

# **THE DISCOVERY OF HYDROTHERMAL VENTS**

**25th Anniversary CD-ROM**

## **The Geochemistry of Ridge Crest Hot Springs**

by

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# The Geochemistry of Ridge Crest Hot Springs

by John M. Edmond

Much of the effort of geologists and geochemists is directed toward understanding past environmental conditions based on the rocks that they produced. This is as true in the study of crystalline rocks\* and ore bodies as in the study of paleoecology. In fact, there is good reason to believe that most of the inorganic processes responsible for the formation of ancient rock types are still active today, but only a time machine could transport us back to the habitats that produced fossil organisms.

The crystalline rocks and ore bodies that we see exposed at the surface were formed in very hot environments and at great depths (and, consequently, high pressures) in the crust under the continents or the ocean. Since these environments still exist today, the barriers to direct examination of inorganic processes are but the technically tractable ones of temperature and depth. On the continents direct observation of high pressure and temperature regimes is possible only by drilling; hence the impetus for the expensive, super-deep drilling programs of the Soviet Union and the United States.

Marine scientists are more fortunate. The process of sea-floor spreading produces very high temperatures at shallow depths in the oceanic crust. The pressure depends on the height of the overlying water column. Fissures and faults associated with the spreading process rapidly expose rocks formed at elevated temperatures. They also act as conduits for the circulating seawater responsible for many of the metamorphic and ore-forming processes in the oceanic crust. Rather than having to drill through 10 to 15 kilometers of solid rock to enter their natural laboratory, marine scientists can get there in specially designed submarines. At present two submarines are active in this kind of investigation. The French submersible *Cyana* was designed by

\* Rocks formed at high temperature and pressure and characterized by crystals of aluminosilicate minerals.

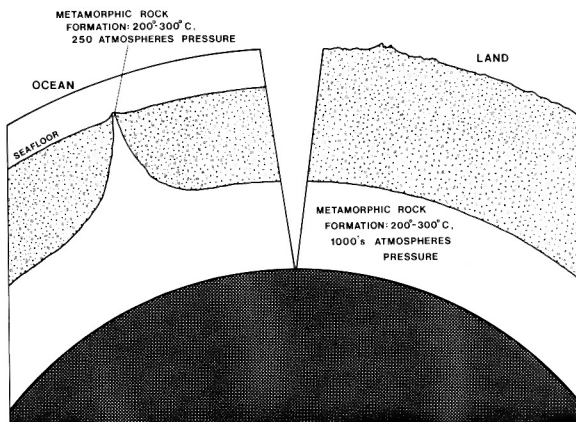


During fissure eruptions along mid-ocean ridges, lava from the magma chamber below forms new oceanic crust, which is then carried away from the spreading center by tectonic processes. The fissure eruption shown occurred in Hawaii, but it is believed that similar eruptions take place at mid-ocean ridges. (Photo courtesy of Robert Ballard)

Jacques-Yves Cousteau as a photographic platform. It is highly maneuverable and an excellent exploration tool. However its scientific payload is very limited. The *Alvin*, operated by the Woods Hole Oceanographic Institution (WHOI), is somewhat larger and slower than *Cyana*, and is a real weight lifter. The sampling programs whose results are described in this article were carried out by *Alvin*; however, a number of the study areas were first identified by *Cyana*.

## The Origin of Hot Springs

As a general rule, void spaces in rocks are filled with water. When molten material from the mantle



Location of metamorphic rock formation in oceanic and continental crust. The formation of these rocks and associated ore deposits requires high temperatures and pressures found only deep within the earth or at the bottom of the ocean.

intrudes into the crust, this water is raised to high temperatures and, if there is sufficient permeability, will convect to the seafloor, where it forms hot springs. On land, much of the hot water recirculates back into the rocks. Coupled with the great compositional heterogeneity common in the continental crust, this recirculation makes interpretation of the chemistry of such springs very difficult.

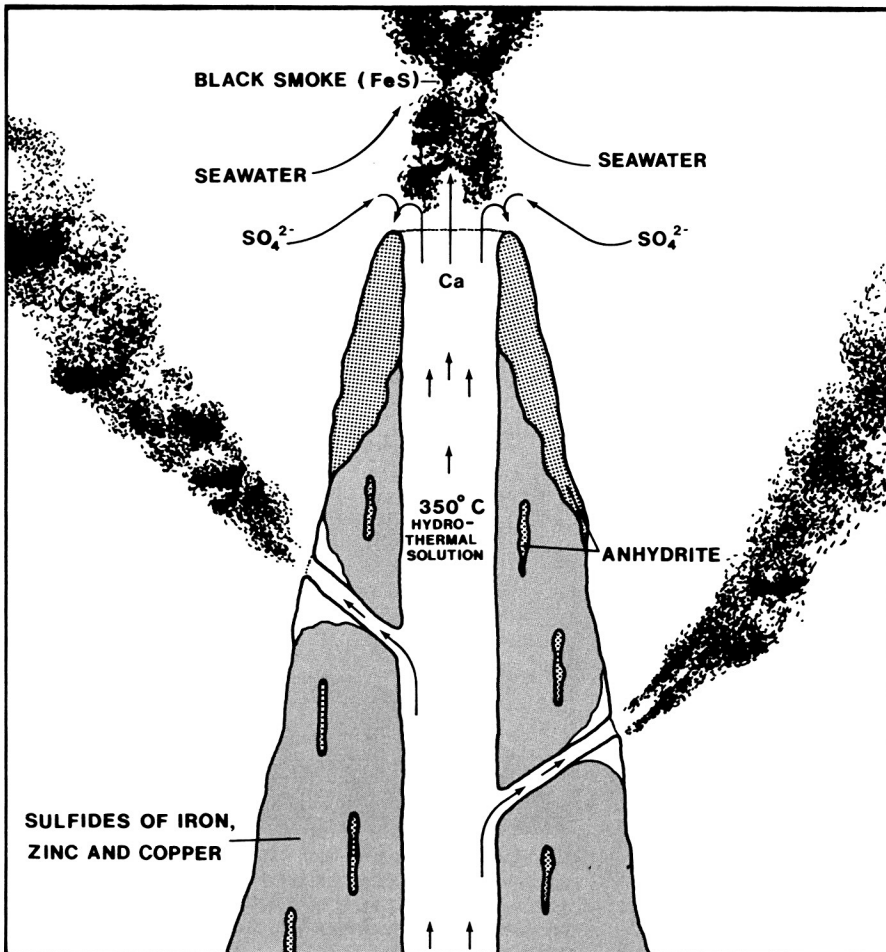
At mid-ocean spreading centers, the chemistry is more straightforward. Seawater enters the highly permeable crust through tectonically induced faults and through contraction cracks caused by rapid cooling. The heated seawater exits through the undersea vents, rises through the water column above the vent orifices, and dissipates. Consequently, the chemistry is not complicated by recirculation. Furthermore, the basaltic rocks that form the oceanic crust are of relatively uniform composition. This combination of factors greatly simplifies the interpretation of the chemistry.

In addition, since the two reactants—basalt and seawater—are so well characterized chemically, laboratory experimental work on the system is greatly facilitated and has become a useful constraint on interpretation and modeling.

The pervasive influence of hydrothermal activity in young oceanic crust was first established from geophysical and geochemical investigations of the sea floor in the axial zone.\* There, the purely conductive heat loss was found to be much lower than expected in a volcanically active area. Dredged rocks showed evidence of extensive reaction by the original lavas with seawater, often at elevated temperatures. Veins of sulfide minerals are common in these rocks. However, progressing from regional information of these types which integrate the effects of the hydrothermal activity over quite long time periods to locating presently active systems required the combination of bathymetric, navigational, and survey tools on a scale much more extensive than previously attempted in oceanography.

Hot springs were first conclusively located and directly sampled in 1977 at the Galápagos Spreading Center in the eastern equatorial Pacific. Previous exploration in the area had provided

\* The area of the ridge characterized by contemporary volcanic activity—generally only a few hundred meters wide.



*Black smokers form by the precipitation of anhydrite ( $\text{CaSO}_4$ ) and iron-zinc-copper sulfides. The hot solutions exiting the smoker are buoyant relative to the surrounding cold seawater, and consequently will rise and disperse into the water column. (Adapted from Scientific American, April 1983)*

detailed Seabeam\* bathymetric charts, evidence of temperature and chemical anomalies in the water column, and even photographs (taken by Scripps Institution of Oceanography's unmanned Deep Tow research vehicle) of a cluster of large clams! Additional surveys in 1977 using the ANGUS camera sled system operated by Robert Ballard of WHOI (see page 7) yielded more pictures of organisms and also of yellow and orange stains on the basalts—presumably caused by hydrothermal effluents. The unusual life forms and stains proved to be manifestations of actively venting hot springs. The smell of rotten eggs in the laboratory on the *Knorr* when the first water samples were opened immediately revealed that the food chain supporting the organisms is based on chemosynthesis (see page 73). The vent fluids have high concentrations of hydrogen sulfide (H<sub>2</sub>S). Certain kinds of bacteria can break down this gas metabolically to form oxides of sulphur, releasing energy in the process. The ridge crest ecosystems are based on such reactions. The diversity and uniqueness of the fauna encountered was unequivocal evidence that hydrothermal activity had to be ubiquitous on young crust. Otherwise how could such a community have evolved and been maintained?

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\* A commercial version of a U.S. Navy sonar mapping system.

### The Formation of Ore

The highest temperatures encountered at the Galápagos site in 1977 and on a subsequent revisit in 1979 were less than 20 degrees Celsius above the ambient temperature (2.05 degrees Celsius) of the cold Pacific deep water. However, experimental results and the chemical composition of the springs made it clear that the observed temperatures were an artifact of mixing between a very hot primary fluid and "groundwater" indistinguishable in its properties from the local bottom water. Magnesium and sulphate were depleted and lithium, potassium, rubidium, and manganese enriched relative to normal seawater. This is in agreement with experiments that have shown that at temperatures of several hundred degrees Celsius magnesium and sulphate are completely removed from solution and the alkalis and manganese rapidly released from the rock. Extrapolation of the magnesium and sulphate data to zero concentration indicated an end-member temperature of approximately 350 degrees Celsius. The economically important sulphide forming elements, such as copper, are in fact lower in these solutions than in seawater, indicating that these elements are very efficiently stripped from the circulating groundwaters by reaction with the hydrothermal H<sub>2</sub>S.

One's visual impression of the seafloor as observed from *Alvin* was that it is so permeable that

*The geysers and hot springs of Yellowstone National Park are driven by processes similar to those responsible for deep-sea hot springs. The water released by terrestrial hot springs, however, may recirculate downward, complicating the chemical reactions. (Photo by Sheryl Lechner).*



sub-surface mixing should be unavoidable. It was difficult to see how the primary fluid could survive its transit up through the crust from the mantle heat source without dilution in the leaky "plumbing." The piles and pillows of basalt are surrounded by voids, faults, and fissures of various sizes. Hence it was expected that very extensive exploration would be needed before the high temperature end-member would be found and sampled directly. This has proved to be completely wrong! In fact, the Galápagos Rift fields are the only ones found to date where the hottest fluids do not emerge at the surface.

Soon after the 1977 expedition an extinct sulphide deposit was found by *Cyana* on the crest of the East Pacific Rise (EPR) at 21 degrees North just south of the tip of Baja California. Since the sulphide-forming elements are only soluble in the presence of H<sub>2</sub>S at high temperatures, this was the first definite indication that the hot waters could in fact penetrate to the surface. It also confirmed that ore bodies could be formed from such solutions in the modern ocean. In ophiolites (slabs of oceanic crust thrust up onto the continents during collisional events) ore bodies composed of massive lenses of iron-copper-zinc-sulphides are relatively common. They rest directly on pillow basalts, are underlain by strongly mineralized conduits, and are often buried by subsequent lava flows. All this strongly suggested that they formed during hydrothermal activity at spreading centers. The French discovery opened up the prospect of observing the ore forming process directly and of sampling the fluids responsible.

In 1979, the Galápagos site was revisited and exploration continued. However, no high temperature activity was found. That big discovery came on the following *Alvin* dive series at 21 degrees North on the EPR. There, a group of American, French, and Mexican geophysicists discovered the now famous "black smokers." The putative 350 degrees Celsius end-member fluid was debouching from the sea floor.

In a hurriedly organized visit to the site in late 1979, it was demonstrated that *Alvin* could approach the vents safely and collect water samples. Three separate vent fields were found, all with maximum temperatures within a few degrees of 350 degrees Celsius. The central vents were composed of chimneys—tall, hollow spires formed by ore minerals precipitated from the hot fluids. They were surrounded by an extensive halo of low temperature springs of the Galápagos type presumably fed by leaks from the central conduit. Geochemists bless the vent fauna, which, being conveniently large and white, make excellent exploration tools on an otherwise black seafloor. The *Alvin* pilots quickly learned to fly up the "crab gradient" to locate the center of activity.

On a return visit to 21 degrees North in 1981, the black smokers were sampled thoroughly and an additional field discovered. The solutions exiting the vents are acid (pH approximately 3.5) and contain up to 300 parts per million H<sub>2</sub>S. They have about 20 percent as much iron and manganese, lesser amounts of copper and zinc and trace levels of lead and silver. The black smoke is composed of the

sulphide precipitates of these elements (excluding manganese, which is soluble) formed during the turbulent entrainment of the cold alkaline seawater as the hot waters rise above the vents. In the orifices themselves, the 350 degrees Celsius fluids are clear and homogeneous. Since they are more than 50 degrees Celsius below the boiling point at *in situ* pressure (2,500 meters depth; 250 atmospheres), there is no flashing, as in geysers, but rather a steady buoyancy-driven flow of 1 to 1.5 meters a second. The resulting plumes rise to several hundred meters above the ridge crest and are carried away in the regional mid-depth circulation of the ocean. Along this trajectory, the sulphide particles and the manganese react with the oxygen dissolved in the deep water to form hydrous oxides that slowly settle out to accumulate as the metalliferous sediments commonly observed on the flanks of mid-ocean ridges.

The chimneys themselves are up to 20 meters high and several meters in diameter. They have extremely varied shapes and surface morphologies. Generally, they are surrounded by mounds of debris produced by chimney collapse, perhaps induced by local earthquake activity.

Since the discoveries at 21 degrees North, chimney fragments have been identified in a number of commercial ore deposits on land. Although active areas comparable in scale to these commercially exploited ore bodies have not yet been discovered, one can reconstruct the process of their formation. As the talus accumulates, it will be reworked and annealed by the hydrothermal fluids rising through it. Additional ore is probably precipitated below the surface by cold water leaking in from the sides. However, only a small percentage of the mass flux of a given vent is localized in the chimney itself. The overwhelming proportion is lost to the water column as the hot solutions disperse. Thus ophiolite-type deposits are relatively small, on the order of a few million tons of ore.

### Other Ore-Forming Processes

Larger ore deposits associated with volcanic activity are found in sediments over zones of lava intrusion. Such sediment-hosted ore bodies range up to 100 million tons in size and are major producers of base metals. The most famous active examples are the brine pools of the Red Sea. There, the floor of the narrow Red Sea Rift is covered by a thick layer of marine evaporites deposited when this arm of the ocean dried up as the result of closure of the shallow straits off Aden. Hot solutions, probably similar to those at 21 degrees North, issue from the underlying basalts and dissolve the salt to form dense brines that pool in depressions on the bottom. Because the brines do not disperse through the water column, almost all of the metals are retained. Consequently, rich ore deposits are forming at the bottom of the brine pools as metals from the hot solutions precipitate.

Unfortunately, no conceivable submarine could be designed to penetrate these high salinity fluids because of the enormous buoyancy that would have to be overcome and the large difference in density between the brine pools and the seawater.

A submarine dense enough to enter the brine pools would drop like a rock through the overlying seawater and hit the brine pool-seawater boundary with great force. Hence, the ore-forming solutions cannot be sampled directly.

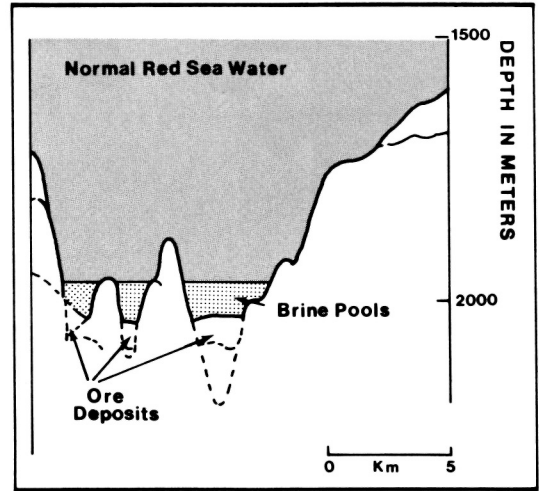
Buried spreading centers also are observed where the ridge axis is adjacent to a source of sediments either from the continents (as in the Gulf of California or off the northwest coast of North America) or near island arcs (for example, the Marianas Trough). So far *Alvin* has visited only one of these sites, the Guaymas Basin in the Gulf of California. There, the axis is covered by several hundred meters of detrital sediment derived from the Mexican mainland admixed with a large amount of biogenic material from the very productive surface waters.

In early 1982, *Alvin* found large mounds on the sediment-covered floor of the Guaymas Basin topped by active hot springs issuing from huge pagoda-like structures. The chemistry of these springs is quite different from those at 21 degrees North. The solutions have a maximum temperature of 315 degrees Celsius, are extremely depleted in magnesium and sulphate (as at 21 degrees North), but are alkaline and have very low abundances of the ore metals. Their most striking features are the high concentrations of ammonia, abundant dissolved hydrocarbons (the water samples smell of diesel fuel!) and the presence of immiscible globules of molten wax.

It appears from the *Alvin* work and from the Deep Sea Drilling Project (DSDP) holes in the basin that this composition results from the reaction of hydrothermal solutions similar to those at 21 degrees North with the sediment column. Dissolution of biogenic carbonate and the breakdown of planktonic carbon at high temperatures produce ammonia and hydrocarbons, which account for the high alkalinity, the "diesel," and the waxes. The high alkalinity induces the precipitation of the ore minerals at depth in the sediments and, unlike the situation at 21 degrees North, retention of the metals is highly efficient. The solutions venting in Guaymas Basin are actually "spent" ore forming fluids. The highly metamorphosed sediments recovered by the DSDP lend strong support to this scenario. Since the sediments themselves act as an additional source of metals to be deposited as sulphides, sediment hosted volcanogenic massive sulphides have great compositional diversity. Depending on the origin of the sediment, a wide range of metal enrichments is possible. The large size of these bodies is the result of the efficiency of the mechanism of ore retention. The biological productivity of the overlying waters is a crucial factor in this efficiency.

### A Continuing Program

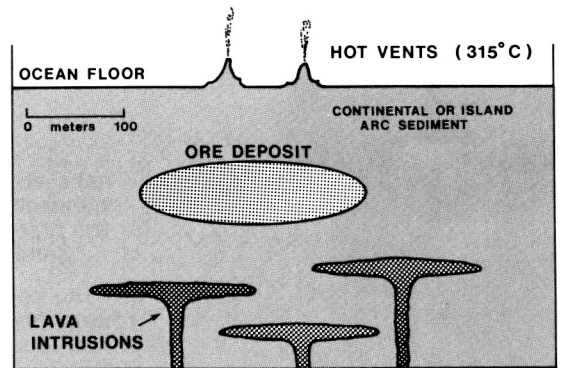
These fundamental insights into the processes of ore formation gained by the study of active systems are leading to major advances in the field of economic geology. The ability of *Alvin* to investigate high pressure and temperature environments in the oceans provides a unique opportunity to unravel the geological and geochemical processes associated with metamorphism and ore emplacement.



Rich ore deposits are forming in brine pools at the bottom of the Red Sea. While metals issuing from black smokers are dispersed over a wide area, metals entering the brine pools are trapped in the dense water and therefore precipitate out in a small area.

The exploration program continues. With the recent conversion for efficiency purposes of *Atlantis II* into the support ship for *Alvin*, a much larger area of the ocean is open for exploration. Work on sediment-starved ridges is continuing with recent dives on numerous black smoker fields between 10 and 13 degrees North on the East Pacific Rise (see page 7). Several groups explored the Juan de Fuca ridge off Oregon and Washington in the summer of 1984. The Guaymas Basin will be revisited in 1985; it is projected that the *Alvin/A-II* will then traverse the Pacific to investigate hydrothermal phenomena occurring on the spreading centers behind the Marianas Arc.

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Metals also may be trapped by sediments located over an area of active volcanism, as at the Guaymas Basin in the Sea of Cortez. Organic matter in the sediments raises the alkalinity of the hydrothermal solutions, causing metals to precipitate out before they reach the surface. (Adapted from *Scientific American*, April 1983).