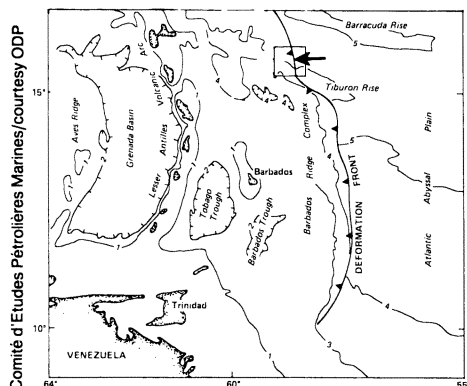


"Hydrogeology is really, really important to geology," says Casey Moore, the project's co-chief scientist, from the University of California at Santa Cruz. "The movement of water through rock controls all kinds of things, and we as geologists have just been studying the rock, the solid material, and not paying any attention to the fluid."



The subduction zone and Ocean Drilling Project site north of Barbados.

As sediment accumulates at the bottom of the ocean, Moore says, it traps ocean water like the pores of a sponge. As the Caribbean plate moves over the Atlantic crust, some of the sediment piles atop the edge of the plate to form an accretionary wedge that is gradually growing eastward; in some places, the wedge is thick enough to create the rolling hills of Barbados. Some of the sediment, however, stays on top of the Atlantic crust as it slides under the Caribbean plate. The pressure of the overriding plate cracks the underlying rock and squeezes out the entrapped ocean water. The water seeps up the cracks into the detachment surface between the two plates. Says Moore, "The water allows [the plates] to slip without building up a lot of strain and therefore [reduces] the potential for a large earthquake."

Because the Atlantic crust sediment lies so deep, the water it releases is much warmer than normal ocean-bottom water. The heat also warms organic matter trapped in the sediment pores, converting it to methane that seeps at least 25 kilometers along the detachment surface up to the ocean's floor, the researchers found. This same mechanism, says Moore, may explain the plumbing network that creates mud volcanoes near Trinidad and feeds the rich biological communities living near submarine vents off the coast of Oregon (SN: 12/15/84,p.374).

As the water squirts out of the sediments, it alters the character of the rock it leaves behind, exchanging minerals in solution for minerals in the rock. "What we're starting out with," says Moore, "are sediments that are on their way to becoming rocks, and we see all these subtle transformations along that path."

— T. Kleist

## Knocking the lead out of gasoline

Now that tetraethyl lead is being phased out as an antiknock additive in gasoline, researchers are beginning to pay closer attention to how lead does its job inside a car engine. Although lead additives have been used for about 60 years, the detailed chemistry of the reactions that take place to eliminate engine knock has remained elusive. Recently, two scientists each proposed a somewhat different theoretical mechanism that may account for lead's effectiveness and could lead to a suitable substitute.

Engine knock occurs when unburnt gases in a car engine's cylinder ignite too soon. Normally, a spark plug initiates a flame that rapidly sweeps through the chamber. But the mixture of air and gasoline at the end of the chamber farthest from the spark plug also gets heated and compressed by the moving flame. As a result, sometimes these "end" gases explode before the flame actually reaches them, upsetting the gasoline's orderly burning. This produces engine knock and a loss of power.

"But if you speed up the flame or slow down the ignition of the gas that's farthest away, then you won't get knock," says physicist Charles K. Westbrook of the Lawrence Livermore (Calif.) National Laboratory. Westbrook and his colleagues have been using a computer to model the chemical reactions that may be going on when a lead compound is added. "If we can understand why lead works," he says, "then maybe we can find something else that will do the job as well."

Lead additives appear to slow combustion mainly by removing hydroperoxyl radicals, highly reactive molecules that form during combustion. Westbrook suggests that microscopic particles of lead oxide, about 50 to 100 angstroms across, form within an engine cylinder after tetraethyl lead breaks down. When active molecules like hydroperoxyl radicals hit these solid particles, they are absorbed and no longer contribute to gasoline combustion.

Chemist Sidney W. Benson of the University of Southern California in Los Angeles, however, contends that the key reactions for removing active molecules occur when all of the species, including lead, are present as gases. He proposes a three-step sequence of elementary reactions that reduces the number of both hydroperoxyl radicals and hydrogen atoms, which are released during the breakdown of gasoline hydrocarbons.

Experiments are needed to settle which of the two proposed mecha-

nisms is dominant. "The problem," says Benson, who has been studying combustion reactions for many years, "is that most of what lead does happens in such a short time that it's hard to get convincing evidence."

Westbrook says previous experiments show that a mist of lead oxide particles does form within a car engine just before it knocks. However, the crucial question of exactly when that happens has not yet been answered. Benson argues that the particles probably form too late to be effective.

"The answer almost certainly is that both [mechanisms] are taking place," says Westbrook. "It's a question of their relative importance."

Nevertheless, both theoretical predictions point to the effectiveness of hydroperoxyl removal for preventing engine knock. "You've got the dossier of the character you're searching for," says Westbrook, "but now you've got to find something that fits that profile."

Based on his results, Benson says, "there should be a lot of metals and a lot of metals in various combinations with other things that could play the same role as lead." The ideal candidate, while preventing engine knock, also would be volatile so that deposits don't build up in cylinders, and it should not affect catalytic converters by poisoning the platinum catalyst.

Presently, petroleum refiners and fuel producers blend a variety of hydrocarbons with gasoline to prevent engine knock. Organic compounds like benzene, toluene and isooctane burn in such a way that premature ignition doesn't occur readily. However, these blending agents are expensive.

Moreover, the occurrence of knock limits how much the gasoline-air mixture in a cylinder can be compressed. A higher compression ratio would increase an engine's fuel efficiency.

Because of the cost- and energy-saving potential of an effective means for preventing engine knock, the Department of Energy (DOE), in cooperation with industry, has for the last few years been sponsoring a research effort to help solve the problem. By using sophisticated instruments and facilities at several national laboratories and elsewhere, DOE-sponsored researchers hope to provide fundamental information about the chemical and physical processes that take place during gasoline combustion. That information, says Marvin E. Gunn of DOE's conservation and renewable energy office, should someday allow fuel producers and engine designers to develop better energy-conserving products.

— I. Peterson