OCN 201 Chemical Oceanography Class Notes, Fall 2014

Hydrothermal vents on the sea floor

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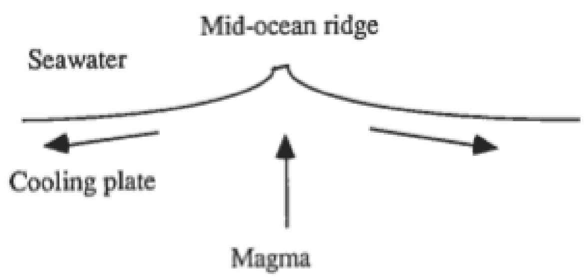
What are hydrothermal vents?

Hydrothermal vents or hot springs are places where high temperature water is coming into the oceans.

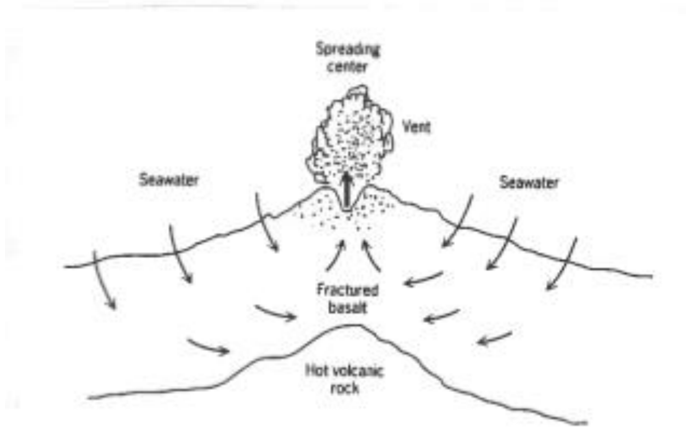
What causes them?

Figure 1 Schematic of a hydrothermal system



The surface of the Earth is composed of a series of rigid plates which are in motion. In some places under the ocean, the plates are moving apart slowly (~ inch/yr) and new ocean floor is being produced in the gap between the plates by the upwelling of hot magma (molten rock) from the interior of the earth. As the plates move apart, the magma that has upwelled moves out to the sides, forms the new seafloor, and it is replaced by more recently upwelled material. As this new seafloor cools, it contracts, and cracks form in it. These cracks link up to produce fractures in the rocks that can go down quite far below the bottom of the ocean.

Figure 2 Cartoon depicting water circulation at a hydrothermal vent site



As shown in figure 2, the cold overlying seawater can penetrate down through these cracks. The seawater finds its way down through the cracks until it starts to encounter hot rock (the magma). When the cold seawater meets the hot rock, of course it becomes heated. Hot water, just like hot air, rises and so the heated seawater starts to rise back up using other cracks until it finally comes out onto the ocean floor through cracks or chimney-like structures. Because of chemicals dissolved in the hot seawater, the areas around where the hot water comes out onto the bottom of the ocean often have lots of marine life associated with them. In the deep ocean where bottom-dwelling animals are spread out very thinly, the hot springs sites have a visual appearance that is very similar to oases in the deserts.

The depth to which the seawater penetrates below the seafloor is determined by the depth of the source of hot magma. By measuring the silica content of the hydrothermal fluid, it is possible to make some estimates of this depth. In some cases, this has been shown to be as deep as 5 km (3 miles) beneath the bottom of the ocean.

The circulation of the seawater can also spread sideways into the older crust. The plates are spreading away from the center and so as you get further away from the ridge axis, the plates are getting older and colder. Some estimates suggest that the circulation may spread as far as 200 km (124 miles) on either side of the ridge axis.

<u>Where vents are found</u>

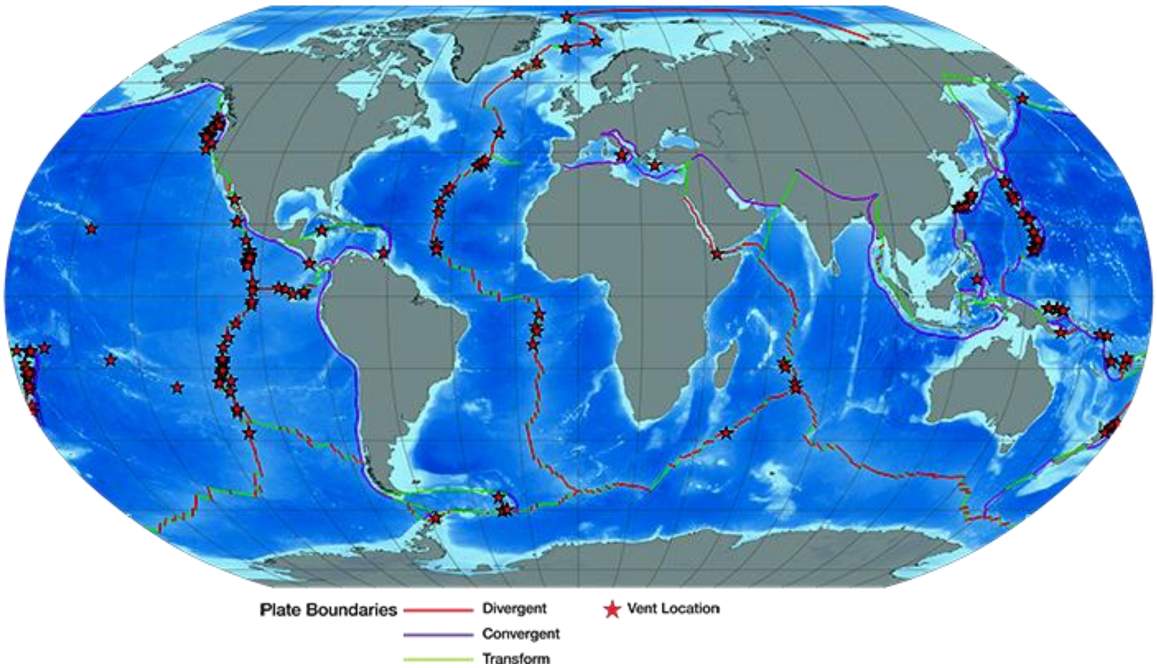
Vents are found anywhere that there is hot magma near the bottom of the oceans. The most common regions that this occurs is along the axial valleys of the mid-oceanic ridge systems, i.e. at the edges of the plates. Since the water can spread out sideways, vents can also be found out on the sides (flanks) of the ridges. Seamounts are also produced by the upwelling of magma from the interior of the Earth so hydrothermal vents can be found associated with these features when they are still in their growth phase. A good example of this is Loihi, the seamount that is growing off the southeast coast of the Big Island. Loihi will probably eventually become the next Hawaiian Island. Currently its summit is about 1000 meters (1/2 mile) below the surface of the ocean. Various scientific expeditions, including using submarines, have found hydrothermal venting taking place near the summit and on the sides of Loihi.

Most of the hydrothermal vents that have been investigated have been more than 2000 meters below the surface of the ocean because this is the depth at which most of the mid-ocean ridges are found. However, there are places where mid-ocean ridges are much shallower. For example, Iceland is formed from, and sits astride the Atlantic mid-ocean ridge. In places like this and also on seamounts, hot springs can occur at much shallower depths.

The idea that high temperature hydrothermal vents might exist on the ocean floor is quite recent, dating from 1965. Indirect evidence for the existence of high temperature hydrothermal vents on the ocean floor began to accumulate as soon as the idea had been proposed in 1965 but it was not until 1977 that any were found and sampled. The first ones were found during the comprehensive geological expedition using the research submarine Alvin to explore the Galapagos Spreading Center (located near the equator in the Pacific Ocean). These scientists located and sampled water from active hydrothermal vents at 2000 meters depth. Part of the reason it took so long to find them is because hydrothermal vents are quite small (~50 meters across) and are usually found at depths of 2000 m or more. Using submarines to find hydrothermal vents is also very inefficient since even with all the lights on the visibility from the submarine is still only about 10 m. With this kind of visibility, trying to locate a feature like a hydrothermal vent that is only 20 -50 meters across is like trying to search the whole of Kapiolani Park for your lost car keys at night with only a small flashlight! More recently locating hydrothermal vents has been done by using packages towed from surface ships that have cameras and chemical sensors attached to them, and only after they have been located are manned submarines used to sample them. As you can imagine, the cost of such work is high and the amount of the ocean bottom can be covered is very limited. For these reasons, only a limited number of regions have been sampled but it is expected that there is active venting along most of the ridge systems and active seamounts.

Figure 3 shows the location of the known hydrothermal activity in 2011. Many additions to this map came as a result of the development of submarines that were capable of diving much deeper than the 4,000m of the original Alvin. In particular the much of the discovery of venting in the back-arc basins and seamount regions around Japan happened since the Japanese Shinkei 6000, a submarine capable of diving to 6000 m, was completed. The newly Most vent sites have been found where seafloor spreading rates (the rate at which the ocean bottom plates are moving apart) are greater than 3 cm/yr. Another aspect of hydrothermal vents sites is that they are often found by locating the animal communities that surround them since these animal communities are much larger than the vents themselves. In fact, the vents themselves are usually only 1-2 meters across while the animal communities can spread out for 10's of meters around them.

Figure 3 Distribution of known deep oceanic hydrothermal vent sites in 2011
Source: Woods Hole Dive and Discover



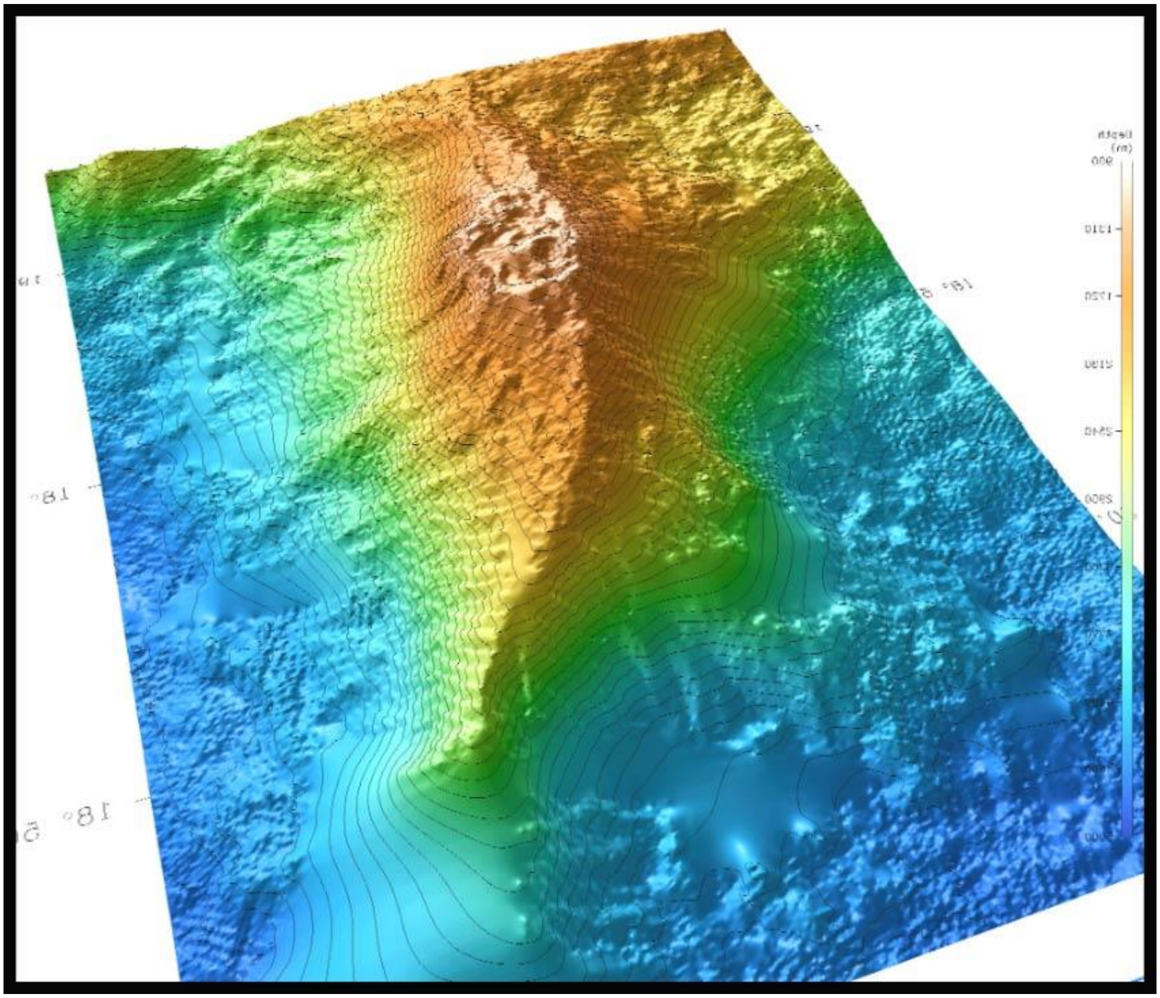
One of the problems of finding vents this way is that we usually find hydrothermal vents with animal communities around them but do not often find ones without animals (even though we know they exist) because they are harder to see. We therefore do not really know how many animal versus non-animal vent sites there are.

<u>Other sites of hydrothermal vents</u>

Seamounts are also produced by the upwelling of magma from the interior of the Earth. Just like at the spreading centers, the new rock will crack as it cools and will allow cold seawater to penetrate down towards the hot rock forming hydrothermal vents. A good example of this is Loihi, the seamount that is growing off the southeast coast of the Big Island. Over the next few million years Loihi will probably become the next Hawaiian Island. Currently its summit is about 1000 meters (1/2 mile) below the surface of the ocean. Various scientific expeditions using the submersible from the Hawaii Undersea Research Laboratory, which is part of the Oceanography Department at UH, have found hydrothermal venting taking place near the summit and on the sides of Loihi.

Figure 4 shows the summit of Loihi, off the SW coast of the Big Island. Previously discovered vents at the summit of Loihi disappeared when a pit crater formed during a series of eruptions in August of 1996. The only animal communities associated with the Loihi vents are mats of bacteria which are not very visible.

Figure 4 Map of the summit of Loihi seamount.



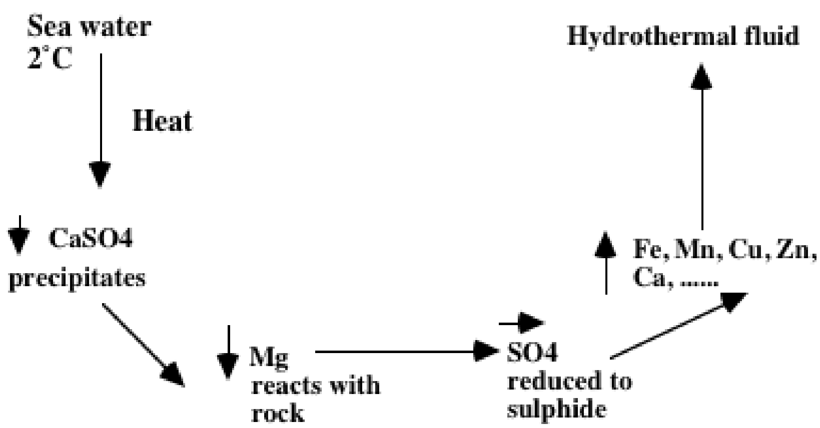
What does the hydrothermal fluid look like?

The seawater that comes up out of hydrothermal vents is very different from the water that goes down.

The hydrothermal fluids are usually very hot (hence their name), with temperatures as high as 380°C (716° F). This compares to about 2-3°C for the ambient seawater at those depths. The boiling point of water is 100°C (212°F) but hydrothermal seawater at 380°C does not boil because of the pressure at the depth at which the vents are found. The boiling point of water is a function of pressure. On the surface of the earth at one atmosphere of pressure, the boiling point of water is 100°C. If you lower the pressure, the boiling point goes down. For example, in Colorado where air pressure is lower because of altitude, the boiling point of water is about 96°C (that's why there are always different cooking instructions on packages for use in the Rocky Mountains). Conversely, if you increase pressure, the boiling point goes up. For example, at 2000 m depth in the ocean (a depth at which vents are found), the total pressure is a little over 200 atmospheres (220 x the pressure at the surface) and the boiling point of water is over 400° C.

At the same time that the seawater is being heated, it is also reacting chemically with the hot magma. The high temperature of the reaction between the seawater and the oceanic basalt results in the addition of many chemicals to the seawater, removal of some and transformation of others. As we shall see later, a further set of chemical changes takes place when hot fluids come back to the seafloor and mix with cold seawater.

Figure 5 Schematic of chemical reaction pathway during hydrothermal circulation



The amount of the chemical alteration processes that occur while the seawater passes through the hydrothermal system can be very important and we will look at each one in turn.

<u>Chemicals that are removed.</u>

The first thing that happens to the cold seawater that starts to descend below the seafloor towards the hot magma is that it is heated. When seawater is heated, calcium sulphate ($CaSO_4$, also known as anhydrite) is precipitated from seawater. This happens because calcium sulphate is less soluble in hot water than in cold, the opposite of how solubility normally goes.

Another chemical that is lost from the seawater is magnesium (Mg). The magnesium in the seawater reacts with the surface of the rock as the seawater passes through, and is removed from the seawater. We will come back to magnesium below when we talk about fluxes.

<u>Chemicals that are added.</u>

There are many elements that are added to the seawater from the rocks but we will just mention a few that have particularly important consequences: iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn).

Table 1

Chemistry of typical hydrothermal vent fluid				
Chemical	Symbol	Hydrothermal fluids (µmol/kg)	Normal seawater (mmol/kg)	Hydrothermal effect on seawater
				Removed
Magnesium	Mg	0	53	All removed
Sulphate	SO_4	0	28.6	All removed
				Enriched
Iron	Fe	1800	<.000001	1.8 million times
Manganese	Mn	1140	<.000005	228,000 times
Copper	Cu	44	<0.00001	4,400 times
Zinc	Zn	40	<0.00001	4,000 times

Table 1 above shows that the concentration of all three of these elements is extremely high in hydrothermal fluids. In the case of iron, the concentration is almost 2 million times the concentration in normal deep saltwater. Manganese is also enriched by more than two hundred thousand times its normal seawater concentration. We shall see below that we can use the tremendous enrichment of these two chemical elements to help find the location of hydrothermal vents.

While not as enriched, the copper, the zinc and iron are the elements which precipitate to form the black smoke that makes up the bulk of the chimney material as we shall see later.

<u>How much do hydrothermal vents contribute to the oceanic chemical balance?</u>

One of the important questions that chemical oceanographers would like to answer is how much do hydrothermal vents contribute to the chemical mass balances of the ocean. Given the previously admitted difficulty of finding hydrothermal vents, it is clearly difficult to make very reliable estimates. For example, there is hydrothermal activity in the Indian Ocean but at this point there are only three known vent sites. Similarly, the Arctic Ocean has a mid-ocean ridge running through it but much of the ocean is permanently covered with ice so it is unlikely that research submarines can ever be used to find hydrothermal activity there. We are left with some indirect ways in which we think we can calculate the total hydrothermal flux into the ocean. These indirect ways rely on a lot of special assumptions about the chemistry of the ocean and the atmosphere and not everybody agrees they are correct. Even though we know that the numbers are not very accurate, they can still be quite useful. Using these calculations, it is possible to come up with some sort of estimates of total global hydrothermal water fluxes. These water fluxes can be combined with the chemical measurements made at specific hydrothermal sites to calculate global chemical fluxes.

Table 2

Comparison of global fluxes from hydrothermal vents to those from rivers

Chemical	River input	Hydrothermal input/removal	Comparative flux: Vent/River
Water	4×10^{16}	1.7×10^{14}	0.4%
Magnesium	5×10^{12}	-8×10^{12}	-160%
Sulfate	4×10^{12}	-4×10^{12}	-100%
Calcium	12×10^{12}	3.5×10^{12}	29%
Barium	10×10^{9}	2.4×10^{9}	24%
Potassium	1.9×10^{12}	1.2×10^{12}	63%
Lithium	$1.4\ \ 10^{10}$	16×10^{10}	11 times

As the table above shows, the water flow through hydrothermal systems is only about 0.4% of that flowing down rivers into the ocean. Put another way, that means that the hydrothermal vent water would have to have 200 times as much of any chemical in it to have the same effect as rivers on the chemistry of the ocean. We can see that for a few elements this is true.

As we mentioned above, the magnesium is removed from seawater during hydrothermal circulation. The total amount of magnesium calculated to be removed from seawater by this process is in fact more (160%) than all the magnesium that is brought into the oceans by the rivers. (The fact that calculated magnesium removal is greater than calculated supply is an immediate demonstration of the inaccuracy in the hydrothermal flux calculations). In the earlier discussion of the residence time of elements in the ocean, it was stated that the fluxes could be calculated by estimation of either the amount going into the ocean or the amount being removed since they must be equal. Before the discovery of hydrothermal vents and the realization that magnesium was lost during the high temperature water circulation, there was a problem with the oceanic magnesium balance. As far as could be calculated then, there did not appear to be enough magnesium being removed from the oceans compared to how much was going in. Now we know that hydrothermal vents are capable of removing just all (or maybe too much!) of the magnesium that comes into the oceans from the rivers.

The table also shows that for some other elements the flux from hydrothermal vents appears to be quite significant. Maybe 25% of all the Ca and Ba; and maybe as much as 92% of all the Li entering the oceans is coming from hydrothermal vents, not from rivers.

What happens to the Fe, Cu, and Zn when the hydrothermal fluid hits seawater is quite interesting.

Chimney Formation

When the high temperature hydrothermal fluid mixes with low temperature seawater, an immediate series of reactions take place.

Calcium which has been put back into the hydrothermal fluid from reaction with the rock (remember the calcium in the downgoing seawater was removed due to $CaSO_4$ formation as this water became heated earlier on), reacts again with the SO_4 in the cold ambient seawater to form more $CaSO_4$ (anhydrite).

The enriched elements iron (Fe), copper (Cu), and zinc (Zn) which coexist with sulphide (which we will talk more about later) in the hydrothermal fluid at high temperature become oversaturated as soon as the hydrothermal fluid mixes with cold seawater. The result of this is that a black "smoke" of Fe, Cu and Zn sulphides form. These sulphides, along with the anhydrite build up to form a chimney. The chimneys will eventually seal up as they continue to grow inward. New chimneys will form and the old ones will fall over to help form large piles of sulphide rubble. If left for long enough, the sulphide material would dissolve but it appears that in some cases the sulphide is preserved. The evidence for this is that since the discovery of the hydrothermal vent systems on the bottom of the oceans, geologists now recognize that most of the major sulphide ore deposits in the world originally came from hydrothermal vent processes. These ore deposits can be massive ranging from 2 to 25 million tons. At this stage, exactly how the sulphide material becomes concentrated in one place and prevented from dissolving is not entirely clear.

Not all hydrothermal vents form chimneys. It appears that in some places the high temperature hydrothermal vent water mixes under the ocean floor with more cold ambient seawater. When this happens, the materials that precipitate to produce chimneys do this below the sea floor and therefore what emerges is usually a clear fluid at much lower temperatures. In fact, the first vents to be sampled in the Galapagos were of this type. It may be that this kind of process, sub-surface dilution of the high temperature end-member is the mechanism by which massive sulphide deposits form.

In addition to precipitation and formation of the chimney, much of the Fe and all of the Mn can escape into the surrounding seawater. The clouds of particulate material that these "smokers" produce form the basis of a means to find hydrothermal vents.

Figure 6 Schematic cross section of a hydrothermal chimney

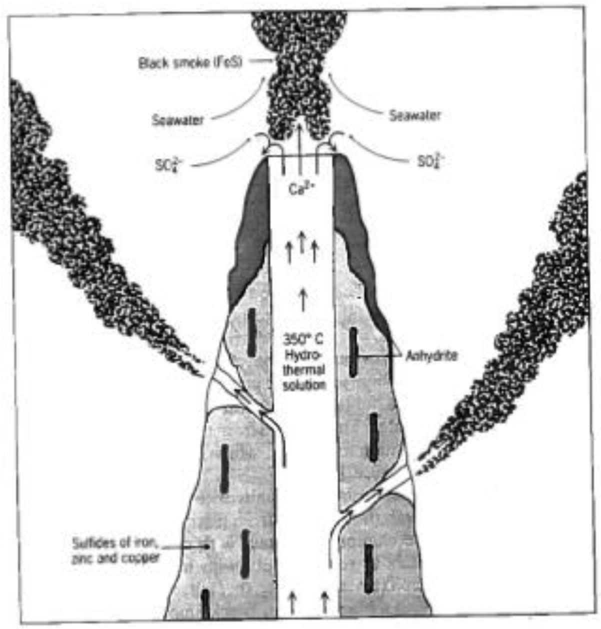


Figure 7 Distribution of manganese in the water above the East Pacific Rise

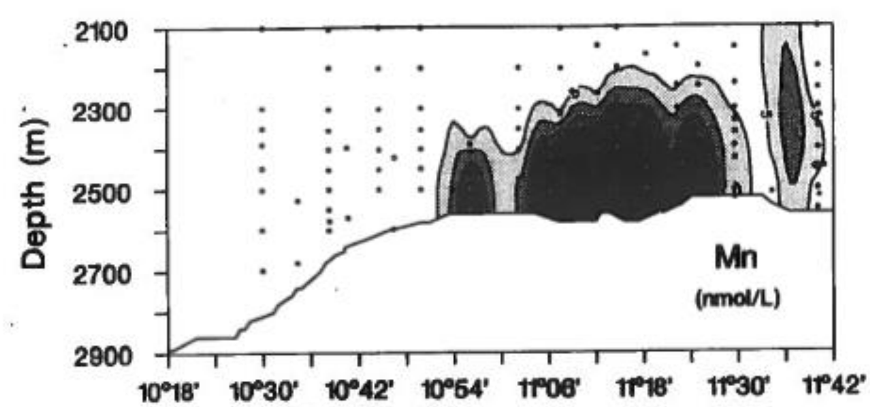
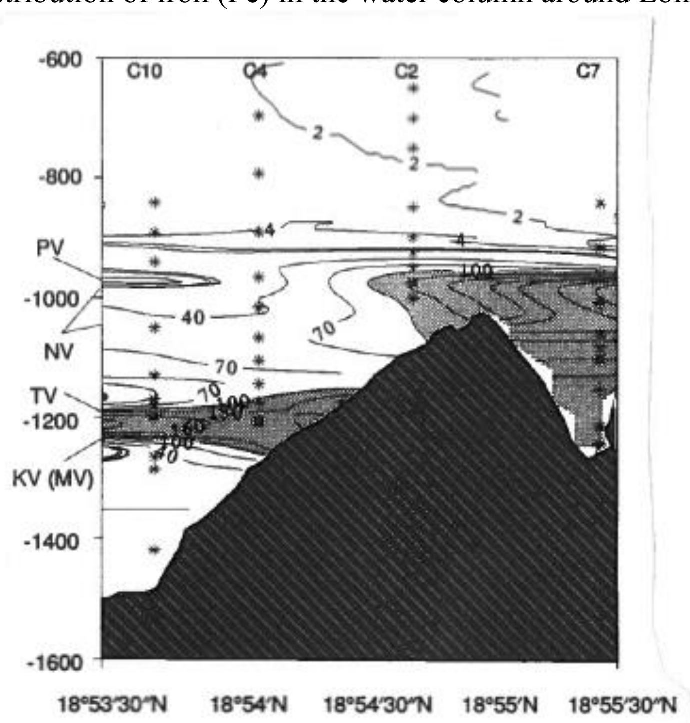


Figure 7 shows a plume of hydrothermal manganese found hovering above the East Pacific Rise between 10 and 12° N. The small dots show where water samples were collected, the shaded dark areas show the regions where the manganese concentrations were high showing the presence of active hydrothermal vents. From the shape of the plume, you can see that the hydrothermal vent water has risen from the vent site up through the water column until by mixing with cold ambient seawater its density has become the same as that of the surrounding seawater. This plume then moves away from the vent source by the prevailing currents, spreading out laterally as it goes. The water samples that were analysed to produce this figure were collected using a rosette sampling system. The rosette is a frame which carries several water sampling bottles. The rosette is towed behind a research ship above the ridge axis. By sending an electrical signal down the wire connecting the rosette to the ship, it is possible to close water bottles one by one--thus providing a series of samples at predetermined places. By collecting water samples over extended sections of the ridge axis, it is possible to map out large areas of the ocean and identify the regions in which hydrothermal vents are likely to be active. These can then be investigated in more detail using submarines. Also important to note is that in this case we are not relying on the animals around the vents to find them.

As Table 1 showed, iron is even more enriched in hydrothermal fluids than manganese and can also be used to "prospect" for hydrothermal vents. The figure above shows the distribution of iron in the water around Loihi seamount. The very high concentrations of iron measured in the water column around Loihi show unequivocally the presence of the hydrothermal vents at about 1000 m.

Figure 8 Distribution of iron (Fe) in the water column around Loihi seamount



They also indicate that there might be venting occurring near 1200 m. Although vents have been found on Loihi at this depth, it was thought that they were dead, i.e., were not venting hydrothermal fluid. The iron data suggests that there are either other vents at this depth or the dead vents have come back to life!

Chemicals that are changed

One of the most important chemicals in hydrothermal fluids is sulphur. During the hydrothermal circulation process, much of the sulphur is removed from the seawater by precipitation as calcium sulphate (anhydrite). Some sulphate, though, remains in the seawater and becomes chemically reduced to sulphide which is present as hydrogen sulphide (this is the same gas that you get from rotten eggs, or from new cars with malfunctioning catalytic converters).

Hydrogen Sulphide

The hydrogen sulphide in the vents is of great significance. The ultimate source of the energy that we or any other organisms use is sunlight. In the case of plants, the connection is direct and obvious. In the case of organisms like ourselves, we gain our energy from eating plants that got their energy from sunlight or other animals that got their energy from eating plants, etc. This is also true in the ocean. Even organisms that live in the bottom of the deep ocean live on food material that has fallen from the surface waters and was originally (directly or indirectly) tied to sunlight for its production.

Until the discovery of hydrothermal vents and the community of animals that live around them, it was thought that **all** animal communities were based on sunlight-derived energy. Chemical energy can also be obtained by oxidizing hydrogen sulphide. In hydrothermal vent fluids, there are bacteria that live by "eating" hydrogen sulphide. These bacteria form the base of the food chain and are in turn eaten by other animals. This chemosynthetic food chain (compared to a photosynthetic food chain which relies on sunlight) is the source of energy for all the animals that live around the hydrothermal vent sites.

The discovery of these communities of animals around these vent sites on the ocean floor 15 years ago was the first time that anyone realised that there were communities of animals whose sole existence depends on hydrogen sulphide, not on sunlight. This has some very profound implications for possible mechanisms for the origin of life on this planet. It has been suggested that hydrothermal vents such as these may have been the places where life first commenced on Earth. This also has profound implications for the search for life on other planets. Currently NASA is planning a mission to ice-covered Europa that would examine the possibility of a liquid ocean below Europa's icy surface. If evidence of a liquid ocean is found NASA then plans to send robotic spacecraft/submarines designed to explore this ocean specifically to look for life forms that might originate from chemosynthesis. < http://sse.jpl.nasa.gov/missions/jup_missns/europa.html>

As was discussed earlier, the existence of the animal communities has in fact aided us in finding these hydrothermal vent sites since they tend to be spread out over a relatively large area around the vents and show up well in photographs. But as you can see from the above, it also means that we only tend to find vent sites which have hydrogen sulphide in the water. We know, though, that there are hydrothermal sites in which there is no hydrogen sulphide in the vent water and hence no animals around the vent--Loihi is an example. This underlines a very crucial point in searching for vent sites. If the only technique for looking for hydrothermal vent sites were by looking for animal communities surrounding them, you would only ever find hydrothermal vents with hydrogen sulphide in them. This point can be generalised to all of science, i.e., the tools used to examine any system influence the results that are found.