

Hydrothermal Minerals

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Hydrothermal deposits of various types are frequently found at or near actively spreading mid-ocean ridges. Polymetallic sulfide deposits occur on the mid-oceanic ridges with fast, intermediate and slow spreading rates; axial and off-axis seamounts and volcanoes; in convergent plate boundaries such as back-arc environments and in sedimented rifts adjacent to continental margins.

The hydrothermal deposits mainly occur in the tectonically active regions, where plates shift and spread creating fissures in the seafloor. Mineralization at the spreading ridges is the result of sea-floor hydrothermal processes involving free circulation of seawater through ocean crust as convection. Heat flow, seafloor fracturing, permeability and fluid composition are the parameters governing the type and extent of mineralization. The chimney like structures are composed of sulfides arising out from deep beneath the Earth's crust. These minerals have been dissolved in hot water (350°C) under great pressures and temperatures. When the water that flows out through the mantle ejects at the mid ocean ridge system, sulfide minerals crystallize from the hot water directly onto the volcanic rocks surrounding the hydrothermal vent leading to the formation of hollow, chimney like sulfide structure through which the hot water continues to flow. The minerals in the hot fluid (manganese, copper, zinc, and iron sulfides) are precipitated out, giving the plumes their smoky appearance.



Fig. 1. Black smoker with sulphides

Hydrothermal mineralization is a part of submarine hydrothermal systems, which are in turn an integral component of global mid-ocean ridge system.

Hydrothermal systems are composed of convection cells in the crust and upper mantle through which seawater freely circulates reacting with magmatic material, which are at high temperatures. The distribution and characteristics of hydrothermal circulation within the oceanic crust are controlled by the thermal regime and the permeability structure, both of which are strongly influenced by magmatic and tectonic processes. Submarine hydrothermal circulation in the oceanic crust and its activity on the ocean floor are fundamental processes controlling the transfer of energy and material from the lithosphere to the hydrosphere. Thermally induced circulation of seawater through the permeable parts of the crust and upper mantle has been estimated to account for 34% of the global oceanic heat flux, corresponding to ~25% of the total heat flux of the Earth. Hydrothermal fluids are discharged along mid-ocean ridges either as high temperature (200-400°C) focused leading to the formation of black smokers and low temperature (<200°C) diffuse fluid flow at white smokers. Fluids also flow off-axis, and are responsible for more than 70% of the hydrothermal heat flux.

Circulation of seawater through the oceanic crust and upper mantle gives rise to a complex series of physical and chemical reactions that lead to the 1) formation of seafloor mineral deposits; 2) alteration of oceanic crust; 3) control of trace element chemistry of oceans and to 4) the existence of unique biological communities. Understanding the influence of hydrothermal processes on ocean chemistry will help in the understanding of the dynamic way in which the planet works as a whole. High temperature black smokers and low temperature white smokers are most spectacular features of active submarine hydrothermal systems. Both these smokers represent upper part of the deposits, which grow on basal hydrothermal mounds. Mounds continue to grow for some time, and consist of hydrothermal sulfide minerals. Mounds are underlain by subsurface stockwork and abundant chimney structures along with hydrothermal minerals such as sulfides and metalliferous sediments. Depending on the temperature of venting fluids, sulfide minerals such as pyrite, chalcopyrite, sphalerite are formed. At the distal sites away from active vents, hydrothermal solutions precipitate as manganese and iron oxides. It is interpreted that, the large quantities of metals ejected from the hydrothermal vents, have been responsible for many of the world's richest ore deposits, such as the

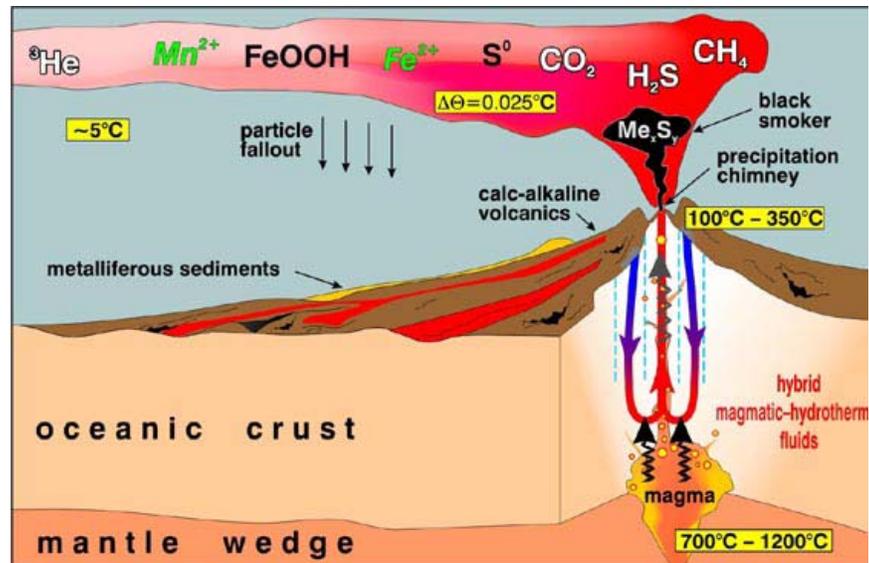


Fig. 2. Schematic cartoon of a venting system on a submarine arc volcano. These systems are driven by magma bodies that range in temperature depending on composition. Dashed lines represent permeable crust into which seawater penetrates to form a hydrothermal circulation cell with ascending fluids discharging at ~100°-350°C depending on depth. Yellow bubbles and saw-tooth arrows represent exsolved magmatic fluid. Some chemicals within volcanic vent fluid may precipitate near the sea floor interface as hydrothermal mineralization. The remaining (most) chemicals will buoyantly rise to form "black smoker" plumes. Hydrothermal plumes are sensed as temperature anomalies or optically detected as light scattered off particles and detected chemically as gas and metal concentration anomalies (Source: www.oceanexplorer.noaa.gov/.../global_220.jpg).

copper ores mined on the island of Cyprus in the Mediterranean Sea.

Circulation Zones

Circulation of hydrothermal fluids is determined by 1) the permeability structure of the ocean crust and 2) the location of the heat source

The process works in 3 phases.

Phase I: In the recharge zone,

1. cold seawater penetrates into the ocean crust
2. Gets heated along its flow path.
3. Strong thermodynamic drive to remove Mg from the fluid into the rock, and acid is produced in the process
4. Drives leaching of other major elements and transition metals from the rock into the hydrothermal fluid.
5. Seawater sulfate is removed from solution by precipitation as anhydrite and by reduction to H₂S

Fluids reach their maximum temperature in the high-temperature reaction zone near the heat source.

Important parameters in determining the high-temperature fluid composition are

- pressure,
- temperature,

- water/rock ratio,
- rock composition,
- recharge fluid composition, and
- reaction time (or residence time).

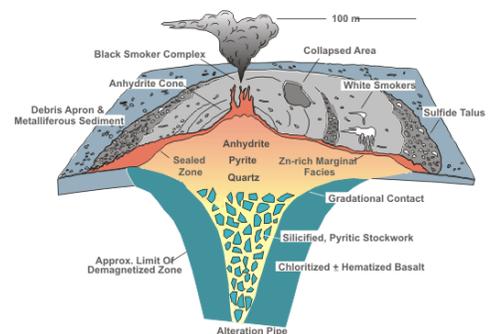


Fig. 3. Types of hydrothermal minerals being formed at various temperature zones

Reactions are fast at high temperature, and fluids may approach equilibrium with a set of alteration minerals. Hot hydrothermal fluids are buoyant and rise toward the ocean floor in the upflow zone. The residence time in this zone is probably very short, but fluids may continue to react with the rock through which they flow. Fluids cool slightly through decompression (adiabatic cooling) and may cool significantly by losing heat to the surrounding rock (conductive cooling) or by mixing with

cold seawater-like fluids below the sea floor. Cooling may cause the hydrothermal fluid to become supersaturated and precipitate secondary minerals (metal sulfides, quartz, etc.), so that the fluid chemistry may change slightly between leaving the reaction zone and arriving at the sea floor.

Hydrothermal vents

Hydrothermal vents are the interface between the hot, anoxic up flow zone and cold, oxidized seawater. When hot fluids mix with cold seawater, many hydrothermal minerals precipitate within seconds to form the dense particle plumes characteristic of **black smokers**.

The particles are predominantly a mixture of sulfides (e.g. pyrrhotite FeS, sphalerite ZnS, chalcopyrite CuFeS₂, etc.) & sulfates (anhydrite CaSO₄, barite BaSO₄). Some of these minerals are formed as part of the chimney structures that build up on the sea floor, while others are formed within the plume and dispersed through the water. Another form of hydrothermal venting is the diffuse vent, where lower temperature fluids exit the seafloor as simmering water through cracks surrounding high-temperature smokers, or in isolated areas venting directly from basalt. The lower temperature fluids generally do not contain enough dissolved metal and sulfide to form "smoke". There is evidence that the cooler diffuse vent fluids are in most cases formed by sub-sea floor mixing of hot, smoker-like fluids with cold seawater-like fluid, and in many cases they must precipitate minerals below the sea floor.

Process of formation

2 complexes viz., sulphide (HS⁻ & H₂S) and chloride (Cl⁻) are important for the transport of ore metals in hydrothermal solution. Both these complexes are capable of transporting large quantities of metals. Deposition of metals from chloride complexes may be due to:

1. Increased H₂S concentration
2. Increased pH (due to boiling)
3. Decreased chloride conc. & decreased temp.

Sulphide complexes are due to:

1. Pressure release and boiling
2. Oxidation which decreases the sulphide contents and the pH

Precipitation of the dissolved constituents in hydrothermal fluid occur when the temperature vary (hot 350°C fluids and near freezing seawater) and it affects the solubility of sulphides & oxides. Stability of the complex ions depends on 1) Pressure change, 2) Reactions between wall rock and solutions. 3) Chemical changes due to mixing of fluids. Transfer of Mg, SO₄²⁻, Na and Cl occurs from seawater to oceanic crust, while

leaching and mass transfer of Li, K, Rb, Ca, Ba, Cu, Fe, Mn, Zn and Si takes place from the oceanic crust to the solutions. Mg reacts with rock forming silicates and liberates H⁺, which enters solution decreasing pH. Hydrogen ion exchanges for cations Ca & K releasing them into the hydrothermal fluid.

The removal of Na from seawater (at <300°C) leads to the formation of analcime and albite (silicate minerals). At temperatures >150°C, K and SiO₂ are leached from mafic rocks. The behaviour of S in the hydrothermal solutions is both complex and critical. The S cycle is determined by the presence of 2 sources and 2 sinks. The source of S resides in both seawater & mafic rocks, while sinks are by deposition of sulphates (barite, anhydrite) and precipitation as sulphides.

Occurrence

Since the time of dramatic discovery of hydrothermal venting fluids along the East Pacific Rise close to the Galapagos Islands during the late 1970s, scientists have found hydrothermal vents along other sections of the world's ocean ridges in the 20 years since that discovery. Hydrothermal deposits including polymetallic sulfides and ferromanganese oxides have been recovered from many locations on the spreading centres (East Pacific Rise, Galapagos Ridge, Explorer Ridge, mid-Atlantic Ridge, Central Indian Ridge), volcanic arc-back-arc basin settings (Tonga-Kermadec Ridge, Manus Basin, Marina Arc, Izu-Ogasawara Arc etc.) and in midplate seamount and guyot regions.

Despite many reports from a variety of locations and geological settings, hydrothermal mineralization from Indian Ocean spreading centers have not been documented for long, mainly because the slow and medium-spreading centers such as the Atlantic and the Indian Oceans were considered less favourable targets in comparison to fast spreading centers such as East Pacific Rise. Massive sulfides and ferromanganese crusts of hydrothermal origin were discovered in an area north of Rodriguez Triple Junction during late nineties. Following this, exploration activities have continued. A compilation of the reported occurrences in the Indian Ocean is shown in Table 1.

Following the initial exploratory cruises to the Rodriguez Triple Junction, wherein the water column and ferromanganese crusts have shown the evidence of past and present hydrothermal activity, two extinct hydrothermal massive sulfide fields have been discovered in the Indian Ocean. In both fields, hydrothermalism has ceased between 11,000 and 13,000 years ago. The first occurrence (Sonne Field, 2850 m water depth) is located in the 4th segment of the Central Indian Ridge, north of the Rodriguez Triple Junction. The second one (Mount Jourdanne, 2940 m

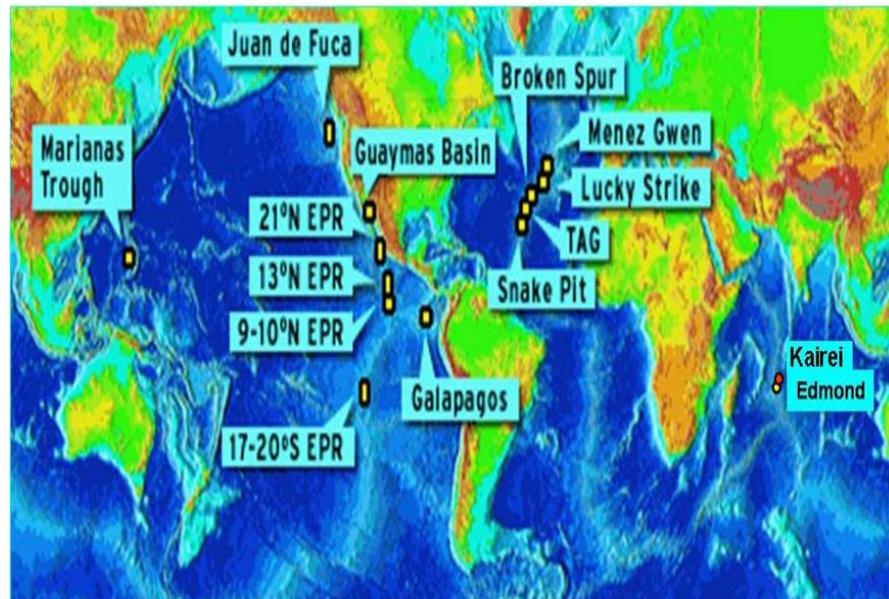


Fig. 4. Worldwide distribution of active submarine vents

ater depth) is located in the 11th segment of the South West Indian Ridge.

The Sonne Field appears to be a typical mid-ocean ridge massive sulfide occurrence with black and white smoker mineralizations; it is now, however, in a state of physical and chemical disintegration, and therefore depleted in anhydrite. The chimney structures were formed by multiple hydrothermal events. Three types of sulfide mineralizations can be distinguished: (1) Cu-rich massive sulfides, (2) pyrite-marcasite massive sulfides, both of which originate from the black smoker activity, and (3) sphalerite- and barite-bearing jasper breccia, this latter obviously having been formed at epithermal temperature conditions. In contrast, the Mount Jourdanne deposit shows a much more complex mineralogy.

Latest discoveries by Chinese scientists (April 2007) are however missing in the following table. In total four new hydrothermal sites were found, three at the SWIR, and one located at the CIR. Each site showed intense signals of turbidity, methane and temperature anomalies in the water column, and supported by hydrothermal influenced sediments and rocks, anemones and white crabs were also occasionally observed at these sites. Besides, two ultramafic complex were located and sampled off-axis of the ridge at SWIR, interestingly, one is located 40km away from the central rift valley.

Exploring the hydrothermal activity

Unlike the land-based mineral deposits and other marine mineral deposits which are lying widespread (placers and manganese nodules) on the seabed, identification of sites with oceanic hydrothermal mineralization is rather difficult and involves specialists from different disciplines. Exploration for a submarine hydrothermal deposit would involve the following activities in sequence.

1. Geophysical and bathymetric surveys for understanding the tectonic setting
2. Sediment sampling for geochemical and mineralogical tracers of hydrothermal activity (Hg, As, Mn, Pb etc.)
3. Water column studies including sampling for temperature anomalies, chemical anomalies such as dissolved and particulate Mn, thermogenic methane, helium from mantle, radon etc. to locate active venting site
4. Seabed sampling for rocks and minerals looking for indications of hydrothermal mineralization
5. TV and still Photographic surveys with real-time imaging on board
6. Submersible/ROVs for direct observations and robot controlled sampling

Table 1. A compilation of reported metallogenesis along the IORS (Source: Banerjee & Ray, 2003)

Sl. no.	Location	Ridge/Back arc	Geologic setting and type of deposit
1.	3°N/60°E	CR	Manganese nodules from the southern part of Carlsberg Ridge. Water depth 3600–4500 m
2.	3°35'N/64°07'E		Magmatic sulphide–oxide mineralization in Carlsberg Ridge rocks. Water depth 3750 m
3.	1°40'S/67°46'E		Presence of hydrothermal sulphide globules in the rocks from Owen fracture zone, North Western Carlsberg Ridge ³¹
4.	5°23.7'S/68°35.1'E	CIR	Magmatic sulphide–oxide mineralization near the Vityaz Fracture Zone. Water depth 3500 m
5.	5°33.90'S/67°53.40'E		Presence of thick ferromanganese crust and nodules from Vityaz Fracture Zone. Water depth 3500 m
6.	19°29'S/65°44'E		Presence of hydrothermal ³ He and manganese plume north of the RTJ. Water depth 2460 m (ref. 4)
7.	23°23.6'S/69°14.4'E		200 km NW of RTJ. Water depth 2800 m (SONNE Hydrothermal Field) Fossil Hydrothermal Field ^{2,3}
8.	23°23.63'S/69°14.43'E		3 km west of the rift axis of the fourth segment of the RTJ. Water depth 2870 m MESO Zone
9.	23°23.38'S/69°14.48'E 24°05.30'S/69°32.03'E 24°06.25'S/69°32.79'E 24°14.30'S/69°40.92'E 24°05.20'S/69°41.65'E 24°00.03'S/69°37.7'E		Extinct Hydrothermal Field first report of massive sulphide from IORS North of RTJ Ferromanganese encrustation with distinct hydrothermal signature. Water depth 2466–3730 m
10.	25°18'S/70°01.23'E		12 miles north of RTJ hydrothermal plumes. Water depth 2300 m
11.	25°19'S/70°03'E		Dive of Shinkai 6500 submersible located heaps of dead shells (at CIR near RTJ). This is the first demonstration of <i>in situ</i> biological communities associated with hydrothermalism along the IORS ²¹
12.	25°19.17'S/70°02.40'E		First hydrothermal vent communities discovered on a volcanic knoll at the eastern crest of an axial valley ~ 22 km north of RTJ. Water depth 2420–2450 m. The same site also locates the active black smoker chimney 'Kairei field' ¹⁴
13.	25°24'S/69°45.36'E and hydrogenetic		Layered Fe–Mn crust from off axis region of the first segment of the CIR, mixed hydrothermal signature. Water depth 2700–2800 m
14.	25°16.30'S/70°08.63'E		SEIR Sediments of SEIR near RTJ show mixed hydrothermal and hydrogenous signature ²⁸
15.	25°50'S/70°E		SWIR Segment of 11 of SWIR, signature of extinct hydrothermal activity along SWIR on the
16.	27°51'S/63°56'E		Mt Jourdanne. Water depth 2941 m
17.	27°46'S/65°08'E 27°55'S/64°27'E		Relict hydrothermal field, east of Melville fracture zone. Water depth 2940 m hydrothermal signature. Water depth 2700–2800 m (ref. 18) 200 km long section within. Water depth 3100–4100 m
18.	27°58'S/63°33'E 30°51'S/59°23'S 31°04'S/58°58'E 31°11'S/58°30'E	Anda- Man Back arc	Evidence of hydrothermal activity in the Andaman Back arc Basin comprising broken parts of chimney structures and rocks with disseminated and vein type metal sulphides. Water depth 2000–4100 m

CR, Carlsberg Ridge; CIR, Central Indian Ridge; SWIR, Southwest Indian Ridge; SEIR, Southeast Indian Ridge

Estimating the resource

Though, the estimation of the continuity of sulfide outcrops and the thickness of deposits of the seafloor is difficult, visual estimates for several deposits on the mid-ocean ridges suggest sizes ranging between 1 to 5 million tonnes. The largest known deposits are found in the neotectonic zone of Red Sea. The Atlantis II Deep, which is one of the larger depressions in the area has proven resources of 94 million tonnes of metalliferous sediments. The lack of knowledge on the thickness of deposits has recently been partially fulfilled during the

deep-sea drilling on the Juan de Fuca Ridge during Leg 139 of Ocean Drilling Program, which has shown that they may contain more than 96 m of massive sulfides at the Middle Valley site. However, individual massive sulfide deposits on the seafloor are estimated to contain 1-100 million tonnes of sulfidic material, which are comparable to the typical volcanic-associated massive sulfide deposits on land. Most of the individual sulfide deposits of the sea floor (e.g., TAG hydrothermal field, Galapagos Rift, Explorer Ridge, Escanaba Trough, Guaymas Basin) contain large quantities of Zn (mostly

between 5 to 20%), Cu (upto 6%) and Pb (upto 12%) and larger than most massive sulfide deposits on land (e.g., Cu+Zn+Pb = 6% in Canada)

Constraints in exploiting these deposits:

- 1) Due to the remote locations of many of the Black Smokers, it makes it very difficult for intensive mining to be undertaken.
- 2) The vertical extension of these deposits are not known, except in areas drilled during ODP.
- 3) The hot vent fluids may hamper any mining activity because of their high temperatures probably inducing tectonic activity such as those seen due to the construction of large reservoirs on land.
- 4) The vent biota, which may host bioactive substances and unique genetic make-up may be permanently lost.

Life in hydrothermal systems

Unique ecosystems: In addition to hosting the economic mineral deposits, deep-sea hydrothermal vents support an extraordinary array of life deep beneath the surface of the oceans. The ecosystems present are the only communities on Earth whose intermediate energy source is not sunlight. The hot water discharged at venting sites is laden with sulfur and minerals, provides an energy source for chemosynthesis and could result in the formation of organic compounds. A unique type of bacteria chemolithoautotrophic hyperthermophilic archaeobacteria thrives in this high temperature environment and requires sulphur as a fundamental part of their metabolisms. Life forms also include tube worms, giant clams and long necked barnacles among others. Hydrothermal systems may be analogous to the environments during which Earth and other planets may have formed, and therefore may provide clues to the origin of life.

Future perspective

Outstanding problems or areas of research in submarine hydrothermal systems are 1) capabilities to understand the relation between volcanic, tectonic and hydrothermal events; 2) temporal variability of hydrothermal systems mainly on the slow-spreading ridges; 3) multidisciplinary studies of known hydrothermal fields in different settings in order to

identify hydrothermal active segments, which are previously unexplored sections of the mid-ocean ridges; 4) quantifying the thermal and chemical fluxes both at high temperature fluid flow and diffuse lower temperature discharge and 5) the genetic make-up of biota thriving in this unique environments. However, the study of hydrothermal systems is still relatively young, and there are many fundamental questions that remain to be addressed in the forthcoming years.

Suggested reading

1. **Seafloor hydrothermal systems: Physical, chemical, biological, and geological interactions** Author(s) :Humphris, S.E.; Zierenberg, R.A.; Mullineaux, L.S.; Thomson, R.E. eds. Source/Publisher: (Geophys. Monographs Ser., 91); American Geophysical Union, Washington, DC, USA. 1995; xiii+ 466 pp
2. **Sea-floor hydrothermal mineralization: New perspectives** Source/Publisher:Econ. Geol. Pub., El Paso, USA. 1993; 361 pp Notes : Special issue: Econ. Geol. Bull. Soc. Econ. Geol. Vol. 88(8); 1993
3. **Hydrothermal processes at seafloor spreading centers** Author(s) :Rona, P.A.; Bostrom, K.; Laubier, L.; Smith, K.L. eds. Source/Publisher: (NATO Conference Series IV: Marine Sciences, Vol. 12); Plenum Press, New York, USA. 1983; xiv+796 pp
4. **Seafloor hydrothermal mineralization** Author(s) :Barrett, T.J.; Jambor, J.L. eds. Source/Publisher:Mineral. Assoc. of Canada, . 1988; 460 pp

Interesting websites to visit:

1. <http://interridge.who.edu/>
2. <http://www.pmel.noaa.gov/vents>