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## MINERAGENESIS AT SEA FLOOR HYDROTHERMAL VENTS

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The similarity of physical and chemical features of hydrothermal fluids sampled in different regions points to a single basic primary composition for almost all oceanic mineral-forming fluids. Hot vents of oceanic rift zones produce solutions closest in composition to such primary fluids. Thermodynamic modelling proves the possibility of formation of such fluids in the process of high-temperature interaction of sea water and basaltic rocks. Hydrothermal solutions form Fe, Zn and Cu-sulfide deposits at their discharge sites on the oceanic floor, if boiling or dilution with cold sea water do not take place during ascent. The compositions of individual ore deposits change in process of their development from mostly Zn to Fe-Cu-sulfide due to secondary redistribution of ore matter within mature deposits, produced by late ore-forming fluids and evolution of fluids themselves. Zn and most trace elements are carried out of inner parts of large ore bodies during recrystallization, leading to the formation of deposits close to most typical continental massive sulfides in mineralogy and structure. In specific geological settings (Gulf of California, Red Sea, etc.) the ore-forming process may become more complicated.

Out of the entire range of mineral-forming processes associated with the activity of hydrothermal vents on the ocean floor, the greatest progress during the last decade has been made in the study of high-temperature processes. The special attention investigators have given these processes is partly due to the fact that high-temperature mineragenesis on the ocean floor results in the formation of contemporary sulfide deposits of Fe, Cu, and Zn many of which are comparable in scale to ancient deposits found on the continents.

There is yet another fact of major importance. The high-temperature (200-350° C) fluids in widely separated mid-ocean, ocean-margin, and intercontinental rifts settings are marked by remarkable uniformity of composition (Table 1). The compositions of low-temperature oceanic fluids suggests that they are the same as the high-temperature fluids, but strongly diluted with cold sea water [8]. Thus, practically all oceanic hydrothermal mineragenesis (allowing for a few exceptions when the

situation is complicated by local geological factors) is due to the action of fluids of a uniform primary composition which can be sampled at the "hot" vents in the rift zones of the ocean. The appreciable collection of experimental data reviewed by Mottl [27] suggests that these fluids, in pure form, also consist of sea water, but with the composition altered as a result of high-temperature interaction with rocks of the ocean floor. While maintaining the overall level of mineralization of sea water in the majority of cases, such fluids are distinguished by high contents of a number of alkali, alkaline-earth, and heavy metals and by the presence of hydrogen sulfide, methane, and hydrogen in the complete absence of Mg, sulfate ion, acid reactions, and reducing properties.

The impossibility of direct examination of the processes forming oceanic hydrothermal fluids beneath the ocean floor has made the use of thermodynamic modelling. The relative simplicity of the geological environments in which the majority of

		East-Pacific Rise		Juan de Fuca	Explorer	Gulf of	Mid-Atlanti	c Ridge
component, ppm	11° N	13° N	21° N	44° N	Ridge	California	23° N	26° N
ם <u></u>	11999-24353	25276-26980	17338-20530	33720-38648	20400-20750	20601-22586	19820	23366
Na <sup>+</sup>	6670-10856	12673-13708	10096-11728	15201-18306		10924-22798	11705-11728	13430
K⁺	729-1283	1072-1162	907-1009	1458-2018	1820-1877	1271-1924	923-934	665
$Ca^{2+}$	424-1412	1784-2192	469-834	3098-3864	1643-1804	1066-1663	381-397	1042
$Sr^{2+}$	3.3-11.8	14.7-15.9	5.7-8.5	20.2-27.3	12.2-12.5	14-22.2	4.4-4.5	8.7
H <sub>2</sub> SiO <sub>3</sub>		6-1273	937-1171	1363-1399	456-811	559-829	1421-1428	1717
Ľi		0.25-4.6	6.2-7.2	77-12.6	5.3-5.5	4.3-7.5	5.9	2.8
Rb		0.12-5.1	2.3-2.8	2.4-3.2	4.7	4.9-7.4	6.0	0.8
Ba			1.1-2.2	0.7-1.2	0.68-0.29	0.96-7.4		
Mn	40.7-50.6	93.5-159	38.4-55	143-246	14.4-15.0	7.3-13	27.0-27.1	54.9
Fe	90-364	224-605	42-136	575-1044	0.56-3.2	1-10	102.3-121.8	91.6
Cu			0.01-2.8	0.1	0.001	<0.001-0.07	0.64 - 1.1	
Zn	2.8-6.8	0.13-6.6	2.6-6.9	39.2-58.8	0.005-0.04	0.007-2.6	3.1-3.3	
$H_2S$	150-415	98.6-279	224-285	102-150	56.2	129-204	201	
T,C	347	317-354	273-350	224-285	306	270-315	335-350	290-321
Hd	3.1-3.7	3.1-3.3	3.3-3.8	3.2	4.6	5.9	3.7-3.9	
Source	Bowers et al.,	Michard et al.,	Von Damm	Von Damm	Tunnicliffe	Von Damm	Campbell	Campbell
	1988 [11]	1984 [26]	et al.,	and Bischoff	et al.,	et al.,	et al.,	et al.,
			1985a [34]	1987 [33]	1986 [32]	1985b [35]	1988 [12]	1988 [12]
Explanation: Value to zero concentratio	es are from an an	alysis of mixtures licate absence of d	s of vent fluids w ata.	ith seawater, reci	alculated to the p	ure composition	of vent water by	/ reduction

TABLE 1. Composition of High-Temperature Mineral-Forming Hydrothermal Fluids of Oceanic Rifts

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FIGURE 1. Change in the composition of the solution during interaction with fresh basalt. Hm) hematite, Qz) quartz, Kln) kaolinite, Ab) albite, Fe-Chl) Fe-chlorite, P) pyrite, Ccp) chalcopyrite, Sp) sphalerite, Bn) bornite, Po) pyrthotite, Gn) galena.

the systems occur and the compositional uniformity of the reacting phases (tholeiitic basalts and sea water) make such investigations feasible. D. V. Grichuk and M. V. Borisov [1] developed a model in which the descending branch of the convective hydrothermal system, corresponding to the entry of sea water into the fracture zone, is represented as a stepwise reactor with progressively increasing temperatures. The pressure was assumed to be uniform (500 bars) since it changes the thermodynamic constants only slightly. The solution (originally sea water) reacts at each step with a given quantity of basalt, with the resulting solution being carried on to the next step, reacting there with a new portion of solid matter. In the calculations, it was assumed that equilibrium between the solution and the association of secondary minerals replacing the basalt is reached at each step.

The results of the modelling are presented in Figure 1. The formation of anhydrite in the lowtemperature portion of the system, due to the heating of sea water supplied to the system, explains the absence of sulfate ion in the resulting hydrothermal solution. An anhydrite-rich zone actually occurs at

depths of 889-1350 m beneath the sea floor within a section of oceanic crust subjected to hydrothermal processes [9]. Sulfide minerals are formed to a lesser extent than the quantity of sulfidic sulfur in the original basalt allows, i.e., leaching (solution and oxidation) of these minerals takes place. In the model, a switch from an oxidized quartzanhydrite-chlorite association to a deoxidized albite-epidote-tremolite association takes place at temperatures of 250-300° C. These generally correspond to two associations of oceanic metabasites revealed by dredging data: one predominantly chloritic and the other predominantly epidoticactinolitic [20]. The most significant discrepancy between the model results and actual observations is the absence of smectites, so characteristic of altered basalts, in the low-temperature region [6]. These minerals were not included in the model because of sufficiently reliable thermodynamic properties are not available. The overall character of both the mineral associations and the resulting solution is in agreement with observations.

When the model is complicated by taking into account the evolution of the fluid over time,



FIGURE 2. Chemical evolution during passage of successive packets ("waves") of fluid through basalt at a temperature of 350° C.

examining the successive passage of packets ("waves") of fluid through rocks of the descending branch of the system (rocks already subjected to alteration), a progression of metasomatic zones downward along the section can be detected [2]. The evolution of the solution in terms of its removal of ore elements from the basalts proceeds in the direction of change from Zn- to Cu-specialization (Fig. 2); this can explain the evolutionary direction of change in mineral composition of ore structures on the sea floor.

Hydrothermal solutions forming at depths on the order of 1-2 km beneath the bottom, corresponding to the final step of the reactor (Fig. 1), can be abruptly cooled in the ascending branch of the hydrothermal system in two cases: If the solutions are diluted with relatively cold water due to lateral replenishment on migration routes or if a drop in hydrostatic pressure to the critical pressure causes them to boil in the channel prior to discharge. In either case, the highest-temperature ore minerals will be deposited in fissures, forming the stockwork mineralization so common in oceanic rift deposits [8].

A diagram of the charges in temperature and pressure of fluid rising to the sea floor, correspond-



FIGURE 3. Change in temperature of mineral-forming solution during ascent to the sea floor [4]. 1) boundary conditions for the existence of sea water in a monophase liquid state and critical point; 2) tentative temperature limit for deposition of sulfides and corresponding depths most typical of the axial portions of active oceanic ridges; 4) approximate courses of temperature and pressure changes of mineral-forming solutions during ascent (vertical and curved lines) and mixing with sea water on discharge (horizontal lines): ABCD) in case when great water depths rule out boiling; ABEFGH and ABEFIJK) in cases involving boiling of solutions carried to completion at temperatures respectively higher and lower than the minimal temperatures for deposition of zinc sulfides; C and G) points corresponding to conditions associated with cessation of deposition of zinc minerals at the sea floor, I) same in the rock stratum.

ing to the second case, is shown in Figure 3. As this diagram suggests, there should be a minimal water depth for each ore mineral at which the mineral can be deposited at the sea floor by incorporation into the massive ore structures; this depth is dependent upon the temperature of formation of the mineral. Thus, formation of zinc sulfides at depths less than 300-500 m is extremely unlikely [4]. This minimal depth will be greater for the high-temperature copper sulfides.

The water depths characteristic of the axial portions of active ocean ridges in most regions allow ore-bearing fluids to reach the sea floor without boiling. If substantial subsurface dilution does not occur, the fluids, upon reaching the floor at a usual temperature of 300-350° C, form massive sulfide orebodies. The "avalanche" character of the processes taking place during the ingress of hot acidic



FIGURE 4. Diagram showing evolution of "black smoker" (modified after [19]). a) Stage of formation of anhydritic "chimney" at sea floor, b) stage of high-temperature hydrothermal activity and formation of sulfide structure, c) stage of diffuse hydrothermal activity. 1) Anhydrite, 2) Cu and Fe sulfides, 3) Zn and Fe sulfides, 4) low-temperature colloform Fe sulfides, 5) veinlet-disseminated mineralization in basalt, 6) flow direction of hydrothermal fluids.

solutions rich in hydrogen sulfide and metals into cold, slightly alkaline, oxygenated bottom water and the important role of kinetic factors complicate the use of the thermodynamic approach. Important results have been obtained by direct observations and sampling using manned submersibles.

Hydrothermal fluids sampled directly at the vents contain a suspension with particle sizes ranging from tens to hundreds of micrometers, with the most abundant components being pyrrhotite, chalcopyrite, sphalerite, wurtzite, pyrite, and anhydrite. The formation of ore structures begins with the creation of an anhydrite "chimney" at the bottom [13]. Caminite, MgSO<sub>4</sub> • 0.4Mg(OH)<sub>2</sub> • 0.2H<sub>2</sub>O, occurs in the form of inclusions in the anhydrite; this is a newly discovered mineral, an endemic form in ore structures [17]. The formation of caminite in hydrothermal systems of the ocean was predicted prior to its discovery on the basis of experiments on the heating of seawater [10]. During the initial period of ore-structure formation, sulfides are predominantly deposited within a "chimney," where the flow of hot fluid from the hydrothermal vent creates fairly high temperature conditions, despite some ingress of cold water through the porous walls of the "chimney." Anhydrite is gradually replaced by sulfides; as a result, growth of the chimney is accompanied by upward movement of the anhydrite margin of the chimney [13]. The formation of mound-like "black smokers" (Fig. 4) proceeds as a result of rapid growth of the "chimney" (up to 7 cm a day, according to data from direct observations [19]) and subsequent collapse, with cementation of fragments by fauna specific to the vents. Fe, Zn, and Cu sulfides quantitatively predominate among the minerals found in the hydrothermal ore structures of the ocean floor (Table 2). Barite and opal are also important components; their proportion is greater in those regions where the concentrations of ore elements in the hydrothermal fluids are relatively low (Explorer Ridge, Axial Mountain on the Juan de Fuca Ridge, Gulf of California, and Marianas Trough).

As the structures grow, diffusive, disseminating penetration of hydrothermal fluids through the previously formed ore mass, accompanied by recrystallization and replacement of mineral aggregates, plays an ever greater role. Fine- and cryptocrystalline colloform dendritic aggregates with organogenic and layered textures predominantly composed of Zn and Fe sulfides (aggregates which are characteristic of small neogenic deposits) are replaced by massive aggregates of cryptocrystalline pyrite and small quantities of chalcopyrite in the internal portions of large, mature structures [5]. The switch from Zn- to Cu-specialization of ores during the evolution of the structures may be due to a change in the composition of the solutions (Fig. 2). When the composition of the hydrothermal fluids is constant, however, "elution" of ore aggregates results in loss of the most mobile components to the external portions of the deposits and (or) to sea water, in addition to recrystallization. Decreases in the contents of the overwhelming majority of

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Mineral	East ] R	Pacific ise	Galapagos	Jua Fuca	m de Ridge	Endeavour	Explorer	Gulf of	Mid-A Ria	tlantic İge
	13° N	21° N	Ridge	44° N	46° N	Ridge	Ridge	California	23° N	26° N
Pyrite	‡	ļŧ		‡	+	+	+	‡	‡	‡
Chalcopyrite	ŧ	ŧ	ŧ	‡	÷	‡	‡	‡	‡ ‡	ŧ
Sphalerite	ŧ	‡	ŧ	ŧ	ŧ	<b>ل</b> ‡	‡	ŧ	‡	‡ ‡
Wurtzite	‡	‡	‡		+	<b>`</b> +				
Marcasite	ŧ	‡	ŧ	+ + +	‡ +	‡ ‡	ŧ	‡	‡	‡
Pyrrhotite	+	‡	÷	‡		+		+ + +	ŧ	+
Isocubanite	‡	‡	+	‡		+	+	+		
Bornite	÷	+							‡	
Covellite	‡	+	÷							‡
Chalcocite	+	+								
Digenite	+	+								‡
Idaite	+	+								
Fahlores		+			+					
Galena		+	+	‡	+	+	+	‡		
Jordanite		+		+	÷					
Fe oxides and hydroxides	ŧ	ŧ	ŧ	+	+		+	‡	‡	‡ +
Lepidocrocite		+		+				+		
Sulfur		‡		+	+			÷	+	

TABLE 2. Minerals of Sulfide Ores Associated with Rift Zones of the Ocean

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Opal		‡	‡	‡	ŧ	‡	<b>+</b> + +	‡ + +		‡
Quartz	+							‡		÷
Smectites								‡		
Talc		+								+
Barite	+	‡	‡	+	‡	+	‡	ŧ		
Anhydrite	ŧ	‡	+	‡	+					ŧ
Gypsum		‡					+	÷		+
Jarosite		‡							+	
Calcite								ŧ		+
Aragonite				+				+		‡
Atacamite	+						+			‡
Mn hydroxides	÷		+		÷		+			
Anglesite		÷								
Caminite		+								
Principal published sources	[18] [23]	[16] [28]	[25] [31]	[21]	[15]	[30]	[14]	[22]	[29]	[7] [7]
Explanation: +++ major mine	sral, ++ comr	non mineral	l, + rare mine	ral.						



FIGURE 5. Concentrations of minor elements in monomineralic fractions of pyrite (a) and chalcopyrite (b) fine- and very fine-crystalline (type 1) and recrystallized (type 2) ore aggregates from 13° N on the East Pacific Rise. Data from neutron-activation analysis by P. A. Baragnov [5]; type 1, average of 2 samples, type 2, average of 4 samples. Ranges of elemental concentrations in individual samples are indicated by vertical lines.

minor elements in mineral grains during recrystallization of oceanic ores, detected by neutronactivation analysis of monomineralic fractions and documented in ancient sulfide deposits on the continents, is direct evidence of such a superposed process [3] (Fig. 5). Apparently, it is this process of "zone refining" which primarily controls the internal structure of the large ore bodies (Fig. 4). In the late stages, the ore bodies finally acquire a massive sulfide composition with a relative small quantity of copper sulfides. It is precisely such a composition, similar to that of the most typical sulfide ores on the continents, which is characteristic of the largest sulfide deposits found in the ocean: in the Galapagos Rift, on the submarine volcanos near the axis of the East-Pacific Rise, and in several other regions.

Retrograde solution of anhydrite in the ore structures takes place in cold sea water after cessation of high-temperature hydrothermal activity. A comparison of the mineral compositions of deposits at the 21° N area on the East Pacific Rise, now growing within a zone of contemporary hydrothermal activity in the axial portion of the rift (Alvin area), and completely formed deposits located approximately 1 km from the axis (the (CYAMEX area) indicates that pyrrhotite and wurtzite practically disappear from the ores after any length of geological time (tens of thousands of years) [28]. Formation of pseudomorphs of sphalerite after wurtzite is characteristic. These minerals are almost never found in ancient sulfide ores of the Cyprus type, which are considered the closest analogs of presentday oceanic deposits. Oxidation crusts are developing on the surfaces of the sulfide bodies. The thickness of this crust cannot be estimated on the basis of existing data, but oxidized ores account for approximately half of the specimens collected by sampling from the surface of an approximately 20,000 year old ore body on a seamount near 13° N on the East Pacific Rise [18].

Thus, the same process, forming for the most part fairly simple mineral paragenesis of sulfide ores, are apparently characteristic of both present-day and (at least in the majority of cases) ancient oceans. Data on individual present-day hydrothermal systems located in specific geological environments suggest that mineragenesis can be significantly more complex than the "base" model described. Interaction of hydrothermal fluids migrating through sediments at rifts with high rates of sedimentation (the Gulf of California, and Gorda and Endeavour ridges), for example, can lead to a portion of the ore matter being deposited in these sediments, forming sulfide-rich interbeds. Lead can be extracted from massive structures at the sea floor by hydrothermal solutions [24]. Mineragenesis takes on a special character in the rift valley of the Red Sea, where ore formation takes place within a brine layer. Other, as yet unknown, variations of the oceanic hydrothermal ore process are in principle possible. Future investigation of the entire diversity of oceanic hydrothermal ore-forming systems is bound to provide data for realistic reconstructions of the conditions of formation of various types of ancient sulfide deposits.

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