Seawater and the Ocean Crust: The Hot and Cold of It

Seventy percent of the earth's crust is beneath the sea. Although geochemists have learned a good deal about how the rocks of the continental crust, the atmosphere, and freshwater affect each other's chemical compositions, little had been known until recently about how seawater and the ocean crust affect each other, if they do at all. In the past it was technologically impossible to recover the right kind of samples from the bottom of the ocean. But now deep-sea drilling and manned submersibles are recovering both rocks and seawater that have been altered by exposure to each other. It seems that parts of the ocean bottom are really quite leaky. This leakiness allows considerable contact between seawater and crustal rock, producing significant changes in both.

A recent development that has received considerable attention from the media, largely because of the biology involved rather than the chemistry, was the discovery and sampling of warm plumes of mineral-enriched seawater emanating from vents on the Galápagos Ridge in the Pacific. These hydrothermal discharges are the long-sought proof that seawater sinks into the crust, reacts with hot volcanic rocks, and rises back to the sea. Analyses of the Galápagos warm springs indicate that reactions between hot rocks and seawater on a global scale help control the chemical composition of the ocean.

Although the samples were collected outside the kind of limelight that accompanied the Galápagos expedition, equally interesting results are emerging from studies of cores of the ocean crust recovered by the Deep Sea Drilling Project's (DSDP) ship *Glomar Challenger*. These studies suggest that all the crust down to about 600 meters depth, the deepest penetration so far, has been altered to some degree by cold, rather than hot, seawater. Apparently, cold seawater has percolated into the crust over millions of years and slowly reacted with the rocks there, producing chemical changes quite different from those occurring at high temperatures. The apparent degree of alteration varies depending on the method of analysis, core location, and the depth in any one core. Thus, geochemists have gone from not being sure if any significant changes were occurring within the ocean crust to having numerous competing processes to sort out.

That the sea floor is permeable to seawater became abundantly clear to DSDP scientists from the start of crustal drilling in 1974. Cracks and veins could be seen in the recovered cores, and it seemed that some parts of the crust are so fractured and fragile that they are largely lost during the drilling operation. This fracturing apparently results from the way new crust is formed. According to the theory of plate tectonics, new rigid crust is formed on either side of mid-ocean ridges as molten rock oozes up into the ridge crest and solidifies. The fresh crust cools slowly as it moves away from the ridge crest at a speed of a few centimeters per year.

The actual mechanics of crustal formation are not understood, but mapping of the ocean bottom and visual inspection of cores have demonstrated the extensive breaking and cracking that the crust is subjected to. Early acoustic sounding methods showed that tremendous zones of deep fracturing, which can stretch the width of an ocean, form perpendicular to the ridge wherever one section of the ridge crest is offset horizontally from another. New instrumentation, such as side-scanning sonar towed near the bottom by a surface ship, has shown that fracturing also occurs on a smaller scale. Apparently, faults spaced 60 to more than 2000 meters apart form parallel to the ridge as the young crust begins its descent from the crest. Direct observation from manned submersibles has revealed even more fracturing and the formation of other kinds of open space between rocks within the median valley, the central depression on the ridge crest where lava actually pours out onto the bottom. Here, piles of volcanic rubble and layers of new sediment are overlaid by fresh lava flows. Fracturing can occur every few meters as rocks adjust to the weight of new lava.

The smallest scale cracking seems to result from thermal stresses during cooling. Douglas Johnson of the University of Texas at Dallas counted the cracks in a DSDP core recovered from 110-million-year-old crust in the Atlantic near Bermuda (Fig. 1). He found that the typical crack in this core was about 2 millimeters wide and 150 millimeters long, and that it occurred about every 2 centimeters. Zones of intense cracking occurred throughout the 247-meter core.

The end result of all this fracturing is that crust on and near the ridge crest is very permeable to seawater. James Kirkpatrick of the University of Illinois estimates that the porosity, or open space, of one core from young (13-million-year-old) crust is on the order of 20 to 25 percent. It would be considerably less if the lava were originally laid out in a single massive sheet rather than as the ropey, toothpaste-like pillow lavas that are typical of the Atlantic. As the crust ages, the most obvious change is the filling of cracks and voids with new minerals deposited from flowing seawater. This reduces the porosity to about 5 percent in an older core, such as the 110-million-year-old one studied by Johnson.

The decrease of porosity with age is reflected in the amount of core that can be recovered. In many cases, only 1 out of every 3 meters of crust drilled could be recovered, the rest having been broken up and lost. The recoveries for some core sections, which were assumed to be zones of rubble or sediment, were much lower. But older cores, welded together by new mineral deposits, sometimes had recoveries of more than 70 percent. Thus, in many cases, zones of cores that have received the most exposure to seawater because of fracturing are the least likely to be recovered.

Filling of porous young crust with new minerals and all other kinds of alteration have, at least in DSDP cores recovered so far, occurred at or near the low temperatures of ocean bottom water. Mineralogists have generally found only those alteration products typical of low temperature conditions. Among the most common alteration products are calcium carbonate that is deposited in the veins and smectite, a type of clay formed by the hydration of glassy basalt at low temperature. Oxygen isotope analyses by James Lawrence of Lamont-Doherty Geological Observatory and by Karlis Muehlenbachs and C. M. Scarfe of the University of Alberta indicate that much alteration took place at a few degrees above zero Celsius, a temperature typical of bottom water. One area of drilling seems to have been altered at a higher temperature, but it was only about 30°C. This is far short of the high temperatures known to occur below the warm springs of the Galápagos Ridge.

There is still no consensus as to just how extensive this low temperature alteration of the recovered cores really is. Opinions vary because assorted measures of alteration are applied to different subsamples of the same core. Approaches used include the determination of the chemical, mineralogical, or isotopic composition of the cores. Each reflects a different process and each process occurs at a different rate, a point not always fully appreciated by the investigators doing the work.

A good example of these differences is the analyses of two cores taken only 400 meters apart but dramatically dissimilar in the amount that they were altered. The highly altered core was taken from a small knoll above the general level of the crust. The fresh, relatively unaltered core was taken from just off the knoll. Thomas Donnelly of the State University of New York at Binghamton believes that this knoll, which remained bare of sediment even after surrounding rock had been covered, acted as a chimney. That is, it conducted seawater that had been slightly warmed by the crust up through the rock. Given the high permeability of the crust, this can happen at any place where the heat of the young rocks warms seawater, causing it to rise into the bottom water while drawing in fresh, colder seawater. The knoll core appears to have been altered by seawater at about 30°C, the warmest alteration encountered so far during drilling.

Donnelly compared the chemical composition of the highly altered core with that of the fresh core and found that significant amounts of several elements had been added to or taken out of the altered rock. A large amount of potassium ion was taken up, and even more calcium was released along with smaller amounts of magnesium and sodium. Some of these changes are just the kind marine chemists have been looking for to help them balance the chemical budgets of the ocean.

For example, one of the more obvious problems has been that much more potassium seems to enter the oceans than is observed to leave it. If this were really so, the potassium concentration of seawater should be rising; but geochemical evidence suggests that it is not. Thus, potassium taken up by cold crust might help balance its removal from the ocean with its input. Donnelly calculates that, if this highly altered knoll represented 3 to 4 percent of the ocean crust, all of the excess potassium could be accounted for. He points out that, although the knoll is unique among the 15 deep penetrations of the crust, 5 of the 50 short cores of the crust recovered from the bottom of sediment cores have also had unusually high potassium contents.

In contrast to the picture of a "very fresh" crust speckled with spots of high alteration shown by chemical studies, mineralogical and isotopic studies seem

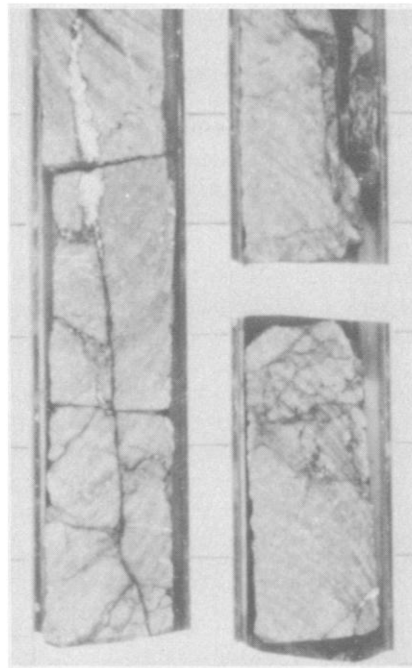

Fig. 1. Core (8 centimeters in diameter) of fractured crustal rock recovered from 110-million-year-old ocean crust. Filling of natural cracks by carbonates (white) and smectite clays (gray) occurred in the presence of flowing seawater. [Source: Douglas Johnson, University of Texas at Dallas]

to show "weak, but pervasive" alteration throughout all parts of the crust that have been sampled so far. Paul Robinson of the University of California at Riverside has identified the minerals present in the "fresh" core taken near the knoll and found that this core too was altered, although weakly, throughout its 366-meter length. The mineralogical compositions of all the cores in the vicinity of the knoll suggest to Robinson that the main chemical changes since the formation of that part of the crust have been the uptake of water, which is a typical weathering reaction, and the loss of calcium and magnesium.

The oxygen isotope data of Muehlenbachs and Scarfe also tend to support the contention that the crust has been slightly altered to great depths. These investigators argue that the relative proportions of oxygen-16 and oxygen-18 can be taken as an indication of the amount of basalt that has been converted to clay because basalt and clay have very different isotopic compositions. They found that all parts of the crust sampled appeared to be altered at least 10 percent and that alteration usually did not decrease with increasing depth. Zones that were once loose rubble had their oxygen isotope compositions changed by up to 60 percent. In fact, Muehlenbachs believes that the exchange of oxygen between seawater and the crust is so extensive that it controls the oxygen isotope composition of the ocean over geologic time.

An effort directed by Jose Honnorez of the University of Miami is now under way to coordinate the varied approaches to the study of low temperature alteration products. The aim is to sort out the different alteration processes and the particular conditions that promoted them. In a pilot study, Honnorez, Muehlenbachs, and Nikolai Petersen of Ludwig-Maximilians-Universität, Munich, have correlated different types of analyses of the same subsamples of a core. They demonstrated a consistent relation between the magnetic properties down a 255-meter core and changes in its chemistry and mineralogy.

Exactly how long fresh cold seawater can circulate through the oceanic crust before the crust is sealed off is not known. The young rock of the ridge crest has no sediment covering and is open to the sea. But as the crust moves away, it cools and accumulates a layer of fine mud and microscopic plankton skeletons that is much less permeable than the fractured crust.

Roger Anderson, Michael Hobart, and Marcus Langseth of Lamont-Doherty think that they have indirect evidence of seawater exchange between the crust and the ocean through 25 million years of accumulated sediments. They measured the temperature of sediments as a function of depth and found that, as the depth increased, it increased nonlinearly. Such anomalous phenomena had been observed before, but it had been thought that heat only flowed through sediment by conduction, not by convection.

The Lamont-Doherty workers, however, tentatively suggest that the temperature gradient is distorted by the convection of warmer water through the sediment and into the bottom water. Their measurements of heat flow by conduction showed patterns of high and low flows. These patterns suggest that heat flow by convection is at work, distorting the normally even conductive heat flow. The observed patterns are of such large dimensions that the convection cells responsible for the patterns must penetrate into the crust. In the 25-million-year-old area, the rising warm water breaks into the bottom water; but in a 55-million-year-old area, where the sediment layer is thicker, it is contained within the sediment-crust system. Evidence for convection cells in the crust and sediment have also been found by Clive Lister's group at the University of Washington and by Kenneth Green and Richard Von Herzen of Woods Hole Oceanographic Institution.

The chemistry of the water trapped in some DSDP sediment cores suggests that, although thick sediment can block water flow, it may still allow exchange of chemicals between the crust and bottom water by means of diffusion. Russell McDuff and Joris Gieskes of Scripps Institution of Oceanography have studied variations with depth in the concentrations of magnesium and calcium in pore waters. These variations, which appear in about one-half of DSDP cores, suggest that calcium is diffusing up from the crust, and that magnesium is diffusing down from the bottom water.

Although the evidence from coring indicates that only low temperature processes have affected the crust, rocks dredged from the sea floor often show the effects of seawater alteration at high temperatures. These rocks, termed greenschists, contain a group of minerals quite unlike the minerals found in crustal cores and are typical of temperatures in the range of 200° to 250°C. These rocks were probably brought to the sea floor from some depth by the large-scale vertical faulting of the crust.

A recent study by Susan Humphris, now at Lamont-Doherty, and Geoffrey Thompson, at Woods Hole, of greenschist samples dredged from the Mid-Atlantic Ridge shows that the chemical changes accompanying the formation of greenschists could be important in global chemical cycles. Significant changes had occurred in the contents of magnesium, calcium, some transition metals, and silica. The chemistry of these alteration products was in reasonable agreement with that deduced for basalts exposed to hot seawater in the laboratory by James Bischoff of the U.S. Geological Survey at Menlo Park and Frank Dickson of Stanford University. But the significance of these changes for the composition of seawater had always been a matter of considerable debate because no one could tell how much of the crust was actually affected by hot seawater.

Warm Spring Chemistry

The discovery last year of hot, mineral-enriched seawater springs on the crest of the Galápagos Ridge has allowed the first estimation of the importance of high temperature crustal alterations to the overall composition of seawater. The discovery followed a sophisticated search for a phenomenon that some believed must exist but no one expected to be as striking as it turned out to be.

After following a trail of subtle clues to a spot 340 kilometers north of the Galápagos Islands, a team of researchers assembled by John Corliss of Oregon State University descended 2800 meters in Woods Hole's submersible *Alvin* into the dark, 2°C waters over the Galápagos Ridge. They were hoping to locate and sample wisps of slightly warmer water, which they expected to be only a degree or so warmer than bottom seawater, as the water rose from the very center of the ridge. Instead, they found plumes of shimmering, sometimes cloudy, warm water pouring from among the bottom rocks. The maximum temperature recorded was 17°C. Even more surprising were the dense colonies of crabs, fish, foot-long clams, giant tube worms, and other exotic animals thriving in the noxious spring waters at ocean depths where normally only an occasional worm scratches out an existence. These animals compose a unique ecosystem that, by feeding on sulfur-loving bacteria, ultimately derives its energy from the geothermal sources beneath the ridge. The

Speaking of Science

Killer Bees: O Death, Where Is Thy Sting?

The popular image of "killer bees" has them attacking humans—and killing them—in a manner reminiscent of the birds in the Alfred Hitchcock movie. Perhaps not surprisingly, many observers, including officials of the United States Department of Agriculture, think that this picture has been overdrawn. Although no one disputes the nasty disposition of the creatures, their main threat appears to be more to the economic health of the beekeeping industry in affected areas than to the public health. In fact, officials of the USDA and scientists studying the problem wince at the name "killer bees," which they think is a misnomer, the result of sensationalized reporting. As Marshall Levin of the USDA put it: "I feel the same way about the term 'killer bees' as the president of General Motors would feel about the term 'killer cars.' "

The preferred name is "Africanized bees," which reflects the origin of the strain. In 1956, a Brazilian geneticist brought a race of African bees (*Apis mellifera adansonii*) to Brazil with the idea of breeding them with the local bees in order to obtain a more productive honey bee for South America. The Brazilian bees, which were derived from European honey bees, were not very vigorous and were relatively poor honey producers in the tropics whereas the African bees were supposed to be industrious workers that made a lot of honey in tropical conditions.

Unfortunately, a few months after their importation, 26 swarms of the African bees with their queens escaped from the apiary where they were being studied. And the hardy, aggressive nature of the bees suddenly became a problem as they began to outcompete, outbreed, and ultimately displace the Brazilian bees in many areas. In the last 21 years the Africanized bees have migrated rapidly in all directions from their point of release.

Africanized bees are more easily disturbed and provoked to attack than are European bees. Despite this—and despite the deadly reputation Africanized bees have acquired—Orley Taylor of the University of Kansas, who has been studying the natural history of the bees for the past 4 years, says that he hears of fewer than a dozen attacks, only some of which are fatal, each year in all the areas of South America that are now inhabited by the bees. (For comparison, at least 40 persons, usually individuals who are allergic to bee venom, die of bee stings annually in the United States.) Although there is no system for reporting such attacks and there could be more that do not come to Taylor's attention, he points out that a phenomenon this hard to track down could not be very widespread.

If the impact of Africanized bees on public health has been slight, their impact on beekeepers has been severe. Taylor says 50 to 60 percent of the beekeepers whose colonies are taken over by Africanized bees quit the job because the invaders are harder to manage than the European bees they are replacing. Beekeepers may need special equipment for handling Africanized bees, such as protective clothing, which is a nuisance in hot climates. They also need to establish their colonies at least 200 meters away from human habitation and domestic animals to minimize the risk of the bees being provoked to attack.

color films from these dives still draw large crowds of viewers, but now the chemical analyses of the water samples are equally alluring to geochemists.

The compositions of the collected hydrothermal waters, being determined principally by John Edmond and his colleagues at the Massachusetts Institute of Technology, show that very high temperature reactions are occurring between seawater and the crust. The amount of silica leached from the rocks into the hydrothermal water indicates that the seawater was heated to 300°C at some point, but it does not boil because of the high pressure at the sea floor. Experiments by Bischoff and Dickson show that the high temperature can generate the observed high acidity, as low as *p*H 3 in the reaction zone, by precipitating magnesium from seawater as sulfates and silicates. Oxygen is also consumed, probably by reaction with iron, producing reducing conditions.

Corliss and Edmond believe that the seawater in cracks perhaps 2 kilometers below the surface is heated by conduction from a magma chamber immediately below the depth of seawater penetration. The hot seawater rises toward the surface, drawing in fresh cold seawater to be heated. Before the hot water can reach the surface, it is diluted by cold water that has percolated into the system at shallower depths. Dilution has no chemical effect on many of the leached elements, such as lithium and calcium. The changes accompanying dilution (decrease in temperature, increase in oxygen content, and increase in *p*H) do affect a number of elements. For example, copper, nickel, and cadmium are totally removed—even the very small amounts present in the initial seawater. They are apparently precipitated as sulfides onto the walls of the cracks. This precipitation process is thought to be responsible for some major mineral deposits, such as those mined for copper on Cyprus. Small veins of copper and zinc sulfide have actually been found in dredge samples.

The behavior of these trace metals, and that of iron and manganese, during dilution in the Galápagos warm springs helps explain the origin of the metal-rich deposits commonly found along ridge crests. In the Pacific, the deposits are sediments highly enriched in iron and manganese with smaller amounts of trace metals. Previous studies have shown that the trace metals are derived from seawater itself, not crustal rocks. A seawater origin can be explained by the removal of leached metals as sulfides and the adsorption of metals from seawater by the iron and manganese as they precipitate and settle into the sediment. In the Atlantic, metal-rich sediments are less common, and manganese is often deposited as extremely pure manganese dioxide coatings on bottom rocks. Edmond suggests that greater dilution of hydrothermal waters, a likely situation in the more fractured Atlantic crust, causes the complete removal of the iron within the crust, leaving the manganese to be deposited alone.

A fortunate circumstance of warm spring chemistry allows some estimation of the importance of hydrothermal discharges in the chemistry of the ocean even though only one spot on the 64,000-kilometer ridge system has been sampled. Along with the other elements leached from the rock, an isotope of heli-

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Another problem for beekeepers is that Africanized bees do not want to stay put in the hive. A colony of Africanized bees may produce as many as 8 swarms per year compared to the one or two produced by a European bee colony. Swarming occurs when a queen, together with her workers and drones, leaves the parent colony to establish a new colony. This divides the population and honey production goes down until the populations go up again. Swarming occurs when conditions are good. When conditions are bad bees tend to abscond entirely as they leave the hive to search for greener pastures. Africanized bees are highly prone to absconding.

In any event, beekeepers eventually can accommodate to the African bees. According to a report from the U.S. National Academy of Sciences, honey production at first decreased but then increased in the areas of southern Brazil where the bees have been established for the longest time. Moreover, bees in these areas apparently have less aggressive characteristics than those in northern Brazil where the African bee takeover is more recent. Presumably, beekeepers in the South have been selecting the gentler strains for breeding.

When Africanized bees swarm or abscond, they often travel long distances, up to an estimated 50 miles before establishing a new home. The fact that the bees have been found on islands 10 to 12 miles from the coast of French Guyana indicates that they can fly at least that far on a single flight.

These flying feats have enabled the Africanized bees to travel great distances since their release. The southward migration has currently ceased in Argentina, but they are still moving northward and have now been spotted in Caracas, Venezuela. They may eventually—perhaps in 10 years—reach the United States, although this is not certain.

Taylor points out that there are many wild bees in Mexico whereas there were few in South America before the Africanized bees moved in. Lack of a vigorous population of indigenous wild bee competitors has been a major factor in the expansion of the Africanized bees throughout South America. Whether they will be able to outcompete and displace the bees of Mexico as readily as they have displaced those of South America is not clear. If they began to breed with and acquire some of the characteristics of the Mexican bees they might also become less aggressive.

Moreover, colder climates may help to block the northward spread of Africanized bees. There are indications from the distribution of the bees in South America that they cannot tolerate the cold as well as European bees. Lack of cold tolerance may have stopped the southward migration in Argentina. Of course, Africanized bees might pick up cold tolerance by breeding with European strains, but this has apparently not yet happened, a fact suggesting that the two strains are not completely compatible genetically.

The USDA Bee Breeding and Stock Center Laboratory in Baton Rouge is exploring ways to moderate the aggressive tendencies of the bees by genetic means should they arrive in this country still as feisty as they are in South America. One promising line of research involves the identification of the pheromones (chemical communicators) that may be responsible for evoking their aggressive behavior. Thomas Rinderer of the Baton Rouge laboratory says that it may be possible to select strains that either produce less of the pheromones or respond poorly to them. Such strains should be gentler and less prone than the Africanized bees to take aggressive defensive action when they are disturbed. The gentle strains might then be used by beekeepers and commercial bee suppliers to breed out the aggressive traits of the immigrant bees.—J.L.M.

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um, helium-3, appears in hydrothermal waters. Helium-3, trapped in the earth since the condensation of the solar nebula, slowly escapes into the ocean from ridges, and then into the atmosphere. It is chemically inert and its total flow into the world ocean from the ridges has been estimated from independent observations. Assuming the proportion of, say, potassium to helium-3 is the same in all hydrothermal waters, the flow of potassium from all warm springs in the ocean can be calculated from the proportion of potassium to helium-3 in the Galápagos springs and the total flow of helium-3 through the ocean. The method is not without possible errors. For example, the proportion of helium-3 to heat content of one of the four Galápagos vent fields is distinctly different from the others, suggesting that the leaching processes can vary from place to place. But a calculation of the flow of heat from ridges, based on the observed proportion of helium-3 to heat, falls between two independent calculations not based on helium-3, lending support to estimations of other fluxes.

Flux calculations for several elements help balance the inputs and outputs of some cycles that had been a bit embarrassing for geochemists, according to Edmond. The large amount of lithium in marine shales, the rock formed from marine muds, had been difficult to explain in light of the relatively small input from rivers, but it appears that hydrothermal waters contribute greater than ten times more than rivers do. All of the manganese deposited in the ocean can be accounted for by hydrothermal activity. And the need for a place to put the magnesium arriving in river water is met by its removal in the hot crust.

Unfortunately, problems with other cycles are not improved and, Edmond points out, some are actually aggravated. Marine chemists have been looking for a source of acid in the ocean to balance the input of alkalinity from the rivers. The net hydrothermal contribution of acidity turns out to be much too small to help. In contrast, the contribution of potassium is so large that its suggested uptake by the cold crust, which before had to accommodate only river-born potassium, would have to be doubled in order to accommodate all the potassium.

The obvious problem for geochemists, now that they have some first-hand evidence about what is going on within the ocean crust, is to find out what the contribution of each process is to the cycling of a particular element. For example, how much potassium, on a global scale, is released by hot rocks beneath the ridge system and how much is taken up by the cold crust? The answers to such questions will require the collection and analysis of many more seawater and core samples, but the prospects for further studies are mixed.

Hydrothermal studies have considerable momentum, and hopes are high that new vent fields will soon be discovered. Expeditions are planned for return visits to all three of the ridge sites that have received close attention, including the Galápagos site. The first phase of joint French-American diving on the East Pacific Ridge at 21° north latitude in April found three large patches of empty giant clam shells and rocks stained by hydrothermal waters in an area with a small apparent temperature anomaly. Elsewhere, other encouraging signs include suggestive variations in helium-3, temperature, and particulate metals suspended in the water, and a bottom photograph of a dense group of sea anemones.

Prospects for extensive deep drilling in the crust are not as bright. The *Glomar Challenger* is scheduled to conduct only limited drilling in the crust during the rest of 1978. No crustal drilling time is specifically allotted during tentatively scheduled operations in 1979 and 1980. The proportion of the post-1980 program devoted to crustal drilling is still very much in doubt.—RICHARD A. KERR