and Staudigel, 1982; Ito et al., 1987).

Initially, an investment in at least one deep hole(>3km penetration into the oceanic crust) will provide the greatest return of information. Development of remote sensing techniques (seismic tomography, magnetotellurics, others?) with which we can extrapolate away from a single drillsite for significant distances will allow an assessment of potential lateral variations in crustal alteration. One site of interest would be on upper Jurassic or lower Cretaceous crust outboard of the Marianas or Bonin trench. A second target would be to deepen holes drilled previously in the western North Atlantic at DSDP Sites 417/418 on 110 Ma crust (Donnelly et al., 1979). Ultimately, the Pacific site could be useful in approaching objective 2 below.

III. OBJECTIVE 2: TOWARDS QUANTIFICATION OF MASS EXCHANGE BETWEEN CRUST AND MANTLE AT SUBDUCTION ZONES

Subduction is the major mass transfer process recycling material from the earth's surface to the mantle (Zindler and Hart, 1986). There is evidence from the chemical and isotopic composition of arc volcanic rocks that sedimentary and probably crustal components are returned to the earth's surface in these regions (Weaver et al., 1986; White and Dupre, 1986; Tera et al., 1986; Monaghan et al., 1988; Ellam and Hawkesworth, 1988), but it is clear that these signals are small in comparison to the total mass of crustal components that appears to be subducted. In particular, volatiles appear to play a role in island arc magma genesis. Both recycled volatiles and non-volatile components probably also play an important role in mantle evolution and generation of mantle chemical heterogeneity (Kay, 1985). It is of great importance to characterize the chemistry and mass of oceanic crustal and sedimentary material that is being supplied to subduction zones, the fraction incorporated in arc igneous-metamorphic complexes following subduction and the composition and mass of material that eventually is assimilated into the mantle (e.g., Karig and Kay, 1981). However, there is a major gap in knowledge of those components needed for understanding the fluxes and mass balance: the composition of the lower parts of the oceanic crust. Thus, an important goal for ODP is to characterize the composition of altered oceanic crust to depths deeper than 500 meters as outlined in Objective 1 above.

At this time it probably is premature to propose a detailed plan for examination of the chemical and mass exchange associated with subduction because general models can be (have been) tested with presently available data and there are no easily quantifiable signals which could provide more stringent constraints. A possible exception is the development of the volatile inventory and models for the distribution of important tracers of both sediment and crustal components needs to be accomplished prior to intensive drilling activity. As stated in objective 1, a major gap in developing such models is knowledge of the alteration characteristics of the lower crust.

In conjunction with these crustal studies the geochemistry of oceanic sediments overlying subducting crust should be investigated in more detail, partly because some of the chemical signals associated with different lithologies are not well characterized, particularly those of some trace elements, rare earths and their isotopes that appear to be important tracers in arc volcanic rocks. However, the interpretation of sediment chemical signals in arc volcanics is by no means

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simple because we do not know the detailed history of the subduction-associated mass balance: the mass of sediment that is accreted, subcreted and/or ultimately subducted to depth in the mantle is not likely to be a steady-state phenomenon.

In addition, more effort should be put into examining the lateral and temporal geochemical evolution of arc volcanic complexes, mainly by field sampling of and/or drilling into the volcaniclastic aprons associated with the arcs, in order to ascertain that there are indeed variations in chemistry of arc volcanics that relate to changes in the nature of subducted lithosphere. In large part, such studies should be confined to oceanic island arcs where crustal contamination signals do not complicate interpretations of volcanic sources. Intriguing chemical signals already known for the Banda, Bonin and Antilles arcs make these possible targets for more intensive study. Our feeling is that if such a program is attempted it should concentrate on understanding one arc system very well; that is, that one or more holes should be drilled outboard of the trench to sample oceanic crust to deep depths as well as holes along the arc volcanic apron and in associated back arc basins.

IV.   OBJECTIVE 3: HYDROTHERMAL OUTPUT AT MID-OCEAN RIDGES THROUGH TIME

Ocean-ridge hydrothermal activity exerts a major influence on the chemical mass balance between upper oceanic crust, seawater and sediments (e.g., Muehlenbachs, 1986). This activity acts as a sink for dissolved chemical species in seawater, (e..g., Mg) which are incorporated into oceanic crust, and a source of other elements added to seawater (e.g., Ca, Sr) and sediments (e.g., Mn, Fe) (e.g., Edmond et al., 1979; 1982). Further, the precipitation of Fe- and Mn-oxides from hydrothermal fluids results in coprecipitation and extraction of other species (e.g., P, As, V) from seawater into the sediment column.

Recent studies of hydrothermal sediment deposits (e.g., Leg 92; Leinen and Rea, 1986) have shown that rates of hydrothermal activity (i.e., chemical exchange) may vary significantly through geologic time. Since this has such a profound effect on the chemical mass balance of so many elements and on important isotopic systems (e.g., Chen et al., 1986) in the oceanic environment it is desirable to quantify the degree to which rates of hydrothermal activity vary both regionally and on a global scale (e.g. VonDamm et al., 1985 a&b).

Two approaches can be applied to increasing our understanding of the magnitude of variations in rates of hydrothermal activity. The first would be to systematically drill new cores to attempt to define the record of hydrothermal sedimentation in specific regions of the ocean basins. An ideal locality for this type of study might be an extension of the Leg 92 Sites to new localities westward of the East Pacific Rise (i.e., onto successively older basement). In each hole complete sediment recovery to basement would provide excellent recovery of proximal to distal hydrothermal deposits with overlapping measurement of the hydrothermal discharge over the 100 Ma interval. The South Pacific is particularly suitable for this type of study because the low eolian sedimentation rates result in minimum dilution of the hydrothermal signal. A second approach would be a more random sampling of the ocean basins, but with a consistent effort to

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recover basal hydrothermal sediments from most ODP sites drilled. Considering the general importance of rates of hydrothermal activity to global mass balance, it would be advisable to attempt to recover the first 5-10 Ma of sediments deposited above basement in any ODP site which drills to basement.

This approach will not unequivocally demonstrate variations in hydrothermal activity because of potential uncertainties in changes in ocean circulation (and sedimentation) patterns. However, such uncertainties can be ameliorated by follow-up coring to document any observed major fluctuations in accumulation of hydrothermal sedimentation. An interesting result of quantifying the distribution of hydrothermal sedimentation as a function of time and space is that this will also provide information about the long-term evolution of mid-level oceanic circulation.

V. OBJECTIVE 4: GEOCHEMICAL SIGNATURES OF CONTINENTAL TECTONICS

The building of mountain ranges and the consequent shedding of continental detritus to the oceans is important for an understanding of tectonics, long term climate change, and for global geochemical cycles (Raymo et al., 1988). Reconstruction of the timing or orogenies and the total mass of material involved in the mountain-building episodes are key problems in tectonics. Ruddiman and Kutzbach (1989) have also suggested that Late Miocene/Pliocene uplift of large regions of Asia and North America were directly responsible for the initiation of the Pleistocene ice ages. Thus mountain building may have important climatic impacts. Finally, measuring the flux of sediment pulses to the oceans will not only help us to understand the role of continents and tectonism in the cycle of aluminosilicate elements but will help us better understand variations in other important geochemical processes. For example, secular variations of Sr isotopes in seawater monitor the competition between weathering of continental material and of oceanic basalts (e.g., Hess et al., 1986). If we can better constrain continental weathering, we can monitor changes in marine hydrothermal alteration through time.

Mountain building in the Neogene can be studied by a program to drill the distal parts of major sediment fans and which uses seismic reflection data to extrapolate this information to thicker portions upslope. High rates of sedimentation in the fan will to a first order date major mountain-building episodes. Provenance of the sedimentary material will confirm that the source was from the mountains themselves. Provided that the fan can be completely drilled, maximum ages for the orogeny can be set. The changing composition of the sedimentary material can track the unroofing of the mountains, and conceivably geobarometric minerals may be preserved in the distal sands. Differences in the composition between distinctive source material and the conjugate fan deposit can be used to infer the exchange with sea water. Finally the significance of these fan deposits with respect to the total detrital sediment flux in the oceans can be assessed.

Areas of interest for drilling include the Bengal and Indus Fans (continuing and extending the goals of legs 116? and 117) and Amazon cone*.

VI. OBJECTIVE 5: GLOBAL VOLCANIC EPISODICITY

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A.   The Cretaceous midplate flood basalt episode. It is now reasonably well appreciated that processes at mid-ocean ridges have had a pronounced influence on seawater, and probably atmospheric, chemistry as the result of direct volatile degassing from the mantle and hydrothermal alteration of oceanic crust. Likewise, volatile outputs at volcanic arcs are deemed as important in the global geochemical cycles of carbon and sulfur among others (e.g. DesMarais, 1985; Sundquist, 1985). However, perhaps one of the most significant outpourings of mantle material yet known occurred in the form of thick midplate basalt flows over a broad area of the central Pacific and Caribbean seafloor during part of the early Cretaceous. These flow series have been observed in seismic records over broad regions of the seafloor, in outcrops on the margins of Central America and northern South America, and in drillholes attempted during DSDP Leg 15 in the Caribbean and Legs 62 and 89 in the Nauru Basin of the Pacific Ocean. Over a large area, the basalt flows reach thicknesses in excess of 1 km, and we have yet to fully penetrate and date the onset of the basaltic activity anywhere. The youngest flows are mid-Cretaceous (Turonian) in age, and extrapolations from the Leg 62 and 89 drilling suggest a Barremian-Aptian age for the onset (see Larson, in press).

The amount of basalt is so massive as to suggest a thermal event of major importance. In fact, it has been estimated that the thermal anomaly and uplift of oceanic crust associated with the regional activity was sufficient to displace an amount of seawater equivalent to 100 meters of sea level rise (Schlanger et al., 1981). In addition, others have suggested that such an event was accompanied by substantial degassing of CO_2 and other volatiles which could have significantly affected atmospheric composition (Arthur et al., 1985). A major increase in pCO_2 related to this "excess" volcanism could explain an apparent global Aptian-Albian climatic warming episode. There are undoubtedly other implications of this event for seawater and sediment chemistry which have yet to be explored. In addition, we need to understand the origin of this peculiar event.

The minimum effort required to approach this problem is to drill at least 2 holes through these massive flows in order to obtain ages for the onset and cessation of the volcanism and further information on the evolution of composition and extent of alteration of the flows. Seismic data and other information could be used to better constrain the extant mass of material on the seafloor. Our suggestion is to return to and deepen the Nauru Basin hole and to drill at least one new site in the eastern Venezuelan and/or Colombian Basin where it appears possible to penetrate the flow series.

B.   Neogene Explosive Volcanic Episodicity. Another achievable objective of interest is to examine evidence for episodicity of explosive arc volcanism during the Neogene and Quaternary. Earlier syntheses of the frequency of volcanic ash layers in DSDP sites for regions outboard of volcanic arcs have suggested that there are peaks in explosive volcanism in the middle Miocene and again in the Pliocene and early Quaternary (Kennett et al., 1977; Verplanck and Duncan, 1987). For various reasons (patterns of distribution of sites, recovery, and dependance on the discrete ash layers rather than the total volume of ash as well as increased preservation potential under higher sedimentation rate regimes), however, it is difficult to ascertain whether the pattern resulted from increased frequency of explosive volcanic events, from increased transport

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efficiency accompanying the Neogene climate deterioration, or both. There are reasons to implicate both factors, but it is important to document possible increases in volcanism because that then may provide clues to a fundamental change in the role of volatiles, for example, as the result of increased rates of sediment subduction or some other cause.

We advocate a program that involves obtaining a number of continuously cored sequences outboard of trenches around the global arc-trench system, where redeposition of volcaniclastic material from the arc is less of a problem, and which will recover at least the Neogene-Quaternary record and older sediments if possible. Sampling of a large number of sites and arcs will alleviate the problem of climatic overprints (for example increased transport efficiency in westerly wind systems) and allow a global outlook. This would also seem to be a perfect application for the Geochemical Logging Tool which could be run in all holes in order to obtain a continuous record of background volcanic material (e.g., Ti/Al ratio variations) as well as possibly detecting important ash layers that might not be recovered. The geochemical logs would provide a rapid and complete set of geochemical data for calculation of ash accumulation rates that could then be interpreted in terms of arc volcanic outputs, in combination with more detailed visual, geochemical and mineralogical studies of core material.

VII.   OBJECTIVE 6: THE GLOBAL CARBON CYCLE

With the present concern over buildup of CO_2 in the atmosphere and global greenhouse warming in response to anthropogenic burning of fossil fuels, there is an increasing need to identify ancient analogues in the sediment record and to identify proxy data that provide indications of the magnitudes of environmental effects that accompanied CO_2 changes in the past (Berner et al., 1983). We know that there have been periods in the Earth's history when there has been massive burial of organic carbon and this has had profound environmental effects. The middle to late Cretaceous was one such period in which massive burial of organic carbon was accompanied by higher than present concentrations of atmospheric CO_2 and an unusually warm global climate and possibly ice-free poles. How are these conditions related to organic carbon-burial? The Cretaceous was also a period of generally high sealevel stands and, therefore, extensive development of shallow shelf seas. In an ice-free world, what was causing global fluctuations in sealevel? The Cretaceous was also a period of rapid plate movement and extensive plate-margin and mid-plate volcanism as recorded in the extensive distribution of seamounts in the western Pacific, and extensive deposits of volcanic ash. Is it possible the Cretaceous sealevel changes were caused by tectonism rather than changes in ice volume as they are today? To what extent did extensive volcanism cause the higher concentrations of atmospheric CO_2? Variations in the Cretaceous carbon cycle have more than just academic implications. Most hydrocarbon deposits, were sourced by Cretaceous organic-carbon-rich sequences. Therefore understanding the origin of these sequences is tantamount to understanding the origin and distribution of most of the of the World's oil, discovered and undiscovered. Variations in the global carbon cycle also have profound effects on the cycles of other elements, especially the nutrient elements (e.g. N, P, and S) as well as a host of trace elements through adsorption, coprecipitation, complex redox reactions, etc. Understanding the carbon cycle also helps to understand the origin and distribution of sediment-hosted metallic and non-metallic

mineral deposits.

Understanding and interpreting variations in the carbon cycle in the past requires a reliable data base to determine the rates, timing, locations, and mechanisms of burial of organic and carbonate carbon in the past. Such data bases include percentages of organic and carbonate in time and space; sources of organic carbon, i.e. whether it is derived from marine or terrestrial organic matter; isotopic composition of carbonate and organic carbon as well as related biogeochemical elements such as N and S; concentrations and distributions of other greenhouse gases such as CH4; concentrations of gases in sediment pore waters; etc. Many of these data bases rely on shore-based studies, but there are some measurements that can and should be made onboard ship. Routine shipboard measurements of carbonate and organic carbon, together with improved chronostratigraphies can provide the data for global fluxes in carbon to marine sediments. Today 80% or more of organic carbon is buried in continental margin settings. Has this been true in the past? What were the fluxes of organic and carbonate carbon to the deep sea in the past? To what extent is this organic carbon derived from terrestrial or marine organic sources? Routine shipboard Roc-Eval (RE) pyrolysis can often provide this information if the concentration of organic carbon is sufficiently high (>0.5%), but more often this information requires more detailed shore-based studies. If rapid, routine shipboard pyrolysis-gas chromatography (PGC) could be developed, a much more extensive data base on the global mass balance of marine and terrestrial organic mater could be established. Routine shipboard measurement of major and trace transition metals (e.g. Fe, Mn, Ni, Co, Cr, Cu, Pb, and Zn) by XRF in organic-carbon-rich sediments and rocks would greatly increase the databases for other biogeochemical cycles.

In summary, we suggest that the program pursue the following:

(1) The routine measurement of carbonate- and organic C.

(2) Rapid techniques for characterization of terrestrial vs. marine OC

(3) The global pore-water methane mass and isotopic fluxes (adequate sampling of pore-water gases at in situ T&P and methods for quantification)

VIII. OBJECTIVE 7: PASSIVE MARGIN BURIAL FLUXES

Carbonate and Organic Carbon burial rates are >50% of global flux, yet virtually no temporal record available; relatively small shifts in loci of deposition that might result from climate and sea level changes could explain a large part of the deep-sea signal, yet we have very little data that bear on this problem.

Approaches to this problem need to be developed that would maximize information derived from a minimal expenditure of drilling time because of the deep holes that will be required. Could decide on optimal locations for relatively few holes that would be complemented by seismic reflection nets allowing extrapolation of sedimentary masses in time and space on important

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margins, with additional information from more extensive industrial sources.

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GEOCHEMICAL LOGGING

I. SUMMARY OF RECOMMENDATIONS

(1) Implement improved procedure for the effective integration of core and log data, requiring XRF and XRD shipboard measurements on samples from log derived key intervals.

(2) Replace JOIDES logging and physical property scientists with JOIDES physical and chemical characterization scientists. Formulate job descriptions.

(3) Quantify intrinsic and field accuracies and precisions for the GLT.

(4) Develop signal enhancement procedure(s) for target GLT vertical resolution of one foot.

(5) Deploy Enhanced Resolution Tool at earliest opportunity.

(6) Include core natural gamma spectral facility on board the JOIDES RESOLUTION.

(7) Investigate the global/regional/local validities of element-to-mineral transforms.

II. INTRODUCTION

In its broadest sense geochemical logging can provide information relating to the chemical composition of the oceanic lithosphere, both solids and fluids, to the way in which the chemical constituents are distributed, and to those dynamic processes which govern fluxes and flowpaths. Thus temperature logs, porosity logs (density, neutron, sonic, resistivity), permeability indicators (e.g., sonic waveform logs) all have an interactive role to play. However, for present purposes we are taking a more specific view by focussing on the Geochemical Logging Toll (GLT), developed and operated by Schlumberger, which has already been widely deployed in the Ocean Drilling Program. We shall consider logs measured using the GLT as " geochemical logs ". In so doing, we shall concentrate primarily on the geochemical evaluation of solid rock as opposed to the interstitial fluids. We shall confine ourselves to inorganic interrogation. Although there are promising indicators from the oil industry that carbon/oxygen ratios measured by the GLT (in inelastic mode) can be used to derive total organic carbon (TOC) in sediments, this ratio has not yet been attempted in ODP.

Here our aims are to assess progress made to date, to evaluate what can be done to improve data quality in the short term, and to identify opportunities for further developing the interpretive technology in the future.

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III.   GEOCHEMICAL LOGS

Properly calibrated geochemical logs form an important part of the scientific legacy of an ODP drill hole. They provide a continuous geochemical signature at in-situ conditions and with a spatial resolution of about 60 centimeters. Geochemical data at this larger scale of measurement constitute a useful basis for the calculation of fluxes. One cannot gross up core data to achieve the same endproduct because of the complementary nature of core and log measurements, i.e., core data have high resolution, but relate to a small volume of rock, whereas log data have lower resolution but relate to a much larger (100 times) volume of rock. The key to successful geochemical characterization is to use the high resolution, and thence greater accuracy and precision, of core data to calibrate the otherwise less accurate and precise log data.

The logs are not as accurate and precise as laboratory data. However, with core calibration the accuracy and precision of the signature can be enhanced. This is an important point because good geochemical logs are often obtained where core recovery is limited, e.g., in (uncased) basement holes, and, therefore, the logs have to provide meaningful interpolation between core data locations. This continuity is essential for complete geochemical surveys of a drill-hole and for the interpretation between sites.

Geochemical logs can provide a geochemical signature in the form of elemental concentrations, mineralogy in terms of a pre-specified mineral domain, and other derived products, such as grain density.

A.   Geochemical Signature.   The geochemical signature takes the form of the absolute concentrations of 12 elements : K, U, Th, Al, Si, Ca, Fe, S, Ti, Gd, H, Cl. The establishment of absolute concentrations of Si, Ca, Fe, S, Ti, Gd, H, and Cl requires post-cruise processing. If core calibration can be incorporated, enhancement of accuracy is possible. Since H and Cl relate primarily to the fluids, they are not considered further. We shall think in terms of a ten element geochemical signature, which can be developed through post-cruise processing.

On board ship, it is possible only to provide a preliminary geochemical signature in the form of absolute concentrations of K, U, Th, and Al and relative concentrations of Si, Fe, Ca, S, H, and Cl. This information can be supplied within real time. It has two important uses:

(1)   It sets in context the significance of geochemical changes as seen in measurements of (discontinuous) cores;

(2)   It serves as a guide to subsequent re-sampling for enhancing the accuracy of subsequent determinations of absolute elemental concentrations.

Accuracy enhancement of the geochemical signature requires controlling laboratory data, such as XRF and XRD. These facilities are underutilized on board ship. This is unfortunate, because core and log data are complementary. Core data have high resolution but sample a small volume. Log data have lower resolution but sample a larger volume. It is possible to derive maximum

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benefits by using the high resolution core data to calibrate the larger sampling log data. This aspect will be developed more fully later.

B.   Mineralogy. The availability of XRF and XRD data allows the controlled progression from geochemical signature to mineralogy. XRF data allow the assumption of the 10 element domain to be verified. XRD data allow on to determine the 5 - 10 most common minerals in order to optimize the inversion process. XRD data also allow the realism of the oxide closure model, used to convert relative elemental concentrations to absolute, for Si, Ca, Fe, S, Ti, and Gd, to be confirmed or otherwise. If these assumptions are all satisfied, the elemental concentrations will be erroneous and the subsequently determined mineralogy will contain artifacts. The key to controlling the interpretation procedure is the effective integration of core and log data.

Schlumberger claim other derived products that can be determined from the mineralogy. Some of these seem intuitively realistic, e.g., grain density and clay types; others are less convincing, e.g., permeability. The only derived product we consider is the mineralogy, and that is viewed as subordinate to the elemental signature for the present purposes.

C.   Case histories of Geochemical Logging in ODP. Here we give an example of the uses of geochemical logging to solve scientific problem within each of the technical working groups established within this workshop, in order to examine future directions of geochemical research within ODP.

        1.   Alteration of the oceanic crust - layer 2:   In Hole 504B, permeability measurements made by pumping below packers inflated in the hole, showed a marked drop in permeability 300 m into the oceanic crust, whereas the porosity values from the electrical resistivity logs indicated continued high porosities. How can high porosities be reconciled with the low permeabilities in the lower pillow basalts of the upper crust? The geochemical logs show strong correlations between high Si and Mg content and low Al and Ca content and high porosity values within this zone of the well. The geochemical logs are detecting the stoichiometry, or the chemical composition, of clay minerals that were precipitated in fractures and pore spaces as a result of the sealing of hydrothermal circulation. Subsequent sampling and laboratory measurement of core samples verified that these alteration zones contain high cation exchange capacitances that account for the "false" porosity factors.

        2.   Chemical fluxes between the crust and the ocean: Also in Hole 504B, the continuous nature of the geochemical log-derived elemental abundances provides a direct measure of the integrated chemical exchange between the basalts and sea water from bottom to top of the well. The integrated differences between the compositions of the freshest dikes from the bottom of the well and the altered basalts from the upper dikes and pillow units show that: there has been a significant addition of Si caused by quartz precipitation at the dike-pillow boundary; Al is depleted in the zone of maximum clay precipitation in the lower pillow basalts; Ca is depleted and Mg enriched from the hydrothermal alteration of basalts, just as predicted from laboratory experiments; significant Fe loss is from black smoker and off axis, ridge flank

advection into the ocean, combined with some primary decrease in Fe and Ti content of the pillow basalts relative to the dike basalts; and the K, which shows strong enrichment in the upper pillow basalts from low temperature alteration, is derived from depletion in the dikes as well as from extraction from circulating sea water.

3.   Global mass balance between subduction and arc volcanism: In the Bonin Arc, geochemical logs record the continuous sequence of arc volcanism back in time. High-K dacites and rhyolites found below high Fe and Mg boninites require a source for the potassium enrichment either from subduction during the Oligocene of high-K sediments or basement rocks, or from massive fractionation of very large volumes of arc tholeiites into boninites and residual dacites.

4.   Paleoceanography: On the western continental margin of Australia, geochemical logs record the sequence of onlap and offlap of sediments caused by the rise and fall of sea level according to what is known from the Vail curve. Chemical changes in the sediments from high Al, Fe, and Ti clastic sediments to high Si sands, then high carbonates, record the fall and rise-again in sea level on the margin.

In the Japan Sea, high frequency cyclicity in Al and gamma-ray logs records the changes in climate on mainland Asia that resulted in changes in the flux of windblown dust deposited on the sea floor. The 41,000 year periodicity of this log-derived cyclicity identifies the climatic forcing function to be Milankewitch orbital perturbations.

5.   Diagenesis: In the continental margin landward of subduction off Peru, the Cl curve from the geochemical logs identified an inversion in pore fluid salinities from more saline fluids above to fresher pore fluids below a prominent seismic reflector. The changes in pore fluid chemistry reflect major causes and effects of diagenetic changes in sediments.

D.   Integration of Core and Log Data. The geochemical logging tool is unable to match accuracy and precision of laboratory data. This is mostly a consequence of the coarser resolution of the tool relative to the size of core samples. Yet, calibrated logs are needed to set core data in perspective. We propose the following strategy for the effective integration of core and log data for optimized interpretation.

The recommended procedure is to use the preliminary geochemical signature, available on board ship in real time, to identify zones of apparent geochemical consistency within each major litho-unit. For each target zone, XRF and XRD data should be determined at regular sampling intervals and averaged over distances that correspond to the vertical resolution of the logging tool. Appropriate weightings, that reflect tool response, should be applied. These and the vertical resolution may vary between the three groups of elements, since K, U, Th, and Al are determined from different tools in the same sonde. The averaged core data (XRF and XRD) provide the basic control on refined interpretations of elemental concentrations of elemental concentrations and thence inferred mineralogy, which becomes available post-cruise.

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This strategy would be better achieved by redefining the job descriptions of the JOIDES logging scientist and the JOIDES physical properties specialist. It is proposed to replace these functions with two integrated functions that cover both logging and laboratory properties. These new functions are: JOIDES Physical Characterization Scientist (responsible for the physical properties log and core measurements); and JOIDES Chemical Characterization Scientist (responsible for geochemical log and XRF/XRD core measurements).

IV. OPPORTUNITIES FOR FUTURE DEVELOPMENTS

A.   Accuracy and precision. There is a need to define the operating limits of accuracy and precision for each element seen by the GLT. Intrinsic accuracy can be determined by comparing measured data with absolute standards, if these exist. Intrinsic precision is governed by statistics of counting. Both accuracy and precision are degraded by the limited vertical extent and degree of physico-chemical constancy of the target beds. Studies directed at defining accuracy and precision should recognize that the intrinsic quantities might be influenced by variations in composition, while the field quantities might be bore-hole specific.

B.   Enhanced Resolution Tools. A scientific wish-list of elemental concentrations that cannot be readily determined using conventional sodium iodide detectors, as in the GLT, might include Ni, Cr, V, Sr, La, and P. The greatly improved spectral resolution attainable with solid state detectors would allow some of these to be measured. Developments in enhanced resolution tools should be closely monitored with a view to deploying them in ODP at the earliest opportunity.

C.   Deconvolution/Signal Enhancement. A sharper spatial resolution for the GLT might be attained either by deconvolution or by using other (high-resolution) logs to specify the boundary conditions. A one-foot (30 cm) vertical resolution would be a useful target. Any such technique would be retroactive, i.e., it could be applied to logs obtained in the past. Among the obvious benefits of a sharper spatial characterization would be better time resolution in sedimentary sequences.

D.   Element-to-Mineral Transform. The applicability of element-to-mineral transforms needs to be established. Is there any case for a global transform and, if not, how extensive an application does a transform have ? Unless these questions are answered, the use of the GLT to establish mineralogy will have limited acceptance. A key issue is the role of XRD calibration. With this control it might be possible to establish optimal transforms for each principal lithology.

E.   Shipboard Measurement. In addition to XRF and XRD, a core gamma spectral facility should be introduced to assist with core-log depth merging and to provide high resolution K, U, Th data. In the longer term, continuous whole-rock bulk-analysis methods should be encouraged.

F.   Logistics of Core-Log Integration. If a casual approach to XRF and XRD data acquisition is allowed to continue, a piecemeal output can be expected. To avoid this situation, specific job descriptions should be developed for the two replacement scientific positions proposed herein. In particular, it should be incumbent upon the JOIDES Chemical

Characterization Scientist to supply all identified XRF and XRD data to the ODP Logging Contractor as input for the advanced (research grade) processing of the GLT data.

V.   CONCLUSIONS

The GLT is at the appraisal stage. We are still learning how to get the best out of it. The recommendations that have been formulated here will contribute to that goal. Geochemical logs do, of course, form but a part of the package of down hole measurements, that are regularly deployed in ODP. The conjunctive use of all core and log data constitutes the optimum strategy for formation evaluation.

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Geochemistry Progress and Opportunities Workshop Attendees
UCLA Conference Center
Lake Arrowhead, CA 92352
January 9 - 12, 1990

Dr. Roger Anderson
Lamont-Doherty Geological Observatory
Columbia University
Palisades, NY 10964
Phone: 914-359-2900 ext. 335
Fax: 914-365-3182

Dr. Michael Arthur
Graduate School of Oceanography
University of Rhode Island
Narragansett, RI 02882-1197
Phone: 401-792-6867
Fax: 401-792-6160

Dr. Paul Baker
Department of Geology
Duke University
Box 6729 College Station
Durham, NC 27708
Phone: 919-684-6450
Fax: 919-684-5833

Dr. Enriqueta Barrera
Department of Geology
University of Michigan
1006 C. C. Little Building
Ann Arbor, MI 48109-1063
Phone: 313-764-4429
Fax: 313-763-4690

Dr. Keir Becker
RSMAS
University of Miami
4600 Rickenbacker Causeway
Miami, Florida 33149-1098
Phone: 305-361-4661
Fax: 305-361-4711

Dr. Garrett Brass
RSMAS
University of Miami
4600 Rickenbacker Causeway
Miami, Florida 33149-1098
Phone: 305-361-4690
Fax: 305-361-4632

Ms. Marta von Breymann
TAMU/ODP
1000 Discovery Drive
College Station, TX 77854-9547
Phone: 409-845-2522
Fax: 409-845-0876

Dr. Lui Chan
Department of Geology and Geophysics
Louisiana State University
Baton Rouge, Louisiana 70803
Phone: 504-388-6439
Fax: 504-388-2302

Dr. Walter Dean
U. S. Geological Survey
Federal Center
Denver, CO 80225
Phone: 303-236-1644
Fax: 303-236-5448

Dr. Eric DeCarlo
Hawaii Institute of Geophysics
University of Hawaii
2525 Correa Road
Honolulu, HI 96822
Phone: 808-948-6473
Fax: 808-949-0243

Dr. Thomas Donnelly
Department of Geological Services
    and Environmental Studies
State University of New York at Binghamton
Binghamton, NY 13901
Phone: 607-777-2264
Fax: 607-775-4000

Dr. Phillip Froelich
Lamont-Doherty Geological Observatory
Columbia University
Palisades, NY 10964
Phone: 914-359-2900   ext. 485
Fax: 914-359-2312

Dr. Joris Gieskes
Marine Research Division (A-015)
Scripps Institution of Oceanography
La Jolla, CA 80225
Phone: 619-534-4257
Fax: 619-534-0784

Dr. Martin Goldhaber
U.S. Geological Survey
Federal Center, Building 25
Denver, CO 80225
Phone: 303-236-1251
Fax: 303-236-3200

Dr. Robert Haddad
UNOCAL Science and Technology Division
376 South Valencia Avenue
Brea, CA 92621
Phone: 714-528-7201 ext.1484
Fax: 714-528-9986

Dr. William Hay
Department of Geology
University of Colorado
Boulder, CO 80302
Phone: 303-586-8552
Fax: 303-492-2606

Dr. Timothy Herbert
Geological Research Division (A-015)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534
Fax: 619-534-0784

Richard Jarrard
Lamont-Doherty Geological Observatory
Columbia University
Palisades, NY 10964
Phone: 914-359-2900   ext.343
Fax: 914-365-3182

Dr. Miriam Kastner
Geological Research Division (A-012)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-2065
Fax: 619-534-0784

Dr. Barry Katz
TEXACO
3901 Briarpark
Houston, TX 77042
Phone: 713-954-6093
Fax: 713-954-6113

Dr. Gary Klinkhammer
Department of Earth, Atmospheric, and Planetary Science
Massachusetts Institute of Technology
Cambridge, MA 02139
Phone: 617-253-8875
Fax: 617-253-3000

Dr. Keith Kvenvolden
U. S. Geological Survey
345 Middlefield Road, M/S 999
Menlo Park, CA 94025
Phone: 415-345-3213
Fax: 415-345-3191

Dr. Frank Kyte
Institute of Geophysics and Planetary Sciences
University of California - Los Angeles
Los Angeles, CA 90024-1567
Phone: 213-825-2015
Fax: 213-206-3051

Dr. John Ladd
National Science Foundation
1800 G Street, NW
Washington, DC 20550
Phone: 202-357-7543
Fax: 202-357-7621

Dr. M. A. Lovell
Department of Geology
Leicester University
University Road
Leicester LE1 7RH
ENGLAND
Phone: (44) 533-52379
Fax: (44) 533-523918

Dr. Mitchell Lyle
Lamont-Doherty Geological Observatory
Columbia University
Palisades, NY 10964
Phone: 914-359-2900   Ext. 672
Fax: 914-365-3182

Dr. Doug Macdougall
Geological Research Division (A-012)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-3294
Fax: 619-534-0784

Dr. Mordeckai Magaritz
Division of Geology
California Institute of Technology
Pasedena, CA 99125
Phone: 818-356-6811 Ext. 6486
Fax: 818-568-0935

Dr. Jon Martin
Geological Research Division (A-012)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-1826
Fax: 619-534-0784

Dr. Judy McKenzie
Geological Institute
ETH-Zentrum
CH-8006 Zurich
SWITZERLAND
Phone: (41) 256-38-28
Fax: (41) 252-7008

Dr. Philip Meyers
Department of Geology
University of Michigan
1006 C. C. Little Building
Ann Arbor, MI 48109-1063
Phone: 313-764-0597
Fax: 313-763-4690

Dr. John Morse
Department of Oceanography
Texas A&M University
College Station, TX 77843
Phone: 409-845-9630
Fax: 409-845-6331

Dr. Richard Murray
Department of Geology and Geophysics
University of California at Berkeley
Berkeley, CA 94720
Phone: 415-642-9116
Fax: 415-643-9980

Dr. James Natland
Geological Research Division (A-012)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-5977
Fax: 619-534-0784

Dr. Sergio Nuti
Consiglio Nazionale d/Ricerch
Piazza Solferino, 2
56126 Pisa
ITALIA
Phone: (50) 41503
Fax: (50) 47055

Dr. Charles Paull
Department of Geology
University of North Carolina
CB# 3315, Mitchell Hall
Chapel Hill, NC 27599-3315
Phone: 919-962-0687
Fax: 919-962-5604

Dr. Clare Reimers
Geological Research Division (A-015)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-2503
Fax: 619-534-0784

Dr. Samuel Savin
Department of Earth Sciences
Case Western Reserve University
Cleveland, Ohio 44106
Phone: 216-368-6592
Fax: 216-368-3016

Dr. Fred Sayles
Department of Chemistry
Woods Hole Oceanographic Institution
Woods Hole, MA 02543
Phone: 508-548-1400 Ext. 2561
Fax: 508-548-1400 Ext. 6128

Dr. Everett Shock
Washington University
Campus Box 1169
1 Brookings Drive
St. Louis, MO 63130-4899
Phone: 314-726-4258
Fax: 314-726-7361

Dr. Bernd Simoneit
College of Oceanography
Oregon State University
Oceanography Admin. Bldg. 104
Corvallis, OR 97331-5503
Phone: 503-737-2155
Fax: 503-737-2064

Dr. Arthur Spivak
Geological Research Division (A-012)
Scripps Institution of Oceanography
La Jolla, CA 92093
Phone: 619-534-3950
Fax: 619-534-0784

Dr. Erwin Suess
GEOMAR Research Center
Wischhofstrasse 1-3
D-2300 Kiel
FEDERAL REPUBLIC OF GERMANY
Phone: (49) 431-7202-232
Fax: (49) 431-7202-239

Dr. Peter Swart
RSMAS
University of Miami
4600 Rickenbacker Causeway
Miami, Florida 33149-1098
Phone: 305-361-4103
Fax: 305-361-4623

Dr. P. F. Worthington
BP Research
Chertsey Road
Sunbury on the Thames TW16 7LN
ENGLAND
Phone: (44) 9327-63263
Fax: (44) 9327-63352

Dr. James Zachos
Department of Geology
University of Michigan
1006 C. C. Little Building
Ann Arbor, MI 48109-1063
Phone: 313-764-1453
Fax: 313-763-4690