

Deep-Sea Mining

Resource Potential, Technical and Environmental Considerations



Chapter 4 Seafloor Massive Sulfide Deposits: Distribution and Prospecting

Georgy Cherkashov

Abstract Discovery of hydrothermal vents and seafloor massive sulfides (SMS) that contain metals of economic importance due to their high concentrations has generated significant interest among researchers as well as entrepreneurs as an alternative source that can be mined in future. This chapter provides a brief historical review of hydrothermal systems, the distribution, geological setting, morphology, composition, and age as well as formation and source of metals in SMS deposits. The chapter also looks at the criteria for recognition and exploration technologies for SMS deposits.

4.1 Introduction

Seafloor massive sulfide (SMS) deposits present the third (and last discovered) type of a short list of deep-sea minerals after ferromanganese nodules and cobalt-rich ferromanganese crusts. The discovery of hydrothermal vents and associated massive sulfides in the end of 1970s was recognized as one of the main events in marine science in the twentieth century. This discovery had not only fundamental but also economic importance due to extraordinary concentrations of metals being discharged from hot vents to the sea bottom. It was confirmed that mid-ocean spreading ridges and arc systems where SMS deposits are accumulated, along with deep-sea basins and seamounts that are hosts of fields of nodules and crusts, have comparable resources with continental metallogenic potential.

Seafloor massive sulfides are considered as modern analogues of land-based volcanogenic massive sulfide (VMS) deposits which were formed over the entire history of our planet evolution from the Archean to the Cenozoic (Hannington et al. 2005; Franklin et al. 2005). VMS provided more than half of the past global production of zinc and lead, 7% of the copper, 18% of the silver, and a significant amount of gold and other by-product metals (Singer 1995). Taking into account relatively short period of geological history for modern SMS accumulation the estimated

G. Cherkashov (🖂)

Institute for Geology and Mineral Resources of the Ocean (VNIIOkeangeologia), Institute of Earth Sciences, St Petersburg State University, St. Petersburg, Russia e-mail: gcherkashov@gmail.com

[©] Springer International Publishing AG 2017

R. Sharma (ed.), Deep-Sea Mining, DOI 10.1007/978-3-319-52557-0_4

resources are not as huge as VMS, nevertheless they are considered as the real source of metals for long-term development of global economy. Also, the technologies for future mining are in process of being designed and methods of metals extraction from SMS already exist being similar to that of VMS.

4.2 Historical Review of Hydrothermal Systems and SMS Deposits Study

The discovery and study of hydrothermal vents and seafloor massive sulfides has a long history of expeditionary researches and theoretical predictions. The initial findings related to the indicators of hydrothermal activity in the near-bottom waters and bottom sediments were hydrothermal plumes and metalliferous sediments.

Anomalies of temperature and salinity in the near-bottom waters were first recorded in the late nineteenth century in the expedition on the Russian vessel "Vityaz" (1886–1889) in the Red Sea. However, this discovery as well as similar data obtained during cruise on the RV "Albatross" (Sweden) from the Red Sea half a century later (1948) was not noticed by the scientific community.

The first samples of metalliferous sediments were recovered from the ocean floor during the famous expedition of the HMS "Challenger" (1873–1876). Sediments characterized by high iron and low aluminum content were dredged near the East Pacific Rise (EPR). Such unusual deposits were collected again in the 1940s on the USS "Carnegie" (Revelle 1944). However, these data did not get an explanation and was overlooked.

Here, the theory of continental drift by Alfred Wegener, published in 1915, should be mentioned revolutionary in its novelty as the discovery of oceanic hydro-thermal systems was an excellent proof of the plate tectonics theory.

Only in the 1960s, Skornyakova (1964) and Boström and Peterson (1966), as well as Bonatti and Joensuu (1966) published papers in which the accumulation of metalliferous sediments and crusts enriched in iron and manganese hydroxides was determined and related to hydrothermal activity. For the first time ancient metalliferous sediments were collected during Leg 2 of the Deep Sea Drilling Project (DSDP) in the basal layer of the sedimentary cover of the Atlantic seabed (Peterson et al. 1970).

Large-scale oceanographic researches in the framework of the International Indian Ocean Expedition (1963–1965) on Research Vessels Discovery, Chain, Atlantis-II and Meteor held in the Red Sea led to the discovery of metalliferous muds in numerous deeps (Miller et al. 1966). It was also found that some deeps contain hot brines up to 180 m thick (Degens and Ross 1969). The explanation for this phenomenon, associated with the dissolution of salt-bearing strata exposed on the rift slopes, was given later (Bäcker 1982).

High-temperature disseminated sulfide mineralization represented by iron and copper sulfides has been detected in the volcanic rock samples dredged from the mid-ocean ridges starting from 1967 (Baturin and Rozanova 1972).

At the same time increasing number of data indicating the presence of unknown sources of energy and metals in the ocean allowed to formulate theoretical background to the discovery of oceanic hydrothermal systems. Sillitoe (1972) suggested the presence of similar complexes in the modern ocean to the ancient ophiolites, which are composed of rocks occurring on the seabed and associated pyrite ores. The idea of the fluid circulation in the oceanic rocks proposed on the basis of differences in the values of the theoretically calculated and the actually observed heat flux in the ocean was suggested by Wolery and Sleep (1976).

Subsequently, more information and new data have been collected. The new sea technology and particularly deep-towed systems and submersibles played key role in the research. In 1976, Kathleen Crane from the Scripps Oceanographic Institute using Deep Tow system got an image of large white clams on black basalts at a depth of 2500 m on the Galapagos ridge. The temperature anomaly of up to 2.5 °C was also observed. Seeps of warm fluids (17 °C) discharging through cracks in the basalt lavas were recorded in the same area in 1977. This seepage zones in basalts were marked by clusters of clams and tubeworms that were later defined as representatives of a special «hydrothermal» fauna (Corliss et al. 1979).

The first sample of the massive sulfide was recovered in 1978 at the 21°N EPR during the international expedition CYAMEX (France, USA, and Mexico) by French submersible Cyana (Cyamex 1978; Francheteau et al. 1979). The presence of sulfide minerals was detected only after the land-based laboratory analysis. Subsequently during the expedition in the following year in the same area with Alvin submersible, the first images of *black smoke* from sulfide chimney standing on a basalt base was recorded with measured temperatures of the discharged fluids being as high as 350 °C (Spiess et al. 1980). Unique biological chemosynthetic communities associated with these hot vents added to the importance of *black smokers* discovery.

The process of the new hydrothermal vents discovery was very dynamic and the initial 5 years all these discoveries were concentrated in the Pacific-at the Galapagos ridge, the northern and southern part of the EPR, and ridges in the north-east Pacific (Gorda, Juan de Fuca, and Explorer). In other oceans, smokers were not found. It was proposed that the hydrothermal system might be formed only in intermediate- and fast-spreading ridges, which included ridges of the Pacific with the full spreading rate between 6 and 18 cm/year. However, the first hydrothermal field was discovered in 1985 at the Mid-Atlantic ridge (MAR) with the spreading rate of less than 4 cm/year. Thus, slow- and ultraslow-spreading ridges which accounts for about 60% of the total length of the mid-ocean ridges (Hannington et al. 2010) have been recognized as promising areas for hydrothermal systems and SMS deposits occurrences as well. The hydrothermal field at the 26°08'N of the MAR was called the TAG as discovered during the project of Trans-Atlantic Geotraverse project (Rona et al. 1986). It was observed that the hydrothermal mound in such a field can attain a size as large as 200 m in diameter and 50-60 m in height. Later it was proved that such large sizes of SMS deposits are specific to the slow-spreading ridges setting.

Other findings of fundamental importance were the discovery of hydrothermal chimneys in the subduction-related volcanic arc systems (Booth et al. 1986). After following several discoveries in arc and back-arc settings (Tonga-Kermadec, Izu-Bonin, Mariana, Manus basin), the connection between hydrothermal systems and convergent zones of oceanic plates has been established (Ishibashi and Urabe 1995; Binns and Scott 1993). Thus, two basic geological settings of hydrothermal systems associated with the boundaries of lithospheric plates have been identified: divergent (the system of mid-ocean ridges) and convergent (the system of island arcs).

Analyses of the samples of massive sulfides testified that a new type of marine minerals, which contains high concentrations of copper, zinc, lead, gold, silver, and rare metals such as cobalt, cadmium, molybdenum, indium, tellurium, selenium, bismuth, and germanium, were discovered.

The detailed history of SMS exploration since the discovery of the first black smokers on the East Pacific Rise can be followed in reviews by Rona and Scott (1993), Lowell et al. (1995), and Ishibashi and Urabe (1995).

4.3 Distribution and Geological Setting of SMS Deposits

The distribution of hydrothermal systems and seafloor massive sulfides has global character (Fig. 4.1). Currently, the number of known sites of hydrothermal activity is close to 500, and it is estimated that the number could increase by three times



Fig. 4.1 Global distribution of hydrothermal systems (from InterRidge at http://www.interridge.org/irvents/)

(Beaulieu et al. 2015). Another estimates of the abundance and distribution of known sulfide deposits in well-studied areas indicate that between 1000 and 5000 large sulfide deposits may exist on the modern seafloor (Petersen et al. 2016). "Geopolitical" statistics shows that from the area that should be explored for SMS deposits, 58% is located beyond the national jurisdiction, 36% within EEZs, and 6% are included in proposals for extensions of continental shelf by different countries (Petersen et al. 2016).

A wide variety ("geodiversity") is typical for SMS deposits related to different geological settings (German 2008; Fouquet et al. 2010). Two global structures— Mid-Ocean Ridges (MOR) and Island Arc Systems (IAS)—could be considered as a first level of geodiversity. Two-thirds of hydrothermal systems are connected with Mid-Ocean Ridges and one-third with Island Arc System, which directly correlates with the length of MOR and IAS (66,000 km and 22,000 km, respectively).

Mid-ocean ridges are characterized by different spreading rates, varying from 1 to 18 cm/year (full rate):

- Ultrafast >12.0 cm/year
- Fast 8.0–12.0 cm/year
- Intermediate 4-8 cm/year
- Slow 2.0–4.0 cm/year
- Ultraslow <2.0 cm/year

The ridges with different spreading rate vary in morphology, segmentation and mode of accretion, as well as geophysical and geochemical characteristics. Variety of hydrothermal deposits (both in terms of the size and composition) of different spreading ridges are considered as the second level of geodiversity of MOR system. In turn, hydrothermal systems in arc environments, the settings in which the majority of ancient VMS districts are thought to have formed (Franklin et al. 2005), are also subdivided on this level. Among them are SMS deposits related to frontal arc volcanoes, arc-related rifts, and back-arc spreading centers. Transitional arc volcanoes and volcanoes in continental margin arcs can also host significant seafloor massive sulfide deposits (Monecke et al. 2014).

Initially the first hydrothermal vents were discovered in the mid-ocean ridge of the East Pacific Rise and maximum number of hydrothermal fields are situated on this global structure. There is a clear link between the frequency of occurrence of vents and their spreading rates, which determines the intensity of magmatic processes. Thus, the magmatic control determines the formation and intensity of hydrothermal processes in a fast- and intermediate-spreading ridges. Another situation occurs in the ranges of conditions characterized by slow- and ultraslow-spreading centers. In this case, the main importance is the tectonic factor.

As a result, there are two types of hydrothermal systems within the mid-ocean ridges, which differ in a number of parameters, the main of which is a resource potential of SMS deposits (Table. 4.1).

The estimates of SMS tonnage within ridges of different spreading rates (Hannington et al. 2010, 2011; Beaulieu et al. 2015; German et al. 2016) show the higher resource potential of slow- and ultraslow ridges comparable with fast- and intermediate ones (Fig. 4.2).

Parameters		EPR	MAR	
Tectonics/magmatis	sm			
Spreading (mm/year)	6–16	<2-4	
Host rocks		Basalts	Basalts, Gabbro-peridotites	
Ore-control structures		Central graben, off-axial smts	AVR, OCC	
SMS deposits				
Age of SMS (years)		$n \times 10^{0} - n \times 10^{3}$	$n \times 10^{0} - n \times 10^{5}$	
Av. size of single mound (m)		$n \times 10^{0}$	$n \times 10^{0} - n \times 10^{2}$	
Av. size of cluster mounds (m)		$n \times 10^1$	$n \times 10^{1} - n \times 10^{3}$	
Distance between hydrothermal		$n \times 10^{0} - 10^{1}$	$n \times 10^{1} - n \times 10^{2}$	
fields (km)				
Estimated resources (t)		$n \times 10^{1} - n \times 10^{3}$	$n \times 10^{3} - n \times 10^{6}$	
Metals	Cu/Zn	Lower	Higher	
	Au	Lower	Higher	

 Table 4.1 Geological setting and parameters of SMS deposits at the East Pacific Rise (EPR) and at the Mid-Atlantic Ridge (MAR)

AVR axial volcanic ridge, OCC oceanic core complex



Fig. 4.2 Expected distribution of seafloor massive sulfide deposits on the mid-ocean ridges as a function of spreading rate (German et al. 2016)

Apparent contradiction between frequency and resource potential of SMS in different spreading rate ridges could be explained by combination of small size but numerous amount ore accumulations within fast- and intermediate-spreading ridges.

The next level of geodiversity is connected with variety of the SMS deposits related to ridges with different spreading rates. The most contrasting diversity could

Structural set	ting					
Mode of accrea	tion					
Symmetrical			Asymmetrical			
Setting in the r	ift zone					
Axial		Off-axial	Off-axial			
Association wi	th OCC/detachmen	ts				
Not associated			Associated			
			Hanging wall	Footwall		
Hosted rocks						
Basalts				Gabbro-peridotites		
E-MORB	N-MORB					
Menez Gwen	Puis des Folles	Krasnov	Semenov			
Lucky Strike	Snake Pit	Peterburgskoye	Ashadze-4	Ashadze-1, 2		
	Broken Spur	Zenith-Victory	TAG	Irinovskoye		
	Squid Forest	Yubileynoye		Logatchev		
		Surprize		Pobeda		
				24° 30′ N		
				Rainbow		

Table 4.2 Geological setting of SMS deposits at the northern equatorial MAR

be observed at the slow-spreading ridges. Based on the mode of accretion and type of hosted rocks, two geological settings of SMS deposits at slow-spreading ridges could be divided: symmetrical mode of accretion with basalts and asymmetrical accretion with gabbro-peridotites (Escartin et al. 2008). The same division of the MAR as a typical slow-spreading ridge is described as "magmatic" (with domination of volcanic processes) and "tectonic" segments where magmatism is reduced and tectonism is dominant (German et al. 2016). Half of the SMS deposits at the Northern Equatorial part of the MAR are associated with basalts at magmatic segments and another half with lower crust and mantle rocks (gabbro-peridotites) of the oceanic core complex (OCC) at tectonic segments (Table 4.2). OCC is tectonically uplifted along detachment faults, which exhume from the footwall deep-seated gabbro-peridotite rocks onto the seafloor and may provide pathways for hydrothermal fluids (Smith et al. 2006; MacLeod et al. 2009; Tivey et al. 2003; McCaig et al. 2007). Basalt-hosted deposits can be located in the axial part of the rift valley; in this case, they are often confined to neovolcanic zones (axial volcanic ridge)-the voungest manifestations of basaltic volcanism. The basalt-hosted deposits could also be located at off-axis setting associated with slopes of the rift valley or tops of the rift mountains. This setting is typical for ultramafic-hosted deposits as well. The last level of geodiversity within slow-spreading ridges is based on the association of SMS deposits with footwall or hanging wall of detachment faults at the tectonic segments of the ridge (Table 4.2).

4.4 Morphology of SMS Deposits

Morphology of SMS deposits depends on the stage of hydrothermal system evolution and varies in different geological settings. Individual active and/or inactive black smokers/chimneys are typical for the initial (immature) stage of SMS deposit formation and have height from few centimeters up to 45 m (Petersen et al. 2016) (Figs. 4.3 and 4.4)

A typical young (up to few thousand years) basalt-hosted active vent field at the Endeavor segment of the intermediate-spreading Juan de Fuca Ridge has been described as follows: "the active vent fields are characterized by steep-sided sulfide edifices that commonly rise several tens of meters above the seafloor and can each contain multiple active points of high-temperature discharge" (Jamieson et al. 2014) (Fig. 4.5).

"Forest-like" chimney accumulations with numerous (up to ten) 30–40 cm high edifices per 1 m² have been observed at ultramafic basement of slow-spreading Mid-Atlantic Ridge (Firstova et al. 2016) (Fig. 4.6). This hydrothermal field (Ashadze-1) is also rather young (7.2 ka) but has different way of occurrence comparable with the same age deposits associated with basalts. Besides smokers, another type of individual hydrothermal edifices—beehive-like diffusers—have been observed at the TAG and other hydrothermal fields (Fig. 4.7).

Over a period of time, chimneys collapse and the sulfide debris accumulates as a mound. The mound-like structures with apron of disintegrated chimneys are widely



Fig. 4.3 Black smoker at the Ashadze-1 hydrothermal field. Photo by ROV Victor in French-Russian expedition Serpentine (2007). Copyright IFREMER



Fig. 4.4 Inactive chimney from the Mid-Atlantic Ridge (Photo V. Malin)



Fig. 4.5 3-D image of the Endeavor Segment of the Juan de Fuca Ridge with sulfide edifices. Bathymetric data were generated from multibeam sonar collected with MBARI AUV D. Allan B and gridded at 1 m. Inset image is of the same scene using shipboard multibeam data gridded at 50 m. At this resolution, sulfide edifices at Endeavor cannot be resolved (Jamieson et al. 2014)



Fig. 4.6 Cluster of small chimneys at the ultramafic-hosted Ashadze-1 deposit (MAR). Chimneys are in different degrees of oxidization. White actinias indicate present-day hydrothermal activity. Photo made by ROV Victor in French–Russian expedition Serpentine (2007). Copyright IFREMER



Fig. 4.7 White smoker (*left*) and diffuser (*right*). Manus Basin. Southwest Pacific (Photo P. Halbach)



Fig. 4.8 Morphology of seafloor massive sulfides in the Pacific ocean (Hannington et al. 1995)

distributed (Fig. 4.8). They have been observed at the Galapagos Ridge, Juan de Fuca Ridge (the Zephyr Mound with a diameter of ~ 90 m and a height of 26 m is the largest single sulfide accumulation so far discovered along the Endeavor Segment (Jamieson et al. 2013)), and at many other sites. But the largest basalt-hosted mounds were discovered at the TAG hydrothermal area where Active and Mir Mounds reach 200 m in diameter and 40–50 m in height.

The large size of these mounds could be explained by long-term process of their formation —up to 50 thousand years (Lalou et al. 1995), which is typical for slow-spreading ridges. A huge mound-like structures are also formed in another geological setting, i.e., within sediment-filled rift valley. Mounds up to 300 m in diameter and 50 m in height are formed where sediments allow for efficient trapping of the metals due to metal precipitation below the seafloor (as in Middle Valley and Okinawa Trough) (Zierenberg et al. 1998; Takai et al. 2012).

The final transformation of SMS accumulation is represented by coalescence mounds and products of their destruction. Morphology of SMS deposit on the matured stage of evolution could be illustrated by Solwara-1 hydrothermal field located in the Bismark Sea (Southwest Pacific). The 3-D image of this best studied ore body prepared for mining operations has been designed based on high-resolution near-bottom bathymetry and EM profiling (Fig. 4.9).

As for basaltic hosted hydrothermal fields, the morphology of ultramafic-hosted sulfide deposits is controlled by several local factors such as depth, phase separation, hydraulic fracturing, and permeability (Fouquet 1997). In ultramafic environments, the discharge is clearly less focused than at basaltic sites. This "diffuse" discharge through more permeable hydrothermally altered ultramafics produces relatively flat deposits without clearly organized mounds. The latter are quite different from basaltic environments where conical mounds are typically formed (Fig. 4.10). In addition,



Fig. 4.9 3-D image of Solwara-1 SMS deposit (Lipton 2012)



Fig. 4.10 Differences in the morphology of deposits and type of discharge between basaltic and ultramafic hydrothermal deposits. Compared to (**a**) basaltic hosted fields, discharge is less focused in (**b**) ultramafic environments, and no real mound is formed; part of the deposit may occur as replacement of the ultramafic rocks (Fouquet et al. 2010)

pervasive near-surface high-temperature circulation generates highly altered areas and enhances subsurface sulfide precipitation, large stockwork mineralization, and completes replacement of the ultramafic rocks by massive sulfides (Fouquet et al. 2010).

One more specific SMS structure found in ultramafic environment at the MAR is "smoking crater" 20–25 m wide and 1–3 m deep with small black smokers on the rim and at the bottom of the crater (Bogdanov et al. 1997; Koschinsky et al. 2006; Fouquet et al. 2008; Petersen et al. 2009). It was suggested that crater shape structure was formed as a result of explosive event due to overpressure conditions inside of the hydrothermal «protomound» (Fouquet et al. 2008, 2010).

4.5 Composition and Aging of SMS Deposits

The composition of hydrothermal sulfide deposits can vary considerably according to the geodynamic environment, the nature of basement rocks affected by hydrothermal circulation, the water depth, the phase separation processes, and the maturity of deposits (Fouquet and Lacroix 2014).

The major minerals forming SMS deposits include iron sulfides, such as pyrite and marcasite, as well as the minerals of the most economic interest—chalcopyrite (copper sulfide) and sphalerite (zinc sulfide). All other minerals of SMS deposits are considered as minor (by-product) ones. According to the name of deposits, most minerals are represented by sulfides but not only: for example, copper oxychloride (atacamite) is widely distributed in SMS deposits at the Mid-Atlantic ridge. The precious metals gold and silver mainly occur in native form. Minor and rare metals either form their own accessory minerals or occur as isomophous phase in another carrier mineral.

Genetically SMS minerals could have primary (generated directly from the hydrothermal fluid) or secondary (formed during alteration of the primary minerals) nature. The zonation of mounds and chimneys is temperature-dependent and involves the replacement of early relatively low-temperature zinc-rich assemblages may with higher temperature copper-rich assemblages. Weathering of SMS on the seabed results in the formation of secondary copper-rich sulfides. High- and low-temperature hydrothermal minerals are recognized as well. High-temperature sulfide minerals often associated with low-temperature precipitates which are predominantly represented by non-sulfide minerals: sulfates, carbonates, and silicates (Table 4.3).

High grade of copper and zinc (up to tens of percent), gold and silver (tens and hundreds of ppm, respectively) in comparison with VMS and other on-land deposits determines economic interest to SMS as a source of these metals. The rare elements—bismuth, cadmium, gallium, germanium, antimony, tellurium, thallium, and indium—which are critical for high-tech industry can significantly enrich some deposits, especially those that were formed at volcanic arcs.

The mean metal content of seafloor massive sulfide deposits with respect to their geological setting demonstrates big varieties (Table 4.4).

The deposits associated with relatively homogenous basalts (in particular on fastand intermediate-spreading ridges) are enriched in zinc, silver, and selenium. SMS

High temperature			Low temperature					
Sulfides		Oxyhydroxides	5					
Iron	Copper	Zinc	Iron	Manganese	Silica	Carbonates	Sulfates	
Pyrite	Chalcopyrite	Sphalerite	Goethite	Todorokite	Quartz	Aragonite	Anhydrite	
Marcasite	Bornite	Wurtzite	Hydrogoethite	Birnessite	Opal	Calcite	Barite	
Pyrrhotite	Chalcosite		Hematite	Vernadite]			
	Isocubanite		Amorphous					

Table 4.3 Minerals of hydrothermal precipitates

		Cu,%	Zn,%	Pb,%	Fe,%	Au, ppm	Ag, ppm
Setting	Ν	(wt%)	(wt%)	(wt%)	(wt%)	(ppm)	(ppm)
Sediment-free MOR	51	4.5	8.3	0.2	27.0	1.3	94
Ultramafic-hosted MOR*	349	17.9	7.1	0.02	24.8	10.0	56
Sediment-hosted MOR	3	0.8	2.7	0.4	18.6	0.4	64
Intraoceanic back-arc	36	2.7	17.0	0.7	15.5	4.9	202
Transitional back-arcs	13	6.8	17.5	1.5	8.8	13.2	326
Intracontinental rifted arc	5	2.8	14.6	9.7	5.5	4.1	1260
Volcanic arcs	17	4.5	9.5	2.0	9.2	10.2	197

 Table 4.4 The mean metal content of seafloor massive sulfide deposits with respect to their tectonic setting

Source: GEOMAR and VNIIOkeangeologia* (Petersen et al. 2016 with additions)

deposits related to mantle rocks are characterized by high values of copper, gold, and cobalt. Sediment-hosted deposits have low concentrations of metals due to the dilution by non-ore material but sometimes are enriched in lead and arsenic. At volcanic arc systems, such as in the western Pacific, the source rocks (mainly andesites and rhyolites) are more variable in composition. It is directly reflected in the composition of the massive sulfides, which are often higher in copper, zinc, lead, silver, and gold.

Regarding geochemical associations, metals are connected with two major elements: copper and zinc. Cobalt, nickel, selenium, and indium are mainly associated with copper, whereas cadmium, lead, arsenic, silver, antimony, and germanium are associated with zinc. Gold shows more complex behavior and may be associated with either copper or zinc.

4.5.1 Age of SMS Deposits

Age of SMS occurrence and duration of ore formation are parameters which characterize maturity of hydrothermal system and determine the size of deposit. The age varies in wide interval: from the first years to hundreds of thousand years depending on the setting of deposit. Short-lived hydrothermal systems with the age up to first thousand years are typical for the fast- and intermediate-spreading ridges as well as for volcanic arc structures (de Ronde et al. 2011; Jamieson et al. 2013). The long-lived systems (tens and hundreds of thousand years) are related to the slow- and ultraslow-spreading centers (Cherkashov et al. 2010). The age of the oldest deposit at the Mid-Atlantic Ridge (Peterburgskoye) is estimated at ca 223 ka (Kuznetsov et al. 2015). The formation of SMS deposits is episodic: active and inactive periods alternate.

4.6 Formation and Source of Metals in SMS Deposits

Seafloor massive sulfide deposits are formed from the hot vents on the seabed as a result of the interaction of seawater with a heat source in the sub-seafloor. The general scheme of the hydrothermal system is given in Fig. 4.11.

It is assumed that the seawater changes its characteristics (especially temperature, redox potential, salinity, and metals content) in the course of the penetration through cracks and circulation in the subsurface of the seafloor. The heated seawater leaches out metals from the surrounding rocks. The chemical reactions that take place in this process result in a hot (up to 400 °C), acidic, reduced and enriched in dissolved metals and sulfur fluid. The hydrothermal circulation is initiated by nearsurface magma chamber. Thus, the first prerequisite of hydrothermal circulation and SMS deposit formation is the existence of the heat source.

The second necessary condition for fluid circulation is the increased permeability of seabed rocks provided by seismic/tectonic activity.



Fig. 4.11 General scheme of hydrothermal system (Jamieson et al. 2016)

These two conditions are realized on the borders of the lithospheric plates, where volcanic and tectonic activity is the most intensive at our planet. Thus, hydrothermal systems in the ocean are related to the main geological and tectonic structures on the seabed—mid-ocean ridges and island arc systems.

Hydrothermal minerals forming chimney and smoke precipitate in zone of hot (up to 400 °C) hydrothermal fluid discharge to the cold (2–4 °C) near-bottom seawater. The color of hydrothermal vents depends on their temperature: black smoke with suspended sulfide minerals has temperature > 300 °C while white smoke with non-sulfide minerals (sulfates and carbonates) is characterized by lower temperature (<200 °C) (Fig. 4.7). A vertical jet-like discharge is replaced by horizontal spreading, after the density of the rising fluid becomes equal to density of the bottom waters at corresponding horizon. This lens of hydrothermal plume usually occurs at a depth of 200–300 m above the bottom. Plume has a thickness of 50–100 m and is characterized by anomalies of transparency/turbidity, gases (methane, hydrogen), and metals (manganese, iron) concentrations. Exploration methods of the active hydrothermal fields with associated sulfide mineralization are based on determination of these parameters in the near-bottom waters (see next section).

Rona (1984) has estimated that only about 5% of the metal amount from hydrothermal fluids accumulates in massive sulfides and 95% disperses as smoke and plume in near-bottom waters with further oxidation and forming layers of metalliferous sediments around hydrothermal fields.

According to the recycling model of SMS formation, the hosted rocks are considered as a source of metals. However, there is geological setting where metals in SMS could be provided by magmatic fluids. This is typical for the sites where seafloor massive sulfide deposits are forming in close association with subductionrelated volcanic centers. Hydrothermal vents at submarine arc volcanoes show clear evidence of the direct input of magmatic volatiles, similar to magmatic-hydrothermal systems in subaerial volcanic arcs (Yang and Scott 1996, 2006).

Thus, for the formation of hydrothermal systems, a combination of two main factors—the magmatic and tectonic—is necessary; the main mechanism leading to the formation of hydrothermal fluids at the mid-ocean ridges is the circulation of seawater in the rocks of the seafloor, while direct magmatic supply of metals is also evident in island arcs environment.

4.7 Criteria for Recognition and Strategy of SMS Exploration

Current exploration for seafloor massive sulfides is based on detection of hydrophysical and geochemical anomalies around hydrothermal fields as well as geophysical anomalies associated directly with ore bodies. Similar methods are used in prospecting of on-land deposits but marine environment dictates specific approaches in their application. The following parameters are used for recognition of hydrothermal systems:

- Hydrological: transparency/turbidity, methane and manganese concentrations in near-bottom waters. These components are characterized by the contrasting anomalies in the plumes above active hydrothermal fields. This approach is based on the fact that the size of anomalous area is considerably higher than the source of this anomaly (hydrothermal field) dimensions.
- Geochemical and mineralogical: metals (iron, manganese, copper, and zinc) and minerals (high-temperature—sulfides, and low-temperature—hydroxides of iron and manganese, sulfates and carbonates) in the sediments. These components form dispersed haloes due to result of fall-out of particles from the plume, same as in process of mass transfer during weathering of sulfide ore bodies. The abovementioned consideration regarding the sizes of anomalies and source of them is true for these type of anomalies as well as for the hydrological ones.
- Geophysical: electric self-potential and magnetic susceptibility in the nearbottom waters. These parameters differ distinctly sulfides from the host rocks and sediments. It is recommended to couple electromagnetic methods to get synergetic effect for prospecting of the SMS deposits.

Currently, exploration for massive sulfide deposits is carried out in two main stages: regional (large-scale) and detailed. Bathymetric and sonar survey for the mapping of the area as well as geological sampling and hydrocast profiling for identification of anomalies in bottom waters and sediments are conducted during the regional exploration stage. Detailed works in the local areas are performed for the groundtruthing of the anomalies and targets revealed on the previous regional stage. Besides sampling of the sulfides, video- and photo profiling for delineation of the deposits are included in the set of methods on this stage.

4.8 Exploration Technologies

Sea technologies used for SMS exploration are based on the criteria for their recognition described in previous section. Here is the brief overview of the technological systems currently applied during cruises either under the conducting of "Contracts with International Seabed Authority for exploration of polymetallic sulfides" or in course of scientific research of oceanic hydrothermal systems.

4.8.1 Hydrological Tools

CTD-rosette system is of considerable use for detection of the hydrothermal plumes generated by hot vents associated with massive sulfides. Plumes can be also detected from water columns surveys using purposefully designed Miniature Autonomous Plume Recorders (MAPRs) instruments that "has revolutionized the international community's ability to explore for hydrothermal activity" (German et al. 2016). MAPRs are used both on vertical profile stations and in conjunction with deep-towed instrument packages (e.g., sonar mapping systems).

4.8.2 Geological Sampling Tools

Different types of grabs (i.e., TV-equipped), cores (gravity, piston, hydraulic, box), and dredges are used to obtain geological samples (rocks, ores, sediments) studied on-board and further in the onshore laboratories.

4.8.3 Remote and Autonomous Operating Vehicles

Towed vehicles (Remote Operating Vehicles—ROV) together with the autonomous (Autonomous Operating Vehicles—AUV) are currently the main technological systems employed on regional and detailed stages for SMS exploration. Deepwater ROVs are linked to a host ship by a load-carry umbilical cable and have modular structure. Depending on the purpose of dive, ROV may be equipped with a manipulator, still/video camera, echosounder, sonar, magnetometer, water sampler, and different sensors that can measure self-potential and other water parameters. AUVs may also carry varied payload sensors such as sonar, echosounder, sub-bottom profiler, laser profiler, magnetometer, and still image camera. The main advantages of unmanned vehicles are their versatility, high efficiency, and safety which cannot be guaranteed in the case of manned submersibles. All these factors make the ROV and AUV most high-tech and demanded complexes in the search for and study of submarine hydrothermal systems.

4.8.4 Drilling Systems

To study the internal structure of the sulfide ore bodies and to estimate their resources drilling is needed. There are two types of drilling systems:

- On-board drilling system (Derrick type)
- Seabed system by using a drilling rig

The first method executed from the specialized vessel allows to drill deep wells and to use Logging-while-Drilling technique. However, this method is extremely complex from a technological point of view and the cost of these works is very high. The using of the second type of drilling systems could be done from non-specialized vessel. This way is more efficient, less expensive, and most widely used in modern practice.

4.8.5 Manned Submersibles

The role of submersibles in the discovery and study of hydrothermal systems is very high. Discoveries and observations made on-board Cyana, Alvin, Pisces, Nautilus, Mir, Shinkai will remain in the history of oceanographic research. Many divers believe that no one device can replace the human eye (especially an expert eye); therefore, each dive of submersible is unique in terms of the information obtained. However, it is clear that the mainstream of ocean technology development is associated with robotic systems.

References

- Bäcker H (1982) Metalliferous sediments of hydrothermal origin from the Red Sea. In: Halbach P, Winter P (eds) Marine mineral deposits. Glückauf, Essen, pp 102–136
- Baturin GN, Rozanova TV (1972) Ore mineralization in the rift zone of the Indian ocean. In: Research of oceanic rift zones. pp 190–202
- Beaulieu SE, Baker ET, German CR (2015) Where are the undiscovered hydrothermal vents on oceanic spreading ridges? Deep Sea Res II. http://dx.doi.org/10.1016/j.dsr2.2015.05.001
- Bogdanov Y, Bortnikov N, Vikentiev I (1997) New type of modern mineral-forming system: black smokers of hydrothermal field at 14°45′ N, Mid-Atlantic Ridge. Ore Deposit Geol 39(1):68–90 (in Russian)
- Bonatti E, Joensuu O (1966) Deep-sea iron deposits from the South Pacific. Science 154(3749): 643–645
- Booth R, Crook K, Taylor B et al (1986) Hydrothermal chimneys and associated fauna in the Manus back-arc basin, Papua New Guinea. Eos 67(21):489–490
- Boström K, Peterson MNA (1966) Precipitates from hydrothermal exhalations on the East Pacific Rise. Econ Geol 61(7):1258–1265
- Cherkashov G, Poroshina I, Stepanova T, Ivanov V, Bel'tenev V, Lazareva L, Rozhdestvenskaya I, Samovarov M, Shilov V, Glasby G (2010) Seafloor massive sulfides from the northern equatorial Mid-Atlantic Ridge: new discoveries and perspectives. Mar Georesour Geotechnol 28:222–239
- Corliss JB, Dymond J, Gordon LI, Edmond JM, Von Herzen RP, Ballard RD, Green K, Williams D, Bainbridge A, Crane K, Van Andel TH (1979) Submarine thermal springs on the Galapagos Rift. Science 203:1073–1083
- Cyamex (1978) Découverte par submersible de sulfures polymétalliques massifs sur la dorsale du Pacifique oriental, par 21°N (projet "Rita"). C R Acad Sci 287:1365–1368
- de Ronde CEJ, Massoth GJ, Butterfield DA, Christenson BW, Ishibashi J, Ditchburn RG, Hannington MD, Brathwaite RL, Lupton JE, Kamenetsky VS, Graham IJ, Zellmer GF, Dziak RP, Embley RW, Dekov VM, Munnik F, Lahr J, Evans LJ, Takai K (2011) Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano, Kermadec Arc, New Zealand. Miner Deposita 46:541–584
- Degens ET, Ross DA (eds) (1969) Hot brines and recent heavy metal deposits in the Red Sea. Springer, New York
- Escartın J, Smith DK, Cann J, Schouten H, Langmuir CH, Escrig S (2008) Central role of detachment faults in accretion of slow-spreading oceanic lithosphere. Nature 455:790–795
- Firstova A, Stepanova T, Cherkashov G, Goncharov A, Babaeva S (2016) Composition and formation of gabbro-peridotite hosted seafloor massive sulfide deposits from the Ashadze-1 hydrothermal field, Mid-Atlantic Ridge. Minerals 6:19. doi:10.3390/min6010019
- Fouquet Y (1997) Where are the large hydrothermal sulphide deposits in the oceans? Philos Trans R Soc Lond Ser A 355(1723):427–440

Fouquet Y, Lacroix D (2014) Deep marine mineral resources. Springer, Heidelberg

- Fouquet Y, Cherkashov G, Charlou JL, Ondreas H, Birot D, Cannat M, Bortnikov N, Silantyev S, Sudarikov S, Cambon-Bonavita MA, Desbruyeres D, Fabri MC, Querellou J, Hourdez S, Gebruk A, Sokolova T, Hoise E, Mercier E, Kohn C, Donval JP, Etoubleau J, Normand A, Stephan M, Briand P, Crozon J, Fernagu P, Buffier E (2008) Serpentine cruise—ultramafic hosted hydrothermal deposits on the Mid-Atlantic Ridge: first submersible studies on Ashadze 1 and 2, Logatchev 2 and Krasnov vent fields. Inter Ridge News 17:15–19
- Fouquet Y, Cambon P, Etoubleau J, Charlou JL, Ondreas H, Barriga FJAS, Cherkashov G, Semkova T, Poroshina I, Bohn M, Donval JP, Henry K, Murphy P, Rouxel O (2010) Geodiversity of hydrothermal processes along the Mid-Atlantic Ridge and ultramafic hosted mineralization: a new type of oceanic Cu-Zn-Co-Au volcanogenic massive sulfide deposit. In: Rona PA, Devey CW et al (eds) Diversity of submarine hydrothermal systems on slow spreading ocean ridges. Geophysical monograph, vol 188. AGU, Washington, pp 297–320
- Francheteau J, Needham HD, Choukroune P, Juteau J, Seguret M, Ballard RD, Fox PJ, Normark W, Carranza A, Cordoba A, Guerrero J, Rangin C, Bougault H, Cambon P, Hekinina R (1979) Massive deep sea sulphide ore deposit discovered on the East Pacific Rise. Nature 277:523–528
- Franklin JM, Gibson HL, Jonasson IR, Galley AG (2005) Volcanogenic massive sulfide deposits: Economic Geology 100th Anniversary Volume: 523–560
- German C (2008) Global distribution and geodiversity of high-temperature seafloor venting. Deep-sea mining: a reality for science and society in the 21st century. Science and policy workshop, 10
- German C, Petersen S, Hannington MD (2016) Hydrothermal exploration of mid-ocean ridges: where might the largest sulfide deposits occur? Chem Geol 420:114–126. doi:10.1016/j. chemgeo.2015.11.006
- Hannington MD, Jonasson IR, Herzig PM, Petersen S (1995) Physical and chemical processes of seafloor mineralization at mid-ocean Ridges. In: Geophysical Monograph, vol 91. AGU, Washington, pp 115–157
- Hannington MD, de Ronde C, Petersen S (2005) Sea-floor tectonicsand submarine hydrothermal systems. In: Hedenquist JW et al (eds) Economic Geology 100th Anniversary Volume, pp 111–141
- Hannington MD, Jamieson J, Monecke T, Petersen S (2010) Modern sea-floor massive sulfides and base metal resources: toward an estimate of global sea-floor massive sulfide potential. Spec Publ Soc Econ Geol 15:317–338
- Hannington M, Jamieson J, Monecke T, Petersen S, Beaulieu S (2011) The abundance of seafloor massive sulfide deposits. Geology 39:1155–1158 http://dx.doi.org/10.1130/G32468.1
- Ishibashi J, Urabe T (1995) Hydrothermal activity related to arc-backarc magmatism in the Western Pacific. In Taylor B (ed) Backarc basins: Tectonics and magmatism. New York, Plenum Press, pp 451–495
- Jamieson JW, Hannington MD, Clague DA, Kelley DS, Delaney JR, Holden JF et al. (2013) Sulfide geochronology along the Endeavour segment of the Juan de Fuca ridge. Geochem Geophys Geosyst. doi: 10.1002/ggge.20133
- Jamieson JW, Clague DA, Hannington M (2014) Hydrothermal sulfide accumulation along the Endeavour Segment, Juan de Fuca Ridge. Earth Planet Sci Lett 395:136–148
- Jamieson JW, Petersen S, Bach W (2016) Hydrothermalism. In: Harff J, Meschede M, Petersen S, Thiede J (eds) Encyclopedia of marine geosciences. pp 344–357
- Koschinsky A et al (2006) Discovery of new hydrothermal vents on the southern Mid-Atlantic Ridge (4S–10S) during cruise M68/1. Inter Ridge News 15: 9–15
- Kuznetsov V, Tabuns E, Kuksa K, Cherkashov G, Maksimov F, Bel'tenev V, Lazareva L, Zherebtsov I, Grigoriev V, Baranova N (2015) The oldest seafloor massive sulfide deposits at the Mid-Atlantic Ridge: 230Th/U chronology and composition. Geochronometria 42(1):100–106
- Lalou C, Reyss JL, Brichet E, Rona PA, Thompson G (1995) Hydrothermal activity on a 10(5)year scale at a slow-spreading ridge, TAG hydrothermal field, mid-Atlantic Ridge 26-degrees-N. J Geophys Res 100:17855–17862

- Lipton I (2012) Mineral Resource Estimate: Solwara Project, Bismarck Sea, PNG. Technical Report compiled under NI43–101. Golder Associates, for Nautilus Minerals Nuigini Inc.
- Lowell RP, Rona PA, Von Herzen RP (1995) Seafloor hydrothermal systems. J Geophys Res 100(B1):327–352
- MacLeod CJ, Searle RC, Casey JF, Mallows C, Unsworth M, Achenbach K, Harris M (2009) Life cycle of oceanic core complexes. Earth Planet Sci Lett 287:333–344
- McCaig AM, Cliff B, Escartin J, Fallick AE, MacLeod CJ (2007) Oceanic detachment faults focus very large volumes of black smoker fluids. Geology 35:935–938
- Miller AR, Densmore CD, Degens ET, Hathaway JC, Manheim FT, Mcfarlin PF, Pocklington R, Jokela A (1966) Hot brines and recent iron deposits of the Red Sea. Geochim Cosmochim Acta 30(3):341–359
- Monecke T, Petersen S, Hannington MD (2014) Constraints on water depth of massive sulfide formation: evidence from modern seafloor hydrothermal systems in arc-related settings, Econ Geol 109:2079–2101. http://dx.doi.org/10.2113/econgeo.109.8.2079
- Petersen S, Kuhn K, Kuhn T, Augustin N, Hékinian R, Franz L, Borowski C (2009) The geological setting of the ultramafic-hosted Logatchev hydrothermal field (14°45'N, Mid-Atlantic Ridge) and its influence on massive sulfide formation. Lithos 112:40–56
- Petersen S, Kratschell A, Augustin N, Jamieson J, Hein JR, Hannington MD (2016) News from the seabed—geological characteristics and resource potential of deep-sea mineral resources. Mar Policy 70:175–187. doi:10.1016/j.marpol.2016.03.012i
- Peterson MNA, Edgar NT, Von der Borch CC, Rex RW (1970) Cruise leg summary and discussion. In: Init Reports DSDP, vol 2. US Govt Print-Office, Washington
- Revelle RR (1944) Marine bottom samples collected in the Pacific Ocean by the "Carnegie" on her seventh cruise. Carnegie Inst Publ 556. Carnegie Inst, Washington
- Rona PA (1984) Hydrothermal mineralization at seafloor spreading centers. Earth Sci Rev 20(1):1–104
- Rona PA, Scott SD (1993) A special issue on sea-floor hydrothermal mineralization; new perspectives; preface. Econ Geol 88(8):1933–1973
- Rona PA, Klinkhammer G, Nelson TA, Trefry JH, Elderfield H (1986) Black smokers, massive sulfides, and vent biota at the Mid-Atlantic Ridge. Nature 321(6065):33–37
- Sillitoe RH (1972) Formation of certain massive sulphide deposits at sites of spreading. Trans Inst Min Metall 81(789):13141–13148
- Singer DA (1995) World class base and precious metal deposits—a quantitative analysis. Econ Geol 90:88–104
- Skornyakova NS (1964) Dispersed iron and manganese in Pacific sediments. Lithol Min Deposit 5:3–20 (in Russian)
- Smith DK, Cann JR, Escartin J (2006) Widespread active detachment faulting and core complex formation near 13 N on the Mid-Atlantic Ridge. Nature 443:440–444
- Spiess FN, Macdonald KS, Atwater T, Ballard R, Carranza A, Cordoba D, Cox C, Diazgarsia VM, Francheteau J, Guerrero J, Hawkins J, Hamon R, Hessler R, Juteau T, Kastner M, Larson R, Luyendik B, Macdougall JD, Miller S, Normark W, Orcutt J, Rangin C (1980) East Pacific Rise; hot springs and geophysical experiments. Science 207(4438):1421–1433
- Takai K, Mottl MJ, Nielsen SHH, Birrien JL, Bowden S, Brandt L, Breuker A, Corona JC, Eckert S, Hartnett H, Hollis SP, House CH, Ijiri A, Ishibashi J, Masaki Y, McAllister S, McManus J, Moyer C, Nishizawa M, Noguchi T, Nunoura T, Southam G, Yanagawa K, Yang S, Yeats C (2012) IODP expedition 331: strong and expansive subseafloor hydrothermal activities in the Okinawa Trough. Sci Drill 13:9–26
- Tivey MA, Schouten H, Kleinrock MC (2003) A near-bottom magnetic survey of the Mid-Atlantic Ridge axis at 26°N: implications for the tectonic evolution of the TAG segment. J Geophys Res 108:2277. doi:10.1029/2002JB001967
- Wolery TJ, Sleep NH (1976) Hydrothermal circulation and geochemical flux at mid-ocean ridges. J Geol 84(3):249–275
- Yang K, Scott SD (1996) Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. Nature 383(6659):420–423

- Yang K, Scott SD (2006) Magmatic fluids as a source of metals in arc/back-arc hydrothermal systems: evidence from melt inclusions and vesicles. In: Christie DM, Fisher CR, Lee S-M (eds) Back Arc spreading systems: geological, biological, chemical and physical interactions, vol 166. American Geophysical Union, Geophysical Monograph, Washington, pp 163–184
- Zierenberg RA et al (1998) The deep structure of a sea-floor hydrothermal deposit. Nature 392(6675):485–488



Georgy Cherkashov is Deputy Director of the Institute for Geology and Mineral Resources of the Ocean (VNIIOkeangeologia, St. Petersburg, Russia) of the Ministry of Natural Resources (since 1996). He holds a Dr. Sci. for research of seafloor massive sulfide (SMS) deposits of the Mid-Atlantic Ridge. He has been the Chief Scientist of 13 oceangoing Russian and international expeditions for prospecting of SMS deposits in the Pacific, Atlantic, and Indian Oceans (1983-2007). He was also the President of International Marine Minerals Society (2011–2012), member of the Legal and Technical Commission of the International Seabed Authority (since 2012) and is Professor at St. Petersburg State University (Marine Geology), part time (since 2005).