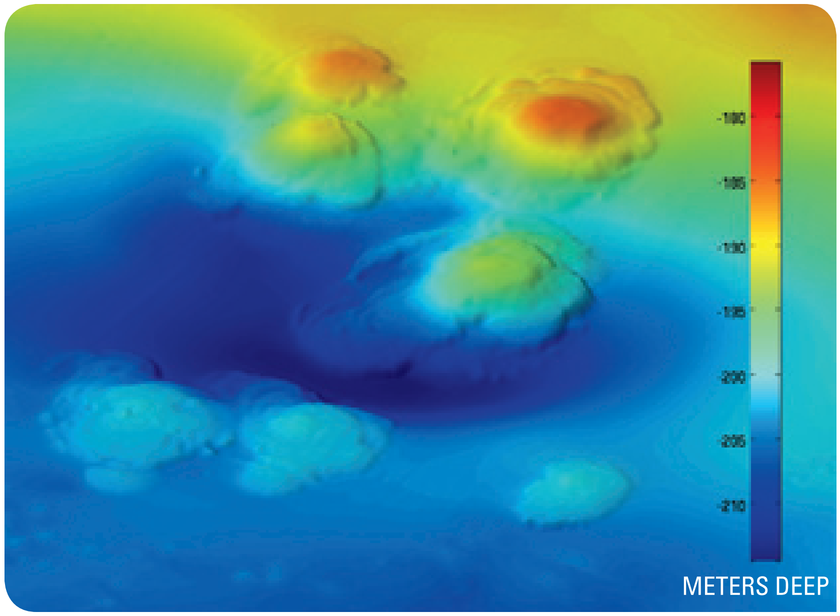
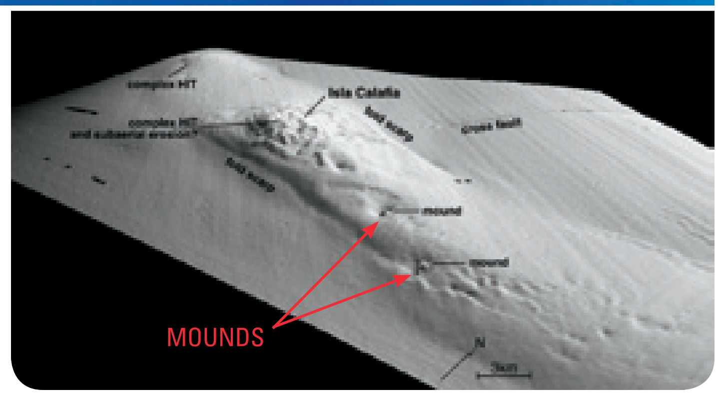
Asphalt Volcanoes on the Ocean Floor

Before Deepwater Horizon, scientists had experience with oil at the seafloor



The *Sentry* Group, WHOI



Ed Keller, UCSB

UCSB scientist Ed Keller analyzed sonar data of the seafloor off Santa Barbara, Calif., and spotted curious mounds. That spurred UCSB colleague Dave Valentine and WHOI chemist Chris Reddy to investigate further, using underwater vehicles to take a closer look and map the mounds (top).

The dome-like mounds poking up in sonar maps of the seafloor caught the scientists' eyes. They stood out in stark contrast to the surrounding environment off the coast of Santa Barbara, Calif.

"They came up very suddenly out of the seafloor," said David Valentine, an earth scientist at the University of California, Santa Barbara. "There were seven of them. The largest we called Il Duomo, and it is about the size of two football fields side by side and as tall as a six-story building."

"Nobody knew what the domes were made of," said Chris Reddy, a chemist at Woods Hole Oceanographic Institution (WHOI).

Valentine's colleague Ed Keller had spotted them, and in 2006 he suggested some possibilities. Large deposits of carbonate rock? Mud volcanoes created by mammoth burps of subsea natural gas? Or, most intriguing to Valentine and Reddy, perhaps they were remnants of oil that had erupted from the seafloor, piled high, and hardened to form something never seen before—volcanoes made naturally out of the same material that people use to pave roads: asphalt.

In 2007, off Santa Barbara aboard the research vessel *Atlantis*, Valentine and Reddy seized an opportunity to use the submersible *Alvin* to investigate the curious mounds. They reported what they found April 25, 2010, in the journal *Nature Geoscience*. We interviewed the two scientists on a bicoastal conference call.

Tell us about the dive to Il Duomo.

Valentine: We dove down, and it took us a few hours to find the mounds. There's no light at that depth. It's only in the artificial lighting of the submarine that you can see the mounds. It looked like something flowing that had solidified in place, very much like lava. A lot of organisms were living on the surface of the mounds.

We were able to use the robotic arm of the submarine to crack off pieces of the rock, and the fact that they cracked off easily told us, well, this is not some really tough rock. This is something like a tar, perhaps. As soon as we ascended back to the *Atlantis*, I knew we had to bring in our oil chemistry guru Chris Reddy to analyze these rocks. Of course, he had worked all the previous night and was sleeping at the time, but that was not going to stop us.

Reddy: One of the undergrads woke me up, saying, "You've got to get on deck and look at this sample that Dave brought up!" I broke off a little piece with some pliers and ground it, like a mortar and pestle, with the back of a Bic pen. I added some nail polish remover, and sure enough, the rock completely dissolved in no time, which immediately said to me that this was tar. And I remember turning to Dave and saying, "We've got to go back! Please take me back there. I want to dive on it."

What happened when you dove to the site?

Reddy: It was an amazing experience flying along in *Alvin* on this relatively unremarkable seafloor, and all of a sudden, this black wall, this mountain, is staring you in the face. There were all types of life forms living on this mountain. It was essentially an oasis. Many life forms like something hard to clamp onto. It was almost like an artificial reef, except it was an asphalt reef.

// SEE THE AUDIO SLIDESHOW @
www.whoi.edu/oceanus/asphalt

We brought a big sample back from the seafloor, as big as Dave and I. I'll never forget that we picked it up off the deck and held it. Had this been cement or rock or marble, we would have been Charles Atlas or Arnold Schwarzenegger times 10.

How did these mounds form?

Valentine: The area around Santa Barbara is very geologically active, because of the movement of the San Andreas Fault. There's an extensive amount of faulting or rupturing in the Earth that allows oil and gas from subterranean reservoirs to seep up to the seafloor and ultimately into the ocean and to the atmosphere.

What we think happened here is that as oils worked their way up and became exposed at the seafloor, little organisms and pieces of sediment began accumulating in the oils and making them heavier. Also some of the oil's lighter, more gasoline-like compounds quickly dissolved into the ocean or wafted away, leaving behind the heavier compounds. The material became heavier than the seawater and began to settle back down to the seafloor. At that point, it began to flow downslope in a way that looks very much like a Hawaiian lava flow.

Nothing exactly like these features has been found before under the sea. The famous La Brea Tar Pits are in some ways an on-land version of this sort of phenomenon.

The La Brea Tar Pits are famous for their preserved fossils. How about Il Duomo?

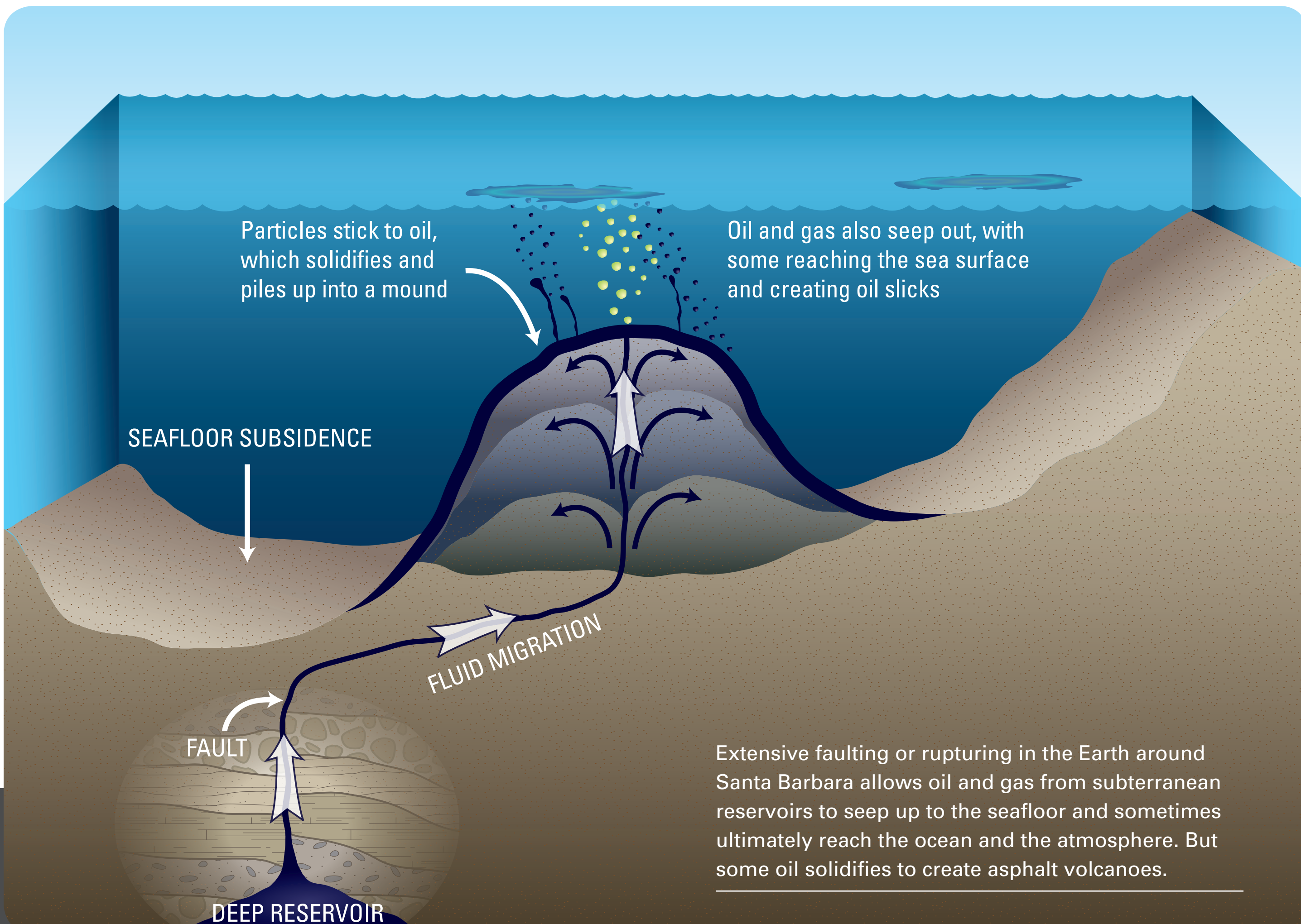
Reddy: Fossil organisms were essentially entombed in the oil from Il Duomo. Dave took a big hunk of rock and washed all the oil away. And what was left over was sand, and in that sand were these little fossils from plankton. Those plankton acted as a clock for us, because we were able to radiocarbon-date their shells. That allowed us to estimate that the eruption that created Il Duomo occurred 30,000 to 40,000 years ago, along with a lot of other big events.

Like what?

Valentine: The Santa Barbara Basin is an excellent chronometer of past events because sediments rapidly deposit into the center of the basin. In those sediments are records of past events in which methane gas rapidly entered the Santa Barbara Basin, even driving it to the point of anoxia, where no oxygen remains in the water, and probably creating a giant "dead zone" for marine life.

Around the asphalt volcanoes are large pits, several times larger than the volcanoes. These are evidence of large pockets of subterranean methane gas bursting at the seafloor.

I suspect that there is a relationship tying together all these features with the eruption of both oil and gas, the anoxia, and probably the movements of faults in the vicinity that set things in motion.



Extensive faulting or rupturing in the Earth around Santa Barbara allows oil and gas from subterranean reservoirs to seep up to the seafloor and sometimes ultimately reach the ocean and the atmosphere. But some oil solidifies to create asphalt volcanoes.

Jack Cook, WHOI

That's fascinating geologically, but what's in it for a chemist who studies oil spills?

Reddy: In my oil-spill experience, I generally study oil that is days, weeks, months, maybe decades old. This was oil I've never seen before. This was a chance to find out what Nature does to oil that has been around for 35,000 years.

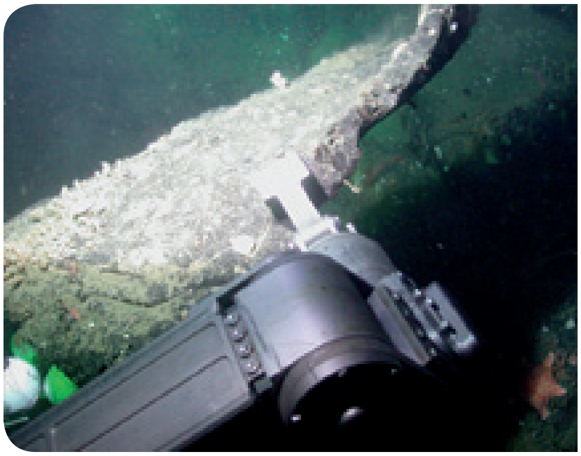
We cracked open a piece of the asphalt, and we immediately felt like we were at a gas station because of the smell. Even though it was so old, it still retained some oil compounds that hadn't been weathered away.

We analyzed some of this oil with advanced technology in my lab called comprehensive, two-dimensional GC×GC gas chromatography (see Page 16). It showed us that Nature had removed many of the compounds in the oil that had been abundant when Il Duomo erupted. And it left behind molecules in the asphalt that had been trace compounds in the oil when it erupted.

When you look at the compounds' chemical structures—how the carbon atoms are attached to each other, and especially in three-dimensional space—you start to get a feeling for why this happened. The compounds that remained are very big molecules, so, for one thing, they don't dissolve in water and get transported away.

In addition, if you could put yourself in the shoes of a microbe, and ask yourself, "Could I eat this molecule?" the answer would be, "No, you can't. It's just too damn big. It's too hard to break it down into digestible bits." So if microbes were to survey the buffet of compounds in oil, they would say, "We can eat this; we can eat that; but, man, we can't eat *that*." And "*that*"—

UCSB graduate student Blair Paul gently scrapes biological specimens from a chunk of asphalt retrieved by the submersible *Alvin* from an asphalt dome on the seafloor. The dome, from an extinct undersea volcano of oil, is now home to a wide range of organisms including brittle stars, worms, and microbes.



The *Alvin* Group, WHOI

Molly Redmond, UCSB

In 2007, the submersible *Alvin*'s manipulator arm breaks off a large piece of rock from an undersea mound called Il Duomo. Dave Valentine (right) of UCSB and Chris Reddy of WHOI could heft it easily, because it turned out to be made of asphalt, the lightweight, solidified residue of oil.

those big compounds—was what we found remaining in the samples. So by looking at these rocks, we learned a lot about how well Nature's microbes can degrade oil.

Valentine: A next step is to closely examine the microorganisms that degrade the oil—maybe even try to find DNA of organisms that were trapped in the asphalt like in the La Brea Tar Pits.

You mentioned that there was a lush variety of life on the volcanoes.

Reddy: Some of the samples we brought back to the surface also had these perfectly cylindrical holes. They looked like they were made by the best drill you could buy at Home Depot. We didn't know what they were. We were sitting there, measuring the holes, taking pictures, and the next thing you know, we see a worm crawling right out of a hole. Are these worms boring into this relatively soft asphalt as a hideout to avoid predators? That's another research project to explore.

What other research can you pursue on these volcanoes?

Valentine: Another future direction would be to drill into these asphalt volcanoes and turn this over to geologists to examine the underlying layers, find out just how far down they go, and figure out exactly what's going on down below—where this oil is coming from and how it's getting there.

We'd also want to determine the abundance and distribution of these features in this region and beyond. How common are asphalt volcanoes? So there are a lot of fascinating questions remaining.

Reddy: In September 2009, we went back with an autonomous underwater vehicle called *Sentry* to search for more areas off Santa Barbara where methane was seeping out of the ocean bottom. *Sentry* was equipped with an underwater mass spectrometer developed by WHOI scientist Rich Camilli, which can detect and identify minute quantities of chemicals in seawater. With that technology, we were able to locate subsurface plumes of hydrocarbons. We couldn't know it at the time, but that cruise turned out to be a practice run for using the same technology nine months later to map the deep hydrocarbon plume from Deepwater Horizon (see Page 28).

Your paper on asphalt volcanoes was published five days after the Deepwater Horizon explosion.

Reddy: At nine o'clock on April 25, I started my day talking to journalists about an oil spill that happened 35,000 years ago. It was ironic: At one point I was speaking to one reporter at a science magazine who wanted to talk about these old volcano eruptions of oil, and then he passed the phone over to a reporter who wanted to talk about Deepwater Horizon. By noontime, it was about half and half, talking about a 35,000-year-old oil spill and a few-days-old oil spill. By five o'clock, my oil-spill work on this 35,000-year-old eruption went extinct. It was a pretty crazy day.

—Lonny Lippsett

This research was funded by the National Science Foundation, the Department of Energy, and The Seaver Foundation.

"This was oil I've never seen before. This was a chance to find out what Nature does to oil that has been around for 35,000 years." — *Chris Reddy*