

Massive Sulphides



The formation and occurrence of sea-floor massive sulphides

Sea-floor massive sulphides (SMS) are deposits of metal-bearing minerals that form on and below the seabed as a consequence of the interaction of seawater with a heat source (magma) in the sub-sea-floor region (Hannington et al 2005). During this process, cold seawater penetrates through cracks in the sea floor, reaching depths of several kilometres below the sea-floor surface, and is heated to temperatures above 400°C. The heated seawater leaches out metals from the surrounding rock. The chemical reactions that take place in this process result in a fluid that is hot, slightly acidic, reduced, and enriched in dissolved metals and sulphur.

Due to the lower density of this evolved seawater, it rises rapidly to the sea floor, where most of it is expelled into the overlying water column as focused flow at chimney vent sites. The dissolved metals precipitate when the fluid mixes with cold seawater. Much of the metal is transported in the hydrothermal plume and is deposited as fallout of particulate debris. The remainder of the metal precipitates as metal sulphides and sulphates, producing black and white smoker chimneys (see box) and mounds (Figure 2).

The minerals forming the chimneys and sulphide mounds include iron sulphides, such as pyrite (often called fool's gold), as well as the main minerals of economic interest. These include chalcopyrite (copper sulphide) and sphalerite (zinc sulphide). The precious metals gold and silver also occur, together with non-sulphide (gangue) minerals, which are predominantly sulphates and silicates. The metals originate from immiscible sulphides, ferromagnesian silicates, and feldspars that make up the volcanic rocks beneath the sea floor (Hannington et al 2005). It has been suggested that rising magmatic fluids may also be a source of ore metals, particularly at sites where hydrothermal systems are producing SMS deposits in close association with subduction zones and island arcs. The enriched magmatic fluid would then mix with the circulating seawater (Yang and Scott 1996; 2006).

Since black smokers were first discovered, more than 280 sulphide occurrences have been identified in all oceans (Hannington et al 2011), indicating that hydrothermal convection is widespread (Figure 3).

Most sulphide occurrences - 65 per cent - have been found along mid-ocean ridges (Hannington et al 2011), with another 22 per cent occurring in back-arc basins and 12 per cent along submarine volcanic arcs. Very few sites – only 1 per cent – have been observed at intraplate volcanoes (Figure 4). Spreading centres (mid-ocean ridges and back-arc basins) have a combined length of 67 000 kilometres (Bird 2003), whereas submarine volcanic arcs have a total length of 22 000 kilometres, 93 per cent of which occurs in the Pacific (de Ronde et al 2003).

At mid-ocean ridges, high-temperature venting occurs mainly in the axial zones of the spreading centres and is associated with basaltic volcanism. At slow-spreading ridges, however, long-lived detachment faults may divert fluid flow away from the ridge axis. The associated sulphide deposits can, therefore, be found several kilometres away from the ridge axis. Volcanic arcs and back-arc basins develop as a result of subduction of oceanic crust at a convergent plate boundary. Hydrothermal systems in these environments are broadly similar to those at mid-ocean ridges. However, the geology and tectonic setting

The colours of smoke

Hydrothermal chimneys discharge various colours of smoke, including black, grey, white, and yellow. The smoke is actually dense clouds of fine particles of sulphide, sulphate, oxide minerals, and/or sulphur, all suspended in seawater. Black smokers have the highest fluid temperatures (greater than 330°C), and the particulates are predominantly sulphide minerals. Particulates associated with white smokers are dominated by sulphate minerals that form at lower temperatures (300-150°C). Grey smokers expel both sulphide and sulphate minerals and form at intermediate temperatures. Yellow smokers occur at several sites that are related to subduction zone processes (volcanic arcs and back arcs). They form at the lowest temperatures and their particulates are mainly sulphur. This colour series also reflects the oxygen content of the fluid, with the amount of oxygen increasing as the mineral form moves from sulphide to sulphur to sulphate.

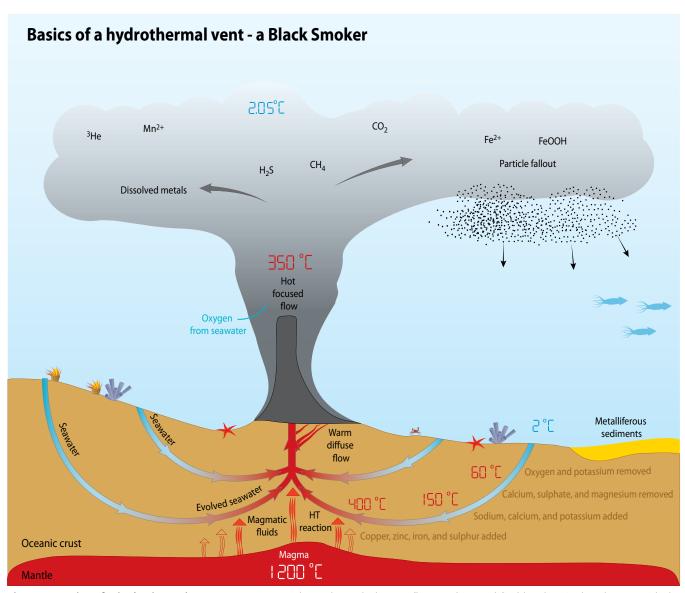
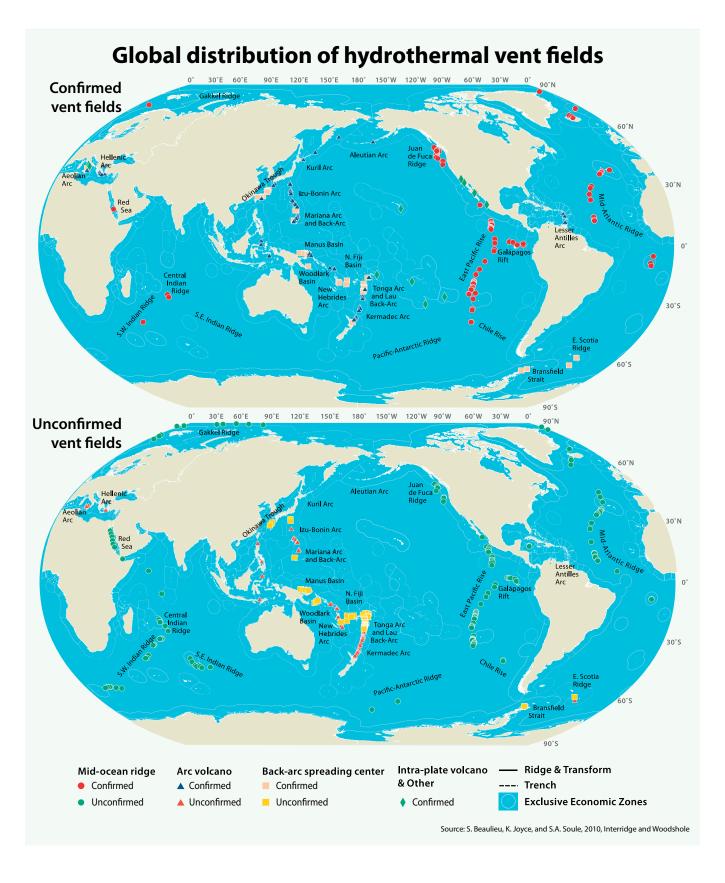
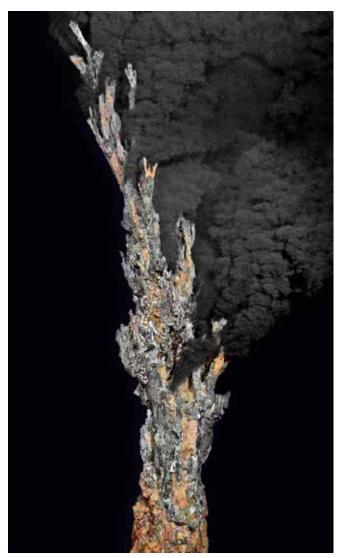


Figure 2. Basics of a hydrothermal vent. Seawater percolates through the sea floor and is modified by chemical exchange with the surrounding rocks and rising magmatic fluid. The altered seawater is released back into the ocean at the vent site and forms a hydrothermal plume. The rising plume mixes rapidly with ambient seawater, lowering the temperature and diluting the particle concentration. The plume will continue to rise through seawater as long as it is less dense than the surrounding seawater. Once the density of the hydrothermal plume matches the density of the seawater, it stops rising and begins to disperse laterally. In a scenario like this, 90 per cent of the metals are lost to the plume and do not take part in the metal deposit formation process.





The largest black smoker discovered to date (since collapsed) measured almost 45 metres high and occurred on the Juan de Fuca Ridge. Following destruction, chimneys have been measured to grow as fast as 30 centimetres per day. The biggest chimneys are generally found on slow spreading ridges (like the Mid-Atlantic Ridge). On fast spreading ridges like the East Pacific Rise, chimneys are rarely more than 15 metres high. Photomosaic of a 5 metre high chimney in the central Atlantic. Image courtesy of GEOMAR.

Figure 3. Global distribution of sea-floor hydrothermal systems and related mineral deposits. Confirmed vents are those where hydrothermal activity has been observed at the sea floor. The unconfirmed sites are inferred to be active based on plume surveys. From version 2.0 of the InterRidge Global Database (Beaulieu et al 2010).

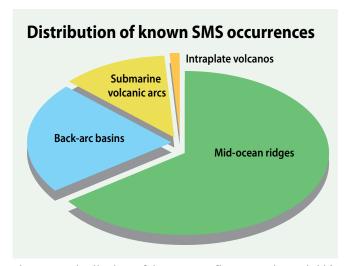


Figure 4. Distribution of known sea-floor massive sulphide occurrences in different environments.

influence the composition of the hydrothermal fluids and also, ultimately, the mineralogy and chemical composition of the associated sulphide deposits. The apparent differences are related to variations in host-rock composition, as well as to direct input of magmatic volatiles and metals into the hydrothermal circulation cell (Yang and Scott 1996; de Ronde et al 2011). The occurrence and distribution of sulphide deposits seems to be related to overall magmatic activity along plate boundaries.

The total number of vent sites that exist on the modern sea floor is not known, although several hypotheses have been used to infer their abundance. Estimates based on Earth's heat flow indicate that approximately one black smoker per kilometre of ridge axis is necessary to explain the heat flux through the oceanic crust (Mottl 2003). The distribution of hydrothermal plumes along the spreading axis and over volcanic arcs has also been used to infer similar values (Baker and German 2004; Baker 2007). It should be noted, however, that the latter approach only considers active hydrothermal fields. Evidence suggests that there are many more inactive sites than active sites (Hannington et al 2011).

Metal concentrations and tonnages

While the number of discoveries of SMS occurrences is steadily rising, most deposits are small in size and tonnage of contained sulphide. Hydrothermal vent systems do not generally incorporate metals into sulphide deposits efficiently. Much of the metal is lost to the hydrothermal plume and dispersed away from the vent sites. Large deposits form only where sediments allow for efficient trapping of the metals due to metal-precipitation below the sea floor (as in Middle Valley and Okinawa Trough; Zierenberg et al 1998; Takai et al 2012) or where hydrothermal

activity occurs for long periods of time, as with sulphide mineralization related to large detachment faults. Based on information about the age of the sulphides and the underlying volcanic crust, it appears that tens of thousands of years are needed to form the largest known deposits, such as the Semyenov and Krasnov deposits of the Mid-Atlantic Ridge (Cherkashov et al 2010). These deposits can be up to several hundreds of metres in diameter and are estimated to have total masses on the order of 5 to 17 million tonnes of contained sulphides.

Geochemistry of massive sulphides in various tectonic settings

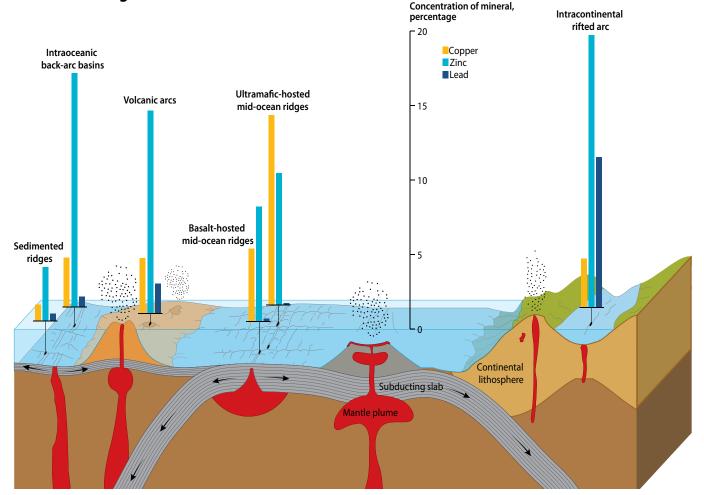


Figure 5. Concentrations of copper, zinc, and lead in sea-floor massive sulphides formed in different geological settings (Source: GEOMAR)

The composition of SMS deposits is highly variable, and not all elements contained in the sulphides are of commercial interest. For example, SMS deposits along the East Pacific Rise and, to some extent, those along the Mid-Atlantic Ridge are primarily composed of iron sulphides that currently have no economic value. In contrast, sulphide occurrences in the southwest Pacific contain concentrations of copper and zinc, which make them more economically attractive (Figure 5). Valuable metals such as gold and silver are trace components of the sulphides but can be highly enriched in some deposits, reaching concentrations of several tens of grammes/tonne for gold and several hundreds of grammes/tonne for silver (Figure 6). Other trace elements - bismuth, cadmium, gallium, germanium, antimony, tellurium, thallium, and indium – are normally contained in SMS in low quantities (at levels measured in grammes/tonne), but can be significantly enriched in some deposits, especially those that form at volcanic arcs. Weathering of old SMS on the seabed can upgrade the metal contents in the deposit due to the formation of secondary copper-rich sulphides.

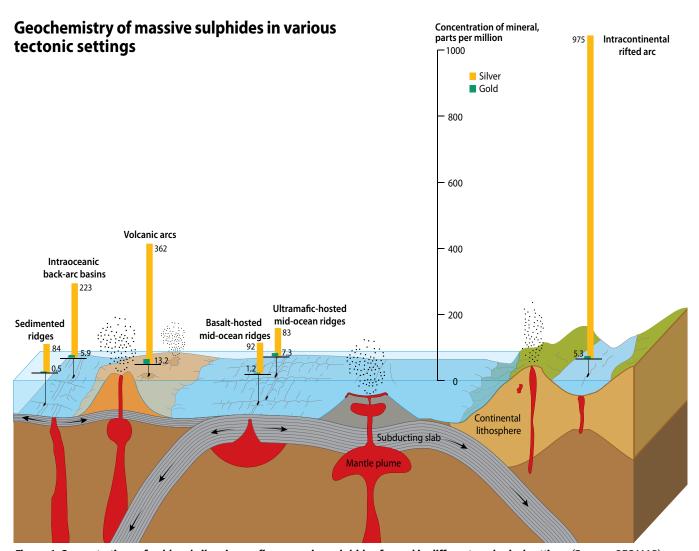


Figure 6. Concentrations of gold and silver in sea-floor massive sulphides formed in different geological settings (Source: GEOMAR)

The geochemical composition of SMS is not only variable on a regional scale, but also varies at the deposit or even hand-specimen scale, reflecting strong gradients in fluid temperatures (Figure 7). Copper-rich minerals typically line the high-temperature upflow zones and fluid conduits. The outer parts of the deposits consist of minerals that are rich in iron and zinc, such as pyrite, marcasite, and sphalerite. These are usually deposited at lower temperatures as the hydrothermal fluid mixes with seawater. As a result of this heterogeneity, the sampling of black smoker chimneys, which commonly show high concentrations of copper, might not be representative of the bulk composition of the deposits. Many published grades of sea-floor sulphide deposits are strongly biased due to sampling of high-temperature chimneys, which are easier to recover than sub-sea-floor mineralization. Unfortunately, with the exception of a few deposits that have been drilled through the Ocean Drilling Program or by commercial or scientific projects, little is known about the interiors of most SMS deposits.

Due to lack of information about the important subsurface component of deposits, it is difficult to estimate the resource potential of most SMS. Initial estimates of the abundance and distribution of sulphide deposits in well-studied areas indicate that approximately 1 000 large sulphide deposits may exist on the modern sea floor (Hannington et al 2011). However, some of the largest deposits, such as those along the central Mid-Atlantic Ridge, are dominated by iron sulphides of no commercial interest. Other factors that affect current commercial viability are water depth, distance to land, and sovereign jurisdiction. An analysis of known deposits indicates that only about ten individual deposits may have sufficient size and grade to be considered for future mining (Hannington et al 2011). However, many smaller, metal-rich deposits could be incorporated into a single mining operation, making mining of these smaller SMS deposits viable.



Figure 7. Examples of sea-floor massive sulphides from various tectonic settings. Pyrite-rich chimney from the basalt-hosted Turtle Pits hydrothermal field, 5° S on the Mid-Atlantic Ridge (upper left). A massive chalcopyrite chimney from the ultramafic-hosted Logatchev hydrothermal field (lower left) and a gold-rich copper-zinc massive sulphide from the PACMANUS field, Papua New Guinea. Note the copper-rich core and the brownish zinc-rich exterior of the sample, exemplifying a typical temperature zonation in SMS. Barite constitutes a major part of this sample (right, scale on sample is 5 cm). Photo courtesy of GEOMAR.

Bismarck Sea sea-floor massive sulphide

The western Pacific is characterized by SMS systems related mainly to westward-dipping subduction zones, which produce hydrothermal activity along back-arc basins and island arcs (Martinez and Taylor 1996).

The Bismarck Sea is a back-arc basin formed in the last three million years by the southward slab rollback of the Solomon Sea Plate under New Britain. Extensive exploration in the Bismarck Sea over the last few years has led to the discovery of numerous active and inactive hydrothermal systems within the national jurisdiction of PNG (Both et al 1986; Tufar 1990; Binns and Scott 1993; Auzende et al. 2000; Binns et al 2002; Tivey et al 2006; Jankowski 2010; Reeves et al 2011). Currently, two SMS systems and two sulphate systems have been documented in the western part of the Bismarck Sea. The active Central Manus spreading centre hosts six SMS systems, while nine SMS systems have so far been located in the eastern Manus Basin, mainly associated with the young volcanic edifices at Pual Ridge and SuSu Knolls (Figure 8). At several other hydrothermally active sites in the Bismarck Sea, no sulphide deposits have been discovered.

The complexity of the tectonic setting within the Bismarck Sea is reflected in the wide range of compositions of volcanic rocks. Overall, the composition of magmas along the Manus Basin changes in a west-to-east direction, from mid-ocean-ridge basalt to more arclike compositions closer to the New Britain Arc (Sinton et al 2003). Chemical changes also occur in the SMS systems themselves, linked to changes in the composition of substrate rocks, water depth, and contribution of magmatic volatiles to the hydrothermal system. Most systems at the Willaumez and Central Manus spread-

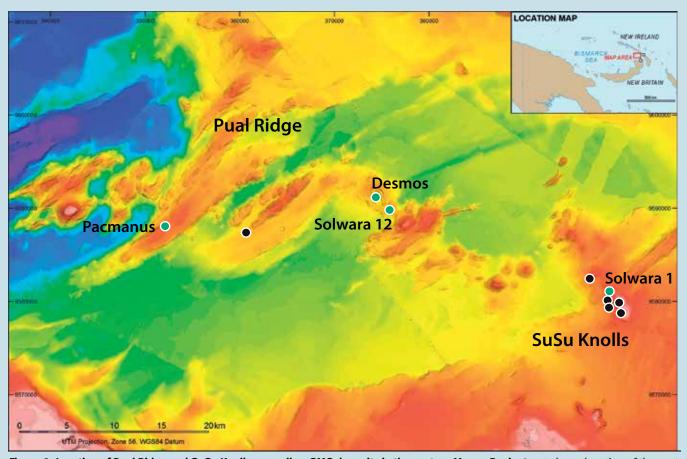


Figure 8. Location of Pual Ridge and SuSu Knolls, as well as SMS deposits in the eastern Manus Basin. Inset shows location of the eastern Manus Basin in relation to major plate tectonic structures.

ing centres are small and consist mainly of scattered zinc-rich chimneys with exit temperatures reaching 302°C (Gamo et al 1996). Systems from the Pual Ridge and SuSu Knolls are distinguished by higher copper, gold, and silver contents (Table 1), making them especially interesting from an economic point of view. At the PAC-MANUS site near the crest of Pual Ridge, discontinuous vent fields occur over a strike length of two kilometres and show exit-fluid temperatures up to 358°C (Reeves et al 2011). While some small mounds are present, scattered chimneys protruding from felsic volcanic rocks characterize most sites. High-temperature venting, up to 332°C (Bach et al 2012), and SMS systems have also been observed at the North Su and South Su sites. There, crosscutting volcanic ridges indicate structural control on melt ascent and fluid migration, a setting common for many ancient land-based sulphide systems. This area also hosts the roughly 2.5-million-tonne Solwara 1 deposit (estimated at 2.6 per cent copper equivalent, or CuEq), over which the southwest Pacific's first mining lease for SMS

mineral extraction has been granted. Additionally, several smaller active and inactive systems have been documented in the vicinity. Solwara 12, another site of commercial interest, is associated with a caldera located between Pual Ridge and SuSu Knolls.

A characteristic feature of many SMS systems in the eastern Manus Basin is the contribution of magmatic volatiles and metals. This is evidenced by the intense alteration of the host lavas, low-pH fluids, occurrence of abundant elemental sulphur at several sites (such as North Su and South Su), and the presence of metal-rich inclusions in host rocks (Yang and Scott 1996). The chemical data from Solwara 1 and Solwara 12 clearly show the difference in resource evaluation between surface sampling and drilling. The sub-seafloor deposits have lower values of both base and precious metals. Present-day exploration techniques mainly search for water column anomalies produced by active vent systems, leaving considerable potential for the discovery of inactive systems in the area.

Location	size/tonnage	Ν _	Cu	Zn	Au	Ag	depth (m)
			wt.%		ppm		
Western Manus Basin							
Solwara 11	-	26	1.6	16.9	1.2	180	1390 - 1450
Solwara 18	-	2	0.3	19.6	0.2	110	1310
Central Manus Basin							
Vienna Woods, Solwara 2	-	215	1.2	21.0	10.0	355	2470 - 2500
Solwara 03	-	31	1.1	21.3	15.2	642	2560 - 2590
Solwara 10	-	12	7.7	15.2	2.5	165	2240
Solwara 14	-	14	1.4	19.2	3.3	97	2240
Solwara 16	-	6	2.1	18.6	2.8	105	2160
Eastern Manus Basin							
Suzette (Solwara 01)	90 000 m ²	250	9.7	5.4	15.0	174	1460
Suzette (Solwara 01)*	1 030 000 t	indicated	7.2	0.4	5.0	23	1460
Suzette (Solwara 01)*	1 540 000 t	inferred	8.1	0.9	6.4	34	1460
North Su	-	4	7.1	1.6	4.8	39	1183
South Su	-	4	7.4	9.2	6.8	191	1309
Solwara 05 (N of North Su)	30 000 m ²	12	6.0	8.3	14.6	282	1635 - 1680
Solwara 09 (west of North Su)	15 000 m ²	17	6.3	10.6	19.9	296	1680
PACMANUS	45 000 m ²	336	7.4	22.5	13.7	267	1650 - 1815
Solwara 12 (near Desmos)	-	10	7.0	22.6	13.7	425	1870
Solwara 12 (near Desmos)*	230 000 t	inferred	7.3	3.6	3.6	56	1870
Solwara 13 (Yuam Ridge)	30 000 m ²	7	9.1	30.7	4.7	546	2000

Table 1: Chemical composition of SMS from the Bismark Sea. For most sites, the average composition of surface samples is given, which might not be representative of the entire deposit. For Solwara 1 and 12, where a resource estimate has been published, the data on surface samples is also provided. (N = number of samples analysed; * = resource estimate based on drilling information; results for PACMANUS include data from Solwara 4, 6, 7, and 8, which are considered here to be part of the same hydrothermal system. Sources: Hannington et al, 2010, 2011; Lipton 2012)

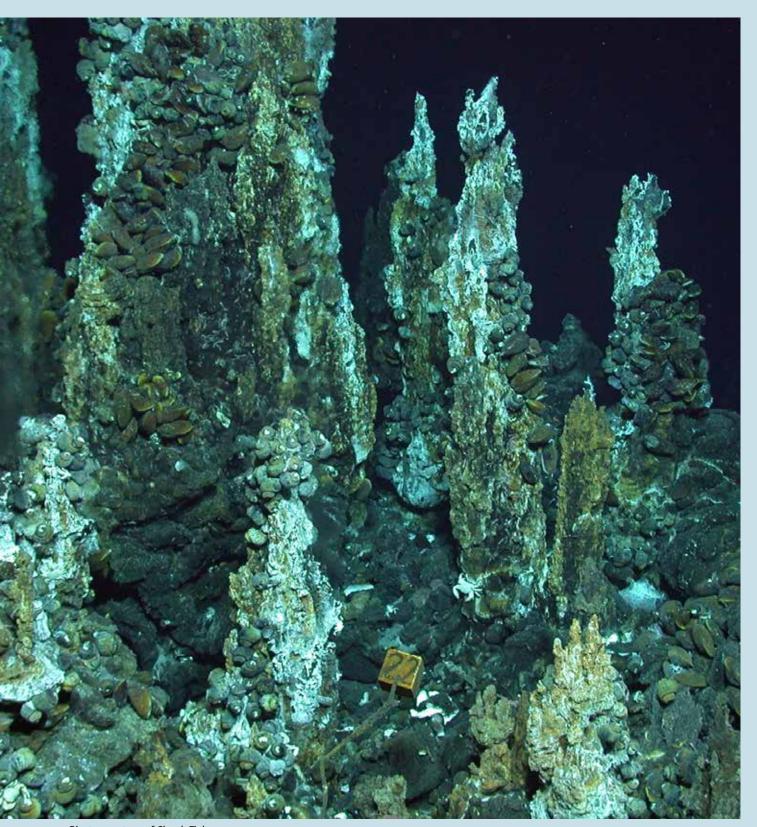


Photo courtesy of Chuck Fisher.

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