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# Specific Features of Massive Sulfide Ore Formation under Submarine Conditions at Various Depths

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The viewpoint that the formation of massive sulfide ores of the Urals on the bottom of water basins is due to the activity of shallow-seated magma chambers has predominated over the past few decades [6, 7]. However, if we take into account recent developments in modeling of the physicochemical evolution of endogenic fluids [5], including the concept of "sulfur intercept" in sulfide ore formation [3, 4], the conventional genetic model illustrates only a particular case of massive sulfide ore formation. As will be shown below, extrapolation of this model to all cases is methodically incorrect because of the omission of near-vertical metasomatic massive sulfide bodies.

Quantitative estimates in this paper are based on the average concentrations of the most abundant volatile components ($H_2O$, $CO_2$, S, Cl, F) in magmatic melts of ultrabasic to silicic composition summarized in [8]. Table 1 shows the average $H_2O/S$ values presented in [8] and our estimates (based on [8]) of possible partial pressure of sulfur and cognate gases relative to their mixtures with water.

In contrast to the previous publications [3–5] based on the relative partial sulfur pressure, the model diagrams shown in Figs. 1 and 2 are based on the relative concentrations of sulfur saturation relative to its mixture with water (Table 1), i.e., the limit weight concentration of sulfur in the fluid gas flow. Overcoming this threshold leads to removal of sulfur into the high-temperature condensate and sulfide deposition. Diagrams in Figs. 1 and 2 show the dependence of the maximum permissible relative sulfur concentration in the fluid flow on temperature and pressure. Such modification of diagrams is not only more convenient for practical use but also more correct, because one can take into consideration the influence of variable molecular compositions of gaseous sulfur (Table 2) on its partial pressure. In previous publications, the relative partial sulfur pressure was calculated at a fixed average content of atoms in the sulfur molecule (see note to Table 1). In the present versions, the contour lines of relative saturation concentrations were obtained by calculating the dependence of fluid pressure $P$, at which the fluid is saturated with sulfur, on the relative sulfur concentration ($K_S = M_S/M_{S+H_2O}$) and temperature $T$:

$$P(K_S, T) = P_{S100\%}(T) \times\left[\left(\frac{K_S}{\mu_S N_S(T)} + \frac{1-K_S}{\mu_{H_2O}}\right)\Big/\left(\frac{K_S}{\mu_S N_S(T)}\right)\right],$$

where $P_{S100\%}(T)$ is the pressure of saturated sulfur vapor at temperature $T$ (Table 2), $\mu_S = 32$ is the atomic mass of sulfur, $N_S(T)$ is the number of atoms in a gaseous sulfur molecule at temperature $T$ (Table 2), and $\mu_{H_2O} = 18$ is the molecular mass of water.

To pass from the total fluid pressure to a possible depth, we assumed that the fluid pressure is five times higher than the lithostatic pressure at a certain depth [8]. This assumption looks quite correct, because the fluid flow requires a pressure gradient, which is maximal in the case of fluid transport by molecular diffusion. Thus, the possible depth shown in model diagrams (Figs. 1, 2) corresponds to the lithostatic equivalent decreased five times due to the correction for excess fluid pressure.

Since the massive sulfide deposits in the Urals are related to cherty–basaltic (spilite–diabase), sodic rhyolite–basalt, and andesite–dacite associations [7], the initial sulfur concentration in magmatic fluid is accepted to be $K_S = M_S/M_{S+H_2O} = 10\%$, which corresponds to the data presented in [8] for basic melts (Table 1).

The massive sulfide deposits of the Urals were formed in rocks located at a shallow depth beneath the water column [7]. This geological setting determines

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**Table 1.** The $H_2O/S$ ratio [8], as well as estimates of probable concentration and partial pressure of sulfur and cognate gases relative to their mixtures with high-temperature water vapor for different magmatic melts

| $SiO_2$ | $H_2O/S$ | Relative concentration ratio $M_S/M_{S+H_2O}$, wt % | Relative partial pressure ratio, % | |
|---|---|---|---|---|
| | | | $\frac{P_S}{P_{S+H_2O}}$ | $\frac{P_{H_2S+SO_2}}{P_{H_2S+SO_2+H_2O}}$ |
| 75.26 | 130 | 0.769 | 0.16 | 0.43 |
| 56.21 | 31 | 3.125 | 0.65 | 1.78 |
| 50.60 | 7.2 | 12.20 | 2.73 | 7.24 |
| 49.29 | 8.3 | 10.75 | 2.38 | 6.35 |
| 42.52 | 4.2 | 19.23 | 4.6 | 11.8 |

Note: In calculation of the relative partial pressure, the average number of atoms $N = 2.78$ in the sulfur molecule at a critical temperature was used. The data reported in [8] are extrapolated over ultrabasic melts.

two specific features of model diagrams: (1) at low pressures, the calculated contour lines of limit sulfur concentrations in the model *PT* diagrams are drastically shifted to the low-temperature region with decrease in depth; (2) the presence of the overlapping water column promotes appearance of the region of forbidden *PT* conditions. If a data point of fluid falls into this region, this implies that all the overlapping water should be transferred into the supercritical vaporlike state. Therefore, the temperature of fluid at its vent on the bottom of water basins cannot be much higher than the critical temperature of water.

Let us compare physicochemical evolution of endogenic fluids in the presence of an overlapping water column of variable thickness. The situation shown in Fig. 1 implies that the fluid is separated from the magmatic melt at 1000°C and $3.5 \cdot 10^8$ Pa and evolves toward a decrease in temperature and pressure. Let us consider release of this fluid under deep-water (water column 5 km, Fig. 1a), moderate depth (1 km, Fig. 1b), and shallow-water (0.2 km, Fig. 1c) conditions. As can been seen, the fluid evolution in these three versions is quite distinct.

Under deep-water conditions (Fig. 1a), the fluid evolution path contains a barrier of forbidden *PT* conditions that corresponds to the contact of a high-temperature fluid with bottom water of the basin. In the situation shown in Fig. 1a, the fluid reaches the forbidden *PT* barrier before intersection of the contour line of the initial sulfur concentration $K_S = M_S/M_{S+H_2O} = 10\%$. Therefore, sulfur release and intense sulfide deposition occur only during the subsequent fluid evolution along the forbidden *PT* barrier. With intersecting contour lines of the maximum permissible concentration of gaseous sulfur in the fluid composition, the excess amount of sulfur is gradually released into the condensate. The outlet to the water neutralization barrier occurs at the maximum permissible concentration of gaseous sulfur equal to ~0.15%. This implies that 98.5% of the bulk gaseous sulfur contained in the fluid is released into the condensate upon the contact of the high-temperature fluid with bottom water. As a result, massive sulfide ore deposits are formed on the oceanic bottom in submarine hydrothermal fields.

Thus, the model shown in Fig. 1a is in full agreement with available observations on sulfide deposition of the black smoker type at a rather great depth (no less than 3–5 km) on the oceanic bottom. At the same time, the forced shift of the fluid evolution path to the low-temperature region is characteristic of temperature ore traps. In contrast to the traps considered previously [3, 4], this case may be defined as a trap of water contact.

However, the shallow-water conditions of island-arc settings are more typical of massive sulfide deposits in the Urals [7]. With decrease in thickness of the water column, the situation changes drastically. The diagram in Fig. 1b demonstrates that if the water column is only 1 km thick, the fluid evolution path enters the sulfur sublimation region located far below the forbidden *PT* barrier and intercepts the contour line of the initial sulfur content in fluid $K_S = M_S/M_{S+H_2O} = 10\%$ approximately at a depth of 1.5 km beneath the oceanic bottom. The outlet to the bottom water zone, i.e., the forbidden *PT* barrier, takes place near the water neutralization barrier.

In the situation shown in Fig. 1b, no more than 5–10% of the bulk gaseous sulfur is released as sulfide mineralization under conditions of bottom hydrothermal fields, whereas 90–95% of gaseous sulfur is lost in the course of exhumation to the basin floor, resulting in the formation of near-vertical metasomatic massive sulfide bodies.

Under shallow-water (Fig. 1c) and subaerial conditions, sulfide deposition in the forbidden *PT* zone is ruled out completely because this zone merges with the water neutralization barrier, where release of sulfur leads to deposition of native sulfur. Sulfides are formed metasomatically at a depth of 300–1700 m, where 95% of the bulk gaseous sulfur is released (Fig. 1c). This diagram is consistent with data on volcanic sulfur deposits

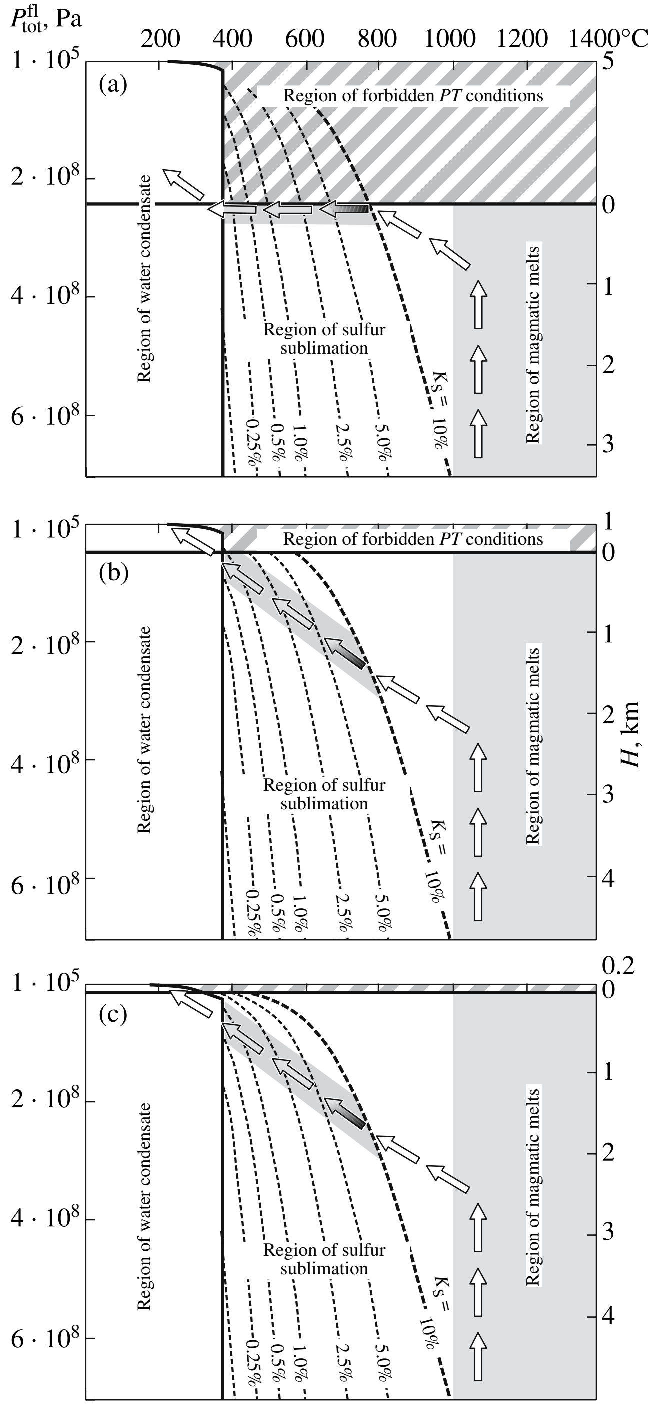

**Fig. 1.** Location of zones of sulfur sublimation and zones of massive sulfide ore formation beneath water columns of different depths: (a) deep-water version (water column 5 km), (b) medium-depth version (1 km), (3) shallow-water version (200 m). Here and in Fig. 2, $P_{tot}^{fl}$ is the total fluid pressure and $H$ is the depth. See text for explanation.

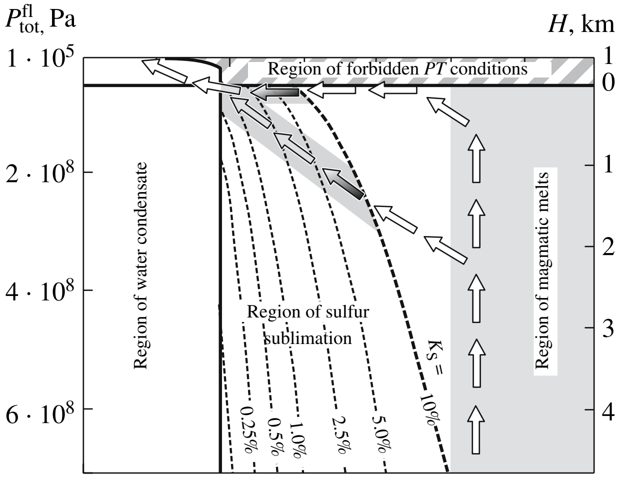

**Fig. 2.** Formation of paleohydrothermal fields with massive sulfide ore and metasomatic orebodies at a medium depth. See text for explanation.

[1], where the near-surface native sulfur grades universally into the underlying sulfide bodies.

This situation is also illustrated by structure of the Gai deposit, where a distinct unit of native sulfur overlies the upper pyrite body [2]. Although the surface portion of the Gai deposit is commonly attributed to supergene alteration, this interpretation is completely ruled out by the abundance of monoclinic modification of native sulfur in this deposit [2]. As was shown by Yushkin [1], the occurrence of monoclinic sulfur is crucial evidence for the primary, volcanic metasomatic origin of the native sulfur.

It should be noted that both near-vertical metasomatic massive sulfide deposits and bottom sulfide mounds of the black smoker type can be formed at a medium depth. Moreover, these orebodies can be formed contemporaneously (Fig. 2). Owing to the effect of the temperature trap, the sulfides are deposited very intensively in hydrothermal fields and confined to local vents. However, under conditions of the medium-deep island-arc setting, the orebodies have a greater chance to be destroyed subsequently in comparison with their deepwater oceanic analogues. As follows from Fig. 2, they are more closely associated with the near-surface fluid-generating active magmatic center and, therefore, may be destroyed during the following cycles of volcanic activity. Furthermore, as the island arc grows, they can be exhumed and eroded.

In summary, it should be noted that although the diagrams shown in Figs. 1 and 2 are rather sketchy, they display an important general tendency. The sulfide deposition of the black smoker type is most typical of deep-water oceanic basins, i.e., where they are actually observed. Under island-arc settings, the significance of hydrothermal fields as temperature ore traps progressively decreases up to the point of their complete disappearance in shallow-water and subaerial settings. The outflow of hydrothermal solutions on the seafloor is accompanied by the deposition of native sulfur grading downward into sulfide bodies. If the thickness of the water column is reduced, the role of near-vertical meta-

**Table 2.** Pressure of saturated sulfur vapor and the average number of atoms in the molecule of gaseous sulfur versus temperature [4]

| Temperature, °C | Saturated vapor pressure, Pa | Average number of atoms in a molecule of gaseous sulfur |
|---|---|---|
| 0 | $4.7423 \cdot 10^{-6}$ | 8.00 |
| 50 | $5.4671 \cdot 10^{-3}$ | 7.85 |
| 100 | $8.3675 \cdot 10^{-1}$ | 7.70 |
| 150 | $2.6842 \cdot 10$ | 7.55 |
| 200 | $2.8064 \cdot 10^{2}$ | 7.40 |
| 250 | $1.6463 \cdot 10^{3}$ | 7.28 |
| 300 | $6.4700 \cdot 10^{3}$ | 7.15 |
| 350 | $1.9430 \cdot 10^{4}$ | 7.03 |
| 400 | $4.9560 \cdot 10^{4}$ | 6.90 |
| 450 | $1.0932 \cdot 10^{5}$ | 6.68 |
| 500 | $2.1314 \cdot 10^{5}$ | 6.45 |
| 550 | $3.8275 \cdot 10^{5}$ | 6.23 |
| 600 | $6.4908 \cdot 10^{5}$ | 6.00 |
| 650 | $1.0629 \cdot 10^{6}$ | 5.65 |
| 700 | $1.6806 \cdot 10^{6}$ | 5.30 |
| 750 | $2.5841 \cdot 10^{6}$ | 4.95 |
| 800 | $3.8246 \cdot 10^{6}$ | 4.60 |
| 850 | $5.5460 \cdot 10^{6}$ | 4.20 |
| 900 | $7.8378 \cdot 10^{6}$ | 3.80 |
| 950 | $1.0880 \cdot 10^{7}$ | 3.40 |
| 1000 | $1.4626 \cdot 10^{7}$ | 3.00 |
| **1040** | $\mathbf{1.8200 \cdot 10^{7}}$ | **2.78** |

Note: The bottom row indicates the critical parameters of sulfur.

somatic sulfide lodes increases. Therefore, the genetic model of massive sulfide deposition on the seafloor (black smoker type), which became popular in the last decades, illustrates only a particular case of the massive sulfide ore formation. Implementation of this model for all cases is methodically incorrect because of the omission of near-vertical metasomatic massive sulfide bodies.

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