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Question From the Classroom

Q. My mother remembers her baby teeth were used in some sort of research study when she was young. What was that all about?

A. Have you ever heard the expression: "You are what you eat?" Well, there's a lot of truth in it.

Perhaps you've never thought about it before, but every atom in your body got there through something you ate. That carbon atom on the tip of your finger might have been in those scrambled eggs you ate a few months back. The iron atom in that hemoglobin molecule passing through your heart right now might have come from yesterday morning's bowl of cereal.

Realizing that people are indeed what they eat, in the late 1950s, researchers at Washington University in St. Louis began a most unusual research project: They asked all local residents to send in their children's teeth (after they had fallen out, of course!). At the time, there were public concerns about the radiation levels caused by all the nuclear weapons tests that were being conducted.

Back then, before we were fully aware of the hazards of radioactive fallout, testing took place out in the open (above ground). If you have ever seen video footage of a nuclear explosion and the resulting mushroom cloud, chances are that footage came from one of these aboveground tests. As it turned out, it was actually the findings of this

baby teeth research project, along with other evidence, that prompted the United States to sign a 1963 international treaty banning aboveground testing.

But why baby teeth? And what were the researchers looking for in those teeth? The answer: strontium. More specifically: strontium-90 (⁹⁰Sr), a radioactive isotope that is one of the dangerous byproducts of nuclear fission. But why would they find ⁹⁰Sr in baby teeth? Take a quick glance at the periodic



table. Where is strontium (Sr) located? In the same group as calcium (Ca). And being in the same group, strontium is chemically very similar to calcium and thus gets taken in and directed to the bones and teeth. The growing bones and teeth of children require large amounts of calcium. So, if a child drinks milk from a cow that has eaten ⁹⁰Sr-contaminated grass, ⁹⁰Sr will be found in the child's teeth.

Natural Abundance of Strontium Isotopes	
⁸⁴ Sr	0.56 %
⁸⁶ Sr	9.86 %
⁸⁷ Sr	7.00 %
⁸⁸ Sr	82.6 %
⁹⁰ Sr	0.00 %

While our bodies naturally contain some strontium, about 300 mg, only a very tiny fraction is normally ⁹⁰Sr. After collecting over 300,000 baby teeth, the researchers showed, however, that this tiny fraction had

increased dramatically during the years that aboveground testing occurred, with radioactivity levels rising above 1400% between 1954 and 1964. Similar studies in other parts of the country reported comparable findings.

And what does one do with 300,000 baby teeth? Those in the St. Louis project were put into long-term storage and completely forgotten. Forgotten, that is, until the spring of 2002, when some scientists were cleaning out an old ammunition bunker and 1.008 3 1 6.5

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found hundreds of shoe-box sized containers filled with baby teeth, 85,000 in all. With each tooth was a card carrying information about the child who lost it. Not having any idea where they came from, the scientists nearly discarded the entire collection. Luckily, someone made the connection to the ⁹⁰Sr research project, and recognized the incredible opportunity to conduct a follow-up study.

Now in their 40s, these individuals were contacted and asked to complete a health history survey to see what correlations might exist between their childhood ⁹⁰Sr levels and their medical records. Concern exists, however, about the validity of such a nonrandom study: After all, who would

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Mg

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Ca

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Sr

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Ba

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Ra

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Sc

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to

71

89

to

103

be more likely to fill out such a survey: a perfectly healthy individual or one with a history of health problems? Similar tooth collection projects are still conducted today.

in an effort to determine whether living in near to a nuclear power plant leads to increased ⁹⁰Sr in the children's teeth.



Question From the Classroom

My mother remembers her baby teeth were used in some sort of research study when she was young. What was that all about?

ChemSumer

Vanilla! It's Everywhere!

Vanilla, it's in everything from hair sprays to soda to chocolate. You might be surprised to learn that the primary flavor compound, vanillin, can be made from rice, beets, wood pulp, and even petroleum.

Teeth Whitening

Pastes, gels, and strips are all available for application, either in a dentist's chair or at home, to whiten teeth. The active ingredient in many whitening products is carbamide peroxide. What is it? How does it work?

Activity: Releasing the Power of Oxygen

No, this isn't an activity from a cheesy infomercial. We'll use two household products to make oxygen and learn about combustion.

Four Cool Chemistry Jobs

You like chemistry, but you're not sure whether it's the career for you. Read about four exciting careers that might change your mind.

Hydrothermal Vents and Giant Tubeworms

Imagine life near a deep-sea vent. It spews hot hydrogen sulfide and other chemicals into the surrounding water. Photosynthesis is impossible in the dark. Food is scarce. What does a giant tubeworm have to do to get a meal around here!?

MysteryMatters

Scanning Electron Microscopy Solves a Mystery: The Mystery of the Pockmarked Paint Job

High-end sports cars are coming off an assembly line with bad paint jobs. Using a scanning electron microscope, a researcher discovers a clue. The answer is "elementary".

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TEACHERS! FIND YOUR COMPLETE TEACHER'S GUIDE FOR THIS ISSUE AT www.chemistry.org/education/chemmatters.html.





COREL

t's almost unbelievable the number of things vanilla is in. Vanilla can be produced from peanuts, grapefruit, cloves, rice bran, and even barrels of crude oil. Originally discovered in Mexican orchids, it has spread from a taste hoarded by royalty into

the flavor in everybody's ice cream sundae. Vanilla is the world's most widely used flavoring, a long-believed aphrodisiac, and a contributor to the manufacture of specialty drugs.

A trip through the average home

turns up vanilla in vanilla extract, room spray, soap, body lotion and massage oil, pudding mix, vanilla-scented candles, potpourri, and, of course, vanilla ice cream—the number-one seller. A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that

> Coca-Cola and Pepsi are going head-tohead in the battle for *vanilla* cola supremacy.

Almost every chocolate recipe calls for it. Tobacco and cattle food are flavored with vanilla, and it is even used in baby food. Where does all this vanilla come from? The United States alone consumes more than 1000 tons of vanilla beans per year, just for "high-end" products. The world demand for vanilla far exceeds the natural supply.

Growth and harvesting

In order to meet demand, planters once carried cuttings of the tree-climbing vines from Mexico to Madagascar and other tropical areas, but the vines did not set pods. *Vanilla planifolia* (old name V. fragrans), which produces 99% of the pure vanilla sold, had been pollinated occasionally by hummingbirds, but mainly by a strain of Mexican Melipona bees. No bees meant no seedbeds and no vanilla. To make matters even more complicated, each flower opens for one day only. In 1841, growers began to hand-pollinate the orchids with a sharp bamboo stick—as they still do—and *V. planifolia* flourished. In Tahiti, vines mutated into a new species, *V. tahitensis*, the other commercial 1%.

Everywhere!

From steamy Mayan jungles to cold Norwegian pulp mills ...

from the Aztec halls of Montezuma

through Europe to Thomas

Jefferson's plantation, one spice

has been there. Chocoholics step

aside, it is vanilla that reigns

supreme as the world's most

widely used flavoring!

By Gail Kay Haines

Today, each ripening vanilla pod is so valuable that it is guarded and sometimes tattooed with its own I.D. number. Picked while green,

s.htm

the large pods have no characteristic smell. First, they must be "killed" in hot water, "sweated" in the sun, dried in the shade, and "conditioned" in a closed box until they turn brown, supple, and fragrant. This process, which promotes enzymatic action to develop the flavor, requires 3–8 months,

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finally yielding long, skinny blackish-brown pods-each weighing about 5 grams-filled with tiny black seeds. From planting to market can take five years, making natural-grown vanilla the second most expensive flavor, after saffron.

Vanillin

Vanillin, C₈H₈O₃, is the major component (about 2%) of "pure vanilla", a complex mixture of four primary and nearly 300 minor chemicals. All four major compounds belong to the group called "aromatics", which means they contain a benzene ring— C_6H_6 with various side chains substituted for hydrogen.

To protect consumers, different types of vanilla have specific legal meanings. Vanillin is only slightly soluble in water, but it dissolves easily in ethanol (ethyl alcohol). Pure vanilla extract is made from chopped vanilla beans, soaked for days or weeks in dilute alcohol. It is the only flavoring to have a U.S. Food and Drug Administration standard of identity. Pure vanilla extract must contain "the extractive material from 13.35 oz. of vanilla beans per gallon and at least 35% alcohol by volume". The extract picks up hundreds of chemicals from the vanilla pod, giving "pure" vanilla its complex taste.

But vanillin is vanillin, whatever the source. In the 1880s German chemists synthesized it as a cheap substitute for vanilla. "Imitation vanilla" is mainly synthetic vanillin. "Natural" vanilla is vanillin from other food sources mixed with a little pure extract. Since



the price differences are huge, chemical tests exist to make sure each product is what the label says. But words do not always mean what they suggest. For instance, "vanilla bean" ice cream may contain, not tiny seeds, but flecks of ground pods left over from the extraction process. Vanillin



Legal Vanillin and Counterfeit Extract

ecause synthetic vanillin is so much cheaper than natural vanillin and not subject to the fluctuations of supply and price that affect natural foods, it offers an inexpensive way for a food producer to impart a vanilla flavor to a food or beverage. Substituting synthetic vanillin for natural vanilla is safe, sensible, and legal-as long as the product is properly labeled as containing artificial vanilla flavoring.

But passing off synthetic vanillin for vanilla extract can be lucrative. A guick trip to the supermarket reveals that vanilla extract can sell for close to \$3.50 per oz., whereas imitation vanilla sells for about \$0.20 per oz. This presents a tempting situation for counterfeiters.

The possibility of cheating means that food chemists must devise a method to determine when a product contains natural or synthetic vanillin. But vanillin is the same chemical compound, whether it originates in the bean or is synthesized from lignin. Standard chemical analysis indicates the identity and quantity of a compound, but usually gives no clues about its sources. In the past few years, researchers have been able to distinguish between vanillin from fossil precursors, such as coal and petroleum, and vanillin of bean origin by using isotopic ratio mass spectroscopy and nuclear magnetic resonance.

The source can be determined by inspecting the carbon atoms in the vanillin with a technique called stable isotope ratio analysis (SIRA). SIRA is based on the fact that not all carbon atoms have the same mass. Of the carbon atoms found in nature, 98.9% have a mass number of 12, and 1.1% have a mass number of 13. Most organic compounds contain these percentages of carbon-12 (¹²C) and carbon-13 (¹³C) atoms. However, the ratio of these isotopes is slightly different for natural vanillin than for synthetic vanillin. The syn-

thetic vanillin is enriched in ¹³C. This happens because of differences in biochemistry of the vanilla orchid and that of most other plants.

The vanilla orchid carries on photosynthesis by a series of reactions known as the Crassulacean pathway. Most plants, however, including trees, use the Calvin pathway, which involves a greater number of chemical reactions. Because ¹³C is heavier than ¹²C, ¹³C reacts more slowly—and less ¹³C is incorporated during each photosynthesis reaction step. Most plants that will eventually become oil, coal, and lignin use the longer pathway. So synthetic vanillin from these sources has a lower percentage of ¹³C. By measuring the ¹³C:¹²C ratio with a mass spectrometer, scientists at the Bureau of Alcohol. Tobacco, and Firearms have been able to identify counterfeit vanilla extract, and federal attorneys have prosecuted unscrupulous suppliers.

But the detective story does not end here. When counterfeiters discovered that chemists could tell the difference between natural and synthetic vanillin by means of isotope ratios, they searched for ways to adjust the ¹³C:¹²C ratio in the synthetic product to more closely match that of natural vanillin. The easiest way is to remove the –OCH₃ group containing ¹²C and replace it with another –OCH₃ group containing ¹³C. But the government chemists were able to spot this ploy by removing the -OCH₃ group and testing for the presence of ¹³C using mass spectrometry.

Adapted from a classic ChemMatters article by R. C. Breedlove, August 1988

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A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that Coca-Cola and Pepsi are going head-to-head in the battle for vanilla cola supremacy.



probably makes up the difference. And although high-fat ice creams require a higher concentration of vanillin because there is less air to deliver the fragrance—no-fat ice creams require the most. A mixture of extract and concentrated vanillin seems to work best.

The scent in your hand lotion is likely synthetic, as is 95% of the world's vanilla supply. Once, most synthetic vanillin came from lignin—the natural polymer removed from wood pulp in papermaking. It was a good use for waste lignin, but the process gave off so much waste sulfuric acid that all such plants in North America have closed due to pollution.

History

The Totonacs, in Mexico, first gathered seed pods of the wild orchid for their unique flavor. They traded pods as vine-grown "money" with the Maya, who paid the beans in taxes to the Aztecs. When Cortez invaded the New World, around 1520, his men named the pods "vainilla" (little sheath) and shipped them home as part of the Aztec treasure. From Spain, vanilla spread across Europe, sometimes as a flavoring for chocolate. Some 250 years later, when Thomas Jefferson was ambassador to France, he brought vanilla back to America. The popularity of ice cream took vanilla flavoring to the top, but chemistry brought it into everyone's life. MIKE CIESIELSK

vanilla-like scent of heliotropin—a compound in Tahitian vanilla—produced a 63% reduction in patient anxiety during MRI scans. Vanilla is one of the three most widely used flavoring/scents to mask the bad taste of medicine, and herbalists are reviving its popularity as a folk remedy to heal and soothe.

For hundreds of years, many people have ascribed aphrodisiac properties to vanilla. European physicians once believed that vanilla could cure sexual ailments and improve performance. Chocolate, also thought to have similar properties was considered "cold", while vanilla was "hot".

Before visiting his harem, the Aztec ruler Montezuma

would consume large quantities of "chocolatl" containing vanilla extract. We'll never know if Montezuma's success with the ladies was a result of the smell of chocolate on his breath or vanilla's aphrodisiac qualities.

Maybe it's not quite that "hot", but modern research has shown men respond to vanilla more than to any other scent. Today, it is appreciated for its mood-lifting, romantic appeal to both sexes. Unless you happen to be a bug. Vanilla scent, alone or with DEET makes a good insect repellent, yet vanilla is used in flypaper, to attract flying pests. Go figure.

Either way, fans of vanilla owe a huge debt of gratitude to chemistry, for making so many sources of vanilla available. Otherwise, this "nectar of the gods", as the Totonacs called it, might still be property of the royal rich. \blacktriangle

Gail Kay Haines is a science writer and book author from Olympia, WA.



Now, vanillin is more likely to be made from petroleum or coal tar. Ethyl vanillin from crude oil—which replaces the methyl (CH₃-) side chain in vanillin with ethyl, (C₂ H₅-)—has a vanilla taste that is 3 times stronger than vanillin, but it is insoluble in butter, caramel, and chocolate. It is used in perfumes and low-fat ice cream. Eugenol from clove oil and guaiacol from coal tar can both be turned into vanillin. As wines and liquors age in oak barrels, alcohol pulls vanillin right out of the wood. Both peanuts and their hulls contain vanillin, which, even at parts per million (ppm) levels, adds a major flavor note. Grapefruit contains vanillin in the ppm range too, but here it causes an "off" taste. In this case, less vanillin tastes better.

Medicinal use

Vanilla even has some medicinal uses. Vanillin is used in the manufacture of medications for Parkinson's disease and high blood pressure. Memorial Sloan-Kettering Cancer Center discovered that the





Scanning Electron Microscopy Solves a Mystery! The Mystery of The Pockmarked Paint Job

By Tim Graham

Small crater-like defects mysteriously began appearing in the paint jobs of high-end sports cars coming off a particular line at a car factory. **Repairing the defects was** very costly. For such a well-established process, the manufacturer was stumped. What could be responsible? **Defective paint? Bad equipment? Sabotage?** Well maybe not sabotage. but no one really knew until a microscopist found the crucial clue.



PHOTODISC

erry Jourdan's day started just like most others. As a research microscopist for one of the largest chemical manufacturers in the world, his job is to evaluate chemical samples using scanning electron microscopy (SEM). Although much of his analytical work is routine, frequently, some very interesting projects come across his desk.

As he rifled through the scheduled work for this particular day, one request immediately caught his attention. A sample of red paint had arrived from one of the major automobile manufacturers for analysis. The red paint pigment manufactured by his company was being used to paint a high-end sports car. The automobile manufacturer was having a problem applying the paint.

Defects, known as craters, were appearing on some of the cars and ruining the quality of the finish. Repainting these cars was a costly and time-consuming repair— a bill that could cost hundreds of thousands of dollars! If his company had supplied a faulty pigment, it would be liable for the cost of the repairs.



Powder (above) and Iguana scales (right).



Great detectives and scientists have a lot in common. Both are armed with powers of deduction and equipment that helps them ferret out and understand clues. Sherlock Holmes had a magnifying glass. Jerry Jourdan had the SEM. He knew that for this type of small-surface defect, the SEM could reveal within minutes clues that would help him unravel the mystery.

Understanding scanning electron microscopy

The SEM is probably as big a mystery to most of us as the paint defect was to Jerry. Here's how it works.

The key behind an SEM's success is the use of electrons instead of light to form an image. The first modern scanning electron microscope was developed in the Cambridge University Engineering Laboratory more than 50 years ago, in 1951.

Whereas an optical microscope produces an image by using lenses to bend light waves, an SEM uses electromagnets to bend an electron beam. This beam is then converted to an image on a computer screen. A beam of electrons is produced by heating a metal filament called a tungsten hairpin gun. (Tungsten is the same metal that is used in incandescent light





Insect wing.

bulbs like the ones you typically use at home.) When voltage is applied, the filament heats up. Negatively charged electrons are emitted from this hot filament and are accelerated toward a positively charged plate. These electrons are then directed through the microscope, where a series of electromagnetic lenses focuses them into a fine beam that eventually strikes the sample.

This entire process must be done under a vacuum because other molecules could absorb electrons that would destabilize the beam. The presence of air could also cause the electron source (tungsten filament) to overheat and burn out.

Once this electron beam strikes the sample, several interactions occur between the beam and the specimen being analyzed. Two such interactions are typical: (1) *secondary electrons* accompanied by X-rays are produced when electrons from the beam are absorbed by the sample and, (2) *backscattered* electrons are formed when the electrons from the SEM beam collide with the specimen and are reflected with little loss of energy. The absorption and reflection of electrons are measured with separate detectors to provide useful information about the specimen being studied.

Secondary electrons

Very much like sonar (sound navigation ranging), which bounces sound waves off the ocean floor to determine the shape of the





 $\ensuremath{\mathsf{SEM}}\xspace/\ensuremath{\mathsf{EDX}}\xspace$ indicate the presence of Zr, Al, Si, and Cl.

seafloor, secondary electrons can be used to map the surface features of a specimen. These secondary electrons are produced when the original higher-energy electron beam knocks electrons out of (ionizes) atoms on the surface of the sample. As the electron beam scans the entire surface of the sample, these secondary electrons are detected and then converted into an image. Areas of greater ionization appear brighter than areas with lower ionization. The resulting three-dimensional image has much higher clarity than an image produced by normal photographic techniques.

X-rays

The secondary electrons emitted from a specimen usually come from one of the lower energy levels in the atoms. Because this leaves a "vacancy" in one of the lower energy levels, an electron from a higher energy position in the atom will "fall" into this vacancy. This results in the release of energy, and typically, this energy appears in the X-ray region of the electromagnetic spectrum. Because Xrays have characteristic energies, unique to the element from which they originated, the identity of an element can be determined. The technique, energy dispersive X-ray analysis (EDX), is typically used to help identify the composition of the contaminant particle(s). SEM/EDX can detect elements at levels as low as 0.1 atomic percent.

Backscattered electrons

SEM produces a second group of electrons called backscattered electrons. These result from the primary electrons from the beam striking the surface of the sample. Measuring these electrons provides an even more complete evaluation of the spec-

imen. When the primary electrons from the beam strike the surface of the sample, backscattered electrons are reflected away from the sample. Atoms with higher atomic number show up brighter on the computer screen. Images produced from backscattered electrons provide useful information about the surface of relatively smooth specimens, but more importantly, give analysts information on the atomic number, and therefore the identity, of the element being bombarded. Scientists can combine the information provided by X-rays, secondary electrons and backscattered electrons to determine the composition of the contaminant. SEM/EDX proves to be a powerful tool in making such determinations.

Back to the mystery ...

When Jerry Jourdan fired up his SEM, analysis revealed the presence of the contaminants aluminum, silicon, chlorine, and zirconium in the red paint samples. What on earth could introduce these elements?

Jerry knew. The answer was "elementary". All of these elements can be found in a very common

household product underarm deodorant!

The active ingredient of many antiperspirant/ deodorants is aluminum zirconium chlorohydrex gly (anhydrous). Silica (SiO₂) is used to provide texture. The SEM data made Jerry suspect that the cratering was due to the interaction of the deodorant solids with the paint during the drying process. Somehow these deodorant solids had made their way into the paint!

Although, Jerry and an investigating team were certain that deodorant was the culprit, it would take further investigation to find the source of the deodorant. The most likely source of these solids was an employee working either in the manufacturing of the pigment or on the auto paint line. Plant officials investigated the process area at the chemical plant to determine whether proper protocols were being followed. They easily determined that the antiperspirant particles did not originate in the manufacturing of the pigment.

Next, officials were dispatched to the automobile facility to monitor the paint application area. A careful review of the data had revealed some additional interesting clues about the cratered paint samples. The damage only occurred on the driver-side fender and hood of the automobile, and only on cars painted during a certain time of the day. These two areas used the same spray nozzle and were operated by a single individual. Hmmm ...

When investigators monitored the operations they found that the auto plant employee who painted this section of the car would have to swing the spray nozzle over the hood, while stretching his entire arm over the



flawed areas of the car. Further monitoring revealed that when the painter did this, flakes from his solid underarm deodorant fell into the freshly applied paint! Once the source of the problem was

identified, new procedures were put into place to prevent this from happening in the future.

Jerry's team had rightly interpreted the SEM/EDX data. It was simply a task of applying some good detective work and logical reasoning to find the origin of the contaminant. In the end, his company was absolved of all responsibility for providing flawed paint pigments.

Tim Graham teaches chemistry at Roosevelt High School in Wyandotte, MI. His most recent article, "Luminol—Casting a Revealing Light on Crime", appeared in the December 2001 issue of *ChemMatters*.





Chem.matters.links

Elemental essays

Test your "elemental" knowledge. What patriotically named element is vital to the operation of smoke detectors? What's the most abundant element in the universe? What element is an aluminum can made of? No, no ... wait that's not right.

Anyway, if you like facts and stories about the elements. Chemical & Engineering News has recently posted 89 essays on the the elements on its website. Don't expect an encyclopedic recitation of facts. Eminent scientists and writers wrote many of the essays about their personal experiences with a particular element or elements. Read the essays to find the answers to the two questions above. They are available as a linked periodic table. http://pubs.acs. org/cen/80th/elements.html

Submit your own SEM sample

That's right! You've read about *scanning electron microscopy* (SEM) in this issue; now you and your class can submit and view your own samples. Professor Scott Chumbley, at Iowa State University, Materials Science and Engineering Department, is hoping to receive requests to view samples from interested students and

teachers who want to operate the SEM over the Web and view samples from their classroom.

> Submitted samples may then appear in the image library with the name of the sample, the name of the student (or class) and school submitting the sample, and a short description of the sample.

> > What can you submit? Lots of things! Samples of insects, common materials, and even pond scum are already available for

viewing. *Take special note:* Not all samples can be viewed in the SEM. Generally, the samples must be dry, nonliving, and capable of being coated with a material to make them electrically conducting.



Contact Scott Chumbley at **chumbley@iastate.edu** if you wish to operate the SEM from your classroom.

If you want to see more SEM images or fill out a submission form,

visit http://www.mse.iastate. edu/microscopy/home.html.

Explore deep sea vents

If you'd like to see more pictures of hydrothermal vents, the *Alvin* submersible, or the giant tubeworm's neighbors, the National Oceanic and Atmospheric Administration (NOAA) has a site for you—http:// oceanexplorer.noaa.gov—with

lots of pictures and information.

Ocean Explorer provides current information on NOAA scientific and educational explorations and activities in the marine environment. Read the log and view pictures from a 2002 NOAA expedition to look at hydrothermal vents.

http://oceanexplorer.noaa.gov/ explorations/02galapagos/ galapagos.html.

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