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MODELING OF GEOCHEMICAL PROCESSES IN THE SUBMARINE DISCHARGE ZONE OF HYDROTHERMAL SOLUTIONS

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The paper reviews the main methods and analyzes modeling results for geochemical processes in the submarine discharge zone of hydrothermal solutions of mid-ocean ridges. Initial data for modeling have been obtained during several marine expeditions, including Russian-French expedition *SERPENTINE* on the research vessel «Pourquoi Pas?» (2007). Results of field observations, laboratory experiments and theoretical developments are supported by the analysis of regression model of mixing between hydrothermal solutions and sea water. Verification of the model has been carried out and the quality of chemical analysis has been assessed; degree and character of participation of solution components in the hydrothermal process have been defined; the content of end members has been calculated basing on reverse forecasting of element concentration, depending on regression character; data for thermodynamic modeling have been prepared. Regression model of acid-base properties and chloridity of mineralizing thermal springs confirms adequacy of the model of double-diffusive convection for forming the composition of hydrothermal solutions. Differentiation of solutions according to concentrations of chloride-ion, depending on temperature and pH indicator within this model, is associated with phase conversions and mixing of fluids from two convection cells, one of which is a zone of brine circulation. In order to carry out computer thermodynamic modeling, hydro-geochemical and physicochemical models of hydrothermal discharge zone have been created. Verification of the model has been carried out basing on changes of Mn concentration in the hydrothermal plume. Prevailing forms of Mn migration in the plume are Mn^{2+} , $MnCl^+$, $MnCl_2$. Two zones have been identified in the geochemical structure of the plume: 1) high-temperature zone (350-100 °C) with prevalence of chloride complexes – ascending plume; 2) low-temperature zone (100-2 °C), where predominant form of transfer is a free divalent ion – lateral plume. Sulfate complex in insignificant quantities (1.5 %) is detected in the lateral plume, whereas hydroxide complex is stable at temperatures 325-125 °C and can only be found in the ascending plume. Results of modeling almost fully correspond to field observations. Verification of thermodynamic model proves its adequacy and allows to make a transition to the next stage of research – examination of geochemical dissipation for key ore components of hydrothermal solutions – Fe, Cu, Zn etc.

Key words: mid-ocean ridge, regression model, thermodynamic modeling, hydrothermal solution, migration forms

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Introduction. From the very discovery of hydrothermal activity in mid-ocean ridges (1977, manned deep-submergence vehicle *Alvin*, Galapagos rift), examination of metal-bearing hydrothermal solutions, forming deep-sea polymetallic sulphides (DPS) rich in Cu, Zn, Pb, Ag, Au and a whole array of other rare chemical elements by the bottom of the World Ocean (hereinafter the Ocean), has become an important part of international research in the field of marine geology. From the viewpoint of applied oceanography, in the course of prospecting for active hydrothermal fields it proved to be a promising idea to examine the structure of near-bottom waters, geochemical and hydrophysical specifics of dispersion halos – hydrothermal plumes near black smokers [1, 2, 4, 6, 7, 9].

In these days deep-sea hydrothermal springs at the ocean bottom arouse great practical interest. It is confirmed by an agreement, signed in October 2012 between Russian Federation and International Sea-Bed Authority (ISA). Russia gained exclusive rights to explore and subsequently develop DPS deposits within the limits of Russian Exploration Region (RER-DPS) in the Mid-Atlantic Ridge (MAR) (12°48'36"–20°54'36"N) [5, 7].

Starting exploitation of seabed mineral resources implies the need to upgrade research methods of hydrothermal springs, including for the purposes of enhancing exploration efficiency. One of important areas of research in this direction is modeling of geochemical processes in the system geothermal fluid – ocean water. Hydrothermal plumes – principal research objects during prospecting for areas of modern ocean mineralization – form in the seabed layers on the mixing line of these two natural solutions. Hydrothermal plumes are complex dispersion halos, characterized by anomalous temperature and amount of suspended particles (turbidity), fluctuations of density, Eh, pH and other parameters [7, 17, 18].



In the process of upgrading methods of hydrothermal spring prospecting, special attention should be paid to examination of water migration of ore components and elements – geochemical reference points in hydrothermal plumes, because they serve as key indicators of modern hydrothermal activity at the ocean bottom [5, 8].

Key features of the geological and geochemical model of suboceanic hydrothermal system. Possible existence of hydrothermal convective system follows from the presence of a heat source – magma chamber, which ensures convection of sea water, as well as from fractured magmatic rocks, acting as permeable medium. Results of field observations, experimental tests and model calculations serve as a base for our understanding of oceanic spring formation [1, 2, 4, 6].

High-temperature metamorphization of sea water, absorbed on the flanks of hydrothermal systems, leads to formation of unsulfated waters devoid of magnesium in the subsoil oceanic structures. It is commonly believed that these waters serve as a source for seabed hot springs and bear the name of terminal solutions (TS) or end members [2, 3, 6, 10, 13, 20].

As the hot fluid progresses through the mass of magmatic rocks, the latter are desalinized and dissolved elements are transferred to the surface (Li, K, Rb, Ca, Cu, Fe, Mn, Zn, Pb, Co, Ni, As etc.). Thus, mineralizing fluid in the discharge zone of a hydrothermal convective system is a product of interaction between oceanic water and rocks composing the oceanic crust.

Physical (experimental) modeling of hydrothermal mineralization in the Ocean and field data. The concept that thermal springs of mid-ocean ridges (MOR) form as a result of high-temperature interaction between sea water and the rocks inside hydrothermal systems is primarily based on abundant data from laboratory modeling, reviewed in 1983 by M.Mottl [17]. Experiments on warming sea water and its exposure to basalts under conditions similar to natural ones showed that the decrease in pH of the solution, associated with Mg absorption by the rocks, leads to desalination of certain elements (including metal ones) and formation of the fluid with the composition really close to natural thermal springs.

As a result of laboratory tests, it was discovered that, when sea water and basalt are warmed to the temperature 300 °C, the solution becomes acidic (pH = 2÷4) and reduced. This causes a dramatic increase in the concentration of such metals, as Fe and Mn. In its turn, ocean water deposition of Mg, incorporated in secondary silicates or mineral associations, including MgSO₄ and Mg(OH)₂, facilitates the formation of H⁺. Ocean water loses magnesium and sulfate ion, and becomes rich in metals and Si. pH value of the solution defines intensity of metal dissolving and formation of mineralizing fluid.

On the whole, field observations confirm results of physical modeling. At the same time, some variations of thermal spring composition have been detected, not only for different regions but also within the same hydrothermal field [2, 6, 7, 20].

Synthesis of physical modeling results and field observations leads to the conclusion that the most acceptable way to explain differences in mineralization of the solutions is offered by the model of double-diffusive convection [2, 12]. It is assumed that near the magma chamber beneath the main convective cell there is a circulation zone of the brine, formed due to differentiation of sea water on the magma contact in the moments of sudden crack opening. Currently, phase conversion and mixing of fluids from two convective cells offer the best explanation of the diversity of observed processes.

Regression model of mixing between mineralizing thermal springs and sea water. Results of field observations, laboratory experiments and theoretical developments are supported by the analysis of regression model of mixing between hydrothermal solutions and sea water in the discharge zone. Concentrations of components in the end members correspond to zero Mg concentration and are defined using graphs and regression equations for individual elements, based on Mg concentration ([element]/[Mg]). For instance, initial point of the trend line [SO₄]/[Mg] indicates zero concentration of both sulfate ion and magnesium in the terminal hydrothermal solutions

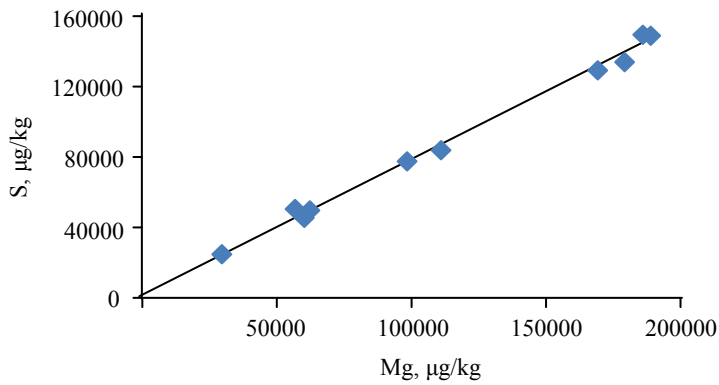


Fig. 1. Dependence of [S] concentration on [Mg] for hydrothermal solutions in several areas of MAR according to *SERPENTINE* expedition data, 2007 [14]

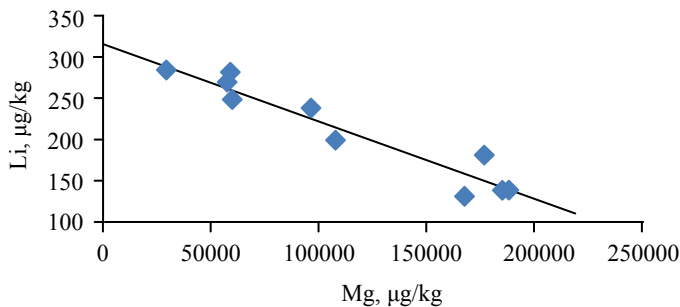


Fig. 2. Dependence of [Li] concentration on [Mg] for hydrothermal solutions in MAR (14°45' N) according to *DiversExpedition* data, 2001 [19]

absence of magnesium in the end member allows to use results of regressions [element]/[Mg] in order to identify groups of elements according to their participation in hydrothermal processes. A positive trend relative to [Mg] indicates that the element comes from sea water, as its concentration decreases with the growth of hydrothermal component and decline in the share of sea water, the same way it does for magnesium. The first group includes Mg, SO₄, U, Mo etc. A negative trend indicates that the element accumulates in the solution as a result of hydrothermal transformations. The second group includes H₂S, Ca, SiO₂, Li, Rb, Mn, Fe, Zn and other elements [2, 6] (Fig.2). Incline of the trend line points to the negative correlation between Li and Mg and reflects the degree of mixing between hydrothermal solution and sea water. Li concentration in the end member amounted to 317 µm/dm³.

3. Calculation of end member concentrations – reverse forecasting of element concentration using trend line (regression equation). Regression models of mixing serve as a calculation base for element concentrations in the terminal hydrothermal solutions that passed through the entire transformation cycle under maximal temperature and pressure inside the hydrothermal system. Adjusted concentrations allow to compare compositions of all end members of submarine hot springs, eliminating the effect of fluid dilution with sea water along the migration routes and in discharge zones. Results of analysis allow to specify fluid composition for observed hydrothermal fields (Fig.2). Calculated end member concentrations can be also used for thermodynamic modeling.

Regression model of acid-base properties and chloridity of mineralizing thermal springs in the Ocean. Assumed end member composition, obtained from the regression model, is widely used to compare compositions of hydrothermal solutions from different areas, when excluding the influence of fluid dilution with sea water. However, one should be very careful when using such calculation data for global geochemical developments. Content fluctuations of hydrothermal solu-

(Fig.1). The start of the trend line in the point with zero S concentration hints at the prevalence of sulfate ion in the system. The shape of the graph corresponds to theoretical notions and confirms the quality of laboratory analysis. It corresponds to the results of physical modeling and allows to contemplate verification of the regression model using independent experimental data. Each observation point on the graph corresponds to a certain magnesium concentration, which reflects the degree of mixing between hydrothermal solution and sea water.

Analysis of regression model allows to address the following tasks:

1. The graph [S]/[Mg] is used to verify the model against results of physical modeling and assess the quality of chemical analysis (Fig.1). Deviation of sulfur concentration from zero allows to make assertions regarding possible presence of other forms of sulfur migration in the system, e.g. H₂S.

2. Determination of the source from which element gets into solution. Ab-

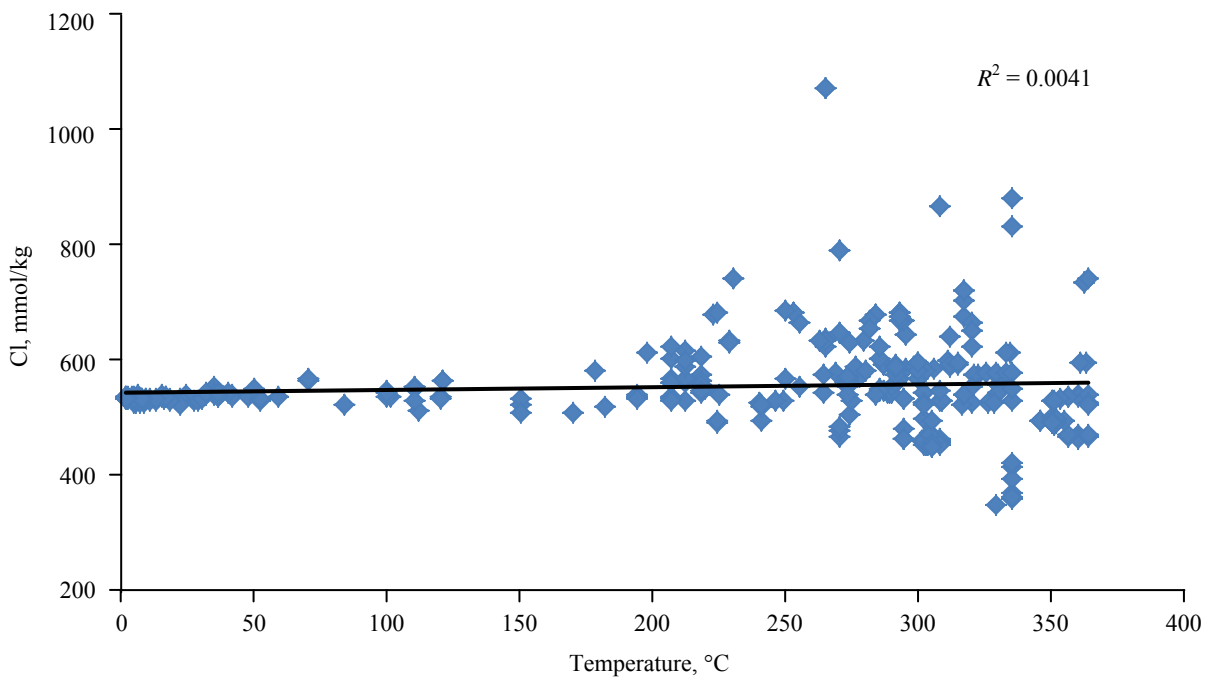


Fig.3. Dependence of $[Cl^-]$ on temperature according to data from hydrothermal solutions sampling

tions can be associated not only with sea water dilution, but also, even to a greater extent, with very unbalanced character of the hydrothermal system. Direct observations have proven the presence of phase conversions in the discharge zones and formation of craters caused by «hydrothermal explosions». Content fluctuations of thermal springs have been instrumentally confirmed for source outfalls [1, 7].

Regression models, constructed for sufficiently large amount of data, allow to offset content fluctuations, resulting from instability of physical and chemical conditions, as well as individual errors of sampling and chemical analysis, and to identify main trends of fluid content formation and interconnections between key indicators. Subsequent analysis was carried out using all currently available initial analytical information without adjustments for end members from author's and global databases [2, 6, 7, 20], including data collected by M.Mottl and available on the website <http://earthchem.org/featured/mott> (Mottl, M.J. (2012), VentDB: Mid-Ocean Ridge Hydrothermal Vent Chemistry Data Collection in the EarthChem Library).

Results of modeling demonstrate a strong tendency for increasing concentration of Cl-ion in oceanic hydrothermal solutions with rising temperature (Fig.3). In different intervals of temperature this connection manifests itself differently. Below 60 °C chloridity of the solution meets the standard for sea water. For higher temperatures (up to 180 °C) both elevated and lowered concentrations of Cl^- can be observed, with the latter ones prevailing. The greatest deviations from $[Cl^-]$ values are observed in the near-bottom oceanic waters for temperatures higher than 180 °C.

Analysis of regression model, linking concentrations of chloride-ion and acidity of hydrothermal oceanic solutions, shows that these parameters are characterized by a negative relationship (Fig.4). The highest values of $[Cl^-]$, significantly exceeding standards for sea water, are observed in acidic solutions with $pH = 2.3 \div 6.0$. The same interval is characterized by visible, but not so significant deviations of the opposite sign. Regression modeling data confirms adequacy of the model of double-diffusive convection, discussed earlier. Differentiation of solutions according to concentrations of chloride-ion depending on temperature and pH indicator within this model is associated with phase conversions and mixing of fluids from two convection cells, one of which is a zone of brine circulation.

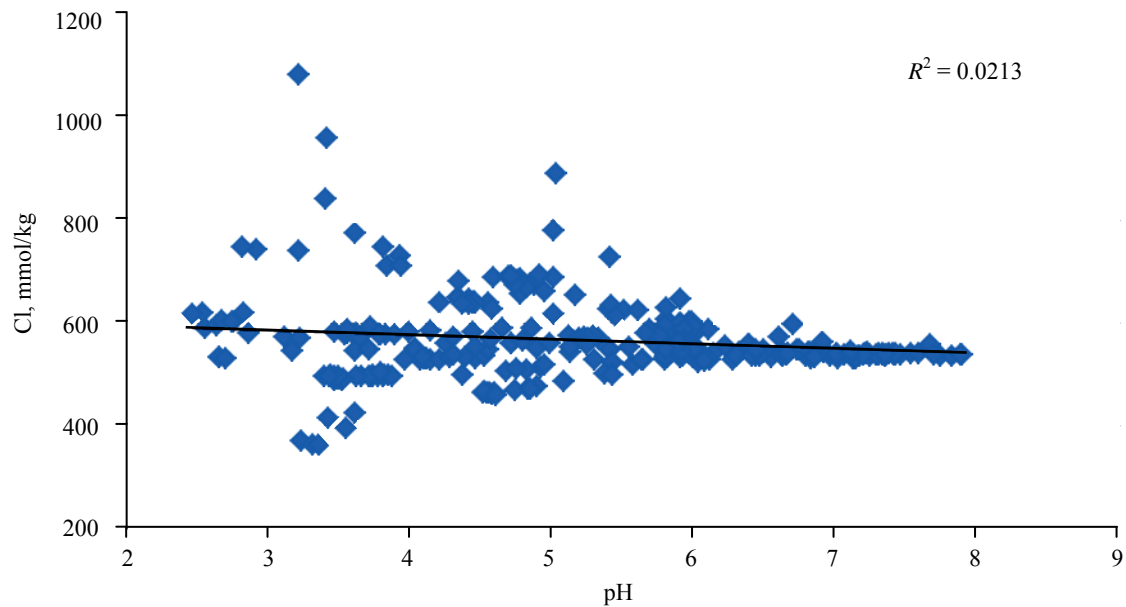


Fig.4. Dependence of $[Cl^-]$ on pH in hydrothermal oceanic solutions

On the other hand, discharge of desalinated waters has also been observed in real time and confirmed by analytical data [7].

It should be added that pH value of the solution defines intensity of metal desalination from surrounding rocks and formation of mineralizing fluid. The second parameter, after water acidity, that plays an important role in metal transfer is the content of chloride-ion, usually related to general mineralization [2, 6].

Results of correlation analysis also point to high negative coefficients of pair correlation between $[Cl^-]$ and pH [5, 7]. Results of carried out thermodynamic modeling confirm that metal transfer primarily occurs in the form of chloride complexes at high temperatures of the solution.

Computer thermodynamic modeling of mixing processes in the discharge zone of hydrothermal solutions. Theoretical justification and procedure of thermodynamic analysis of various geochemical processes, including oceanic geothermal ore genesis, have a longstanding history [3, 10-13, 16]. Hydro-geochemical model of hydrothermal discharge zone by S.M.Sudarikov and M.V.Zmievisky has been under development since 2010. Computer modeling has been carried out by M.V.Zmievisky in the Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, in the laboratory of Geochemical and Hydrothermal Modeling, using HCh software package [10, 11]. Initial data for modeling have been obtained by S.M.Sudarikov and J.-L.Charlou in the course of several expeditions, including collaborative work in the Russian-French expedition *SERPENTINE* on the research vessel «Pourquoi Pas?» [14, 15].

In the process of preparation for thermodynamic modeling, a hydro-geochemical model was constructed, nominally composed of two stages. The first stage corresponds to subsurface mixing of hydrothermal solutions and sea water, the second one – to post-discharge processes occurring in hydrothermal dispersion halos (plumes). Current paper focuses on the modeling results of the second stage conversions.

When constructing a physicochemical model using literature and analytical data, such parameters were assigned as temperature and pressure. Pressure has been assigned as a constant value – 300 atm (30 MPa), which corresponds to pressure at the depth of source location – approximately 3 km. Temperature has been assigned as a variable. Physicochemical model includes liquid, solid and gas phases. The number of dissolved forms of migration for different elements, existing in the system, is 152.

Initial temperature in the observed area of hydrothermal system was 352 °C (temperature of the solution, measured at the source outfall), final temperature 2 °C (temperature of near-bottom waters). Overall the program contains 50 mixing stages with temperature differences of 7 °C. Basing on empirical data and literature, ratios of mixing solutions in the model vary according to a specially developed formula, which takes into account amount of hydrothermal solution, amount of sea water, numbers of mixing stages [5, 8].

It is most reasonable to verify the model against changes in manganese concentrations. Behavior of hydrothermal manganese in the plumes is fairly well understood [2, 7, 18, 19]. Mn dispersion halos are one of the main prospecting indicators of modern hydrothermal mineralization. Dissolved manganese forms the longest dispersion halos in the discharge zones due to its geochemical (migration) characteristics.

Divalent manganese is quite resistant to the oxidizing environment of oceanic near-bottom waters. Besides, manganese does not form sulfide minerals in the zones of oceanic discharge of thermal springs. Hence, mineralization does not affect concentrations of different migration forms of this element in hydrothermal solutions and plumes, which makes modeling results for the dynamics of Mn dissolved forms more reliable.

Analysis of obtained results allows to state that prevailing forms of manganese migration in the plume are Mn^{2+} , $MnCl^+$, $MnCl_2$ (Fig.5). Moreover, geochemical structure of the plume is composed of two zones: 1) high-temperature zone (350-100 °C) with prevailing chloride complexes; 2) low-temperature zone (100-2 °C), where predominant form of transfer is a free divalent ion.

The first zone can be nominally associated with ascending plume with elevated turbulence, the second one – with lateral plume, within the bounds of which manganese in the form of a free divalent ion can be transferred at the distance of dozens of kilometers [18, 19]. Strong presence of sulfate and hydroxide complexes can also be noted (Fig.6). Sulfate complex in insignificant quantities (1.5 %) is detected in the lateral plume, whereas hydroxide complex is stable at temperatures 325-125 °C and can only be found in the ascending plume. These compounds are considered «secondary» forms of migration.

Impact of remaining forms of Mn transfer (e.g., carbonate) appears very small (< 0.5 %), and they are considered «insignificant» (Fig.7).

Presented results demonstrate practically full correspondence between modeling data and field observations. In particular, a great share of secondary and insignificant forms of Mn migration leave the solution with temperature decrease and take part in the formation of hydrothermal manganese crusts, widely occurring in the discharge zones of hydrothermal solutions [2, 4, 6, 17, 20].

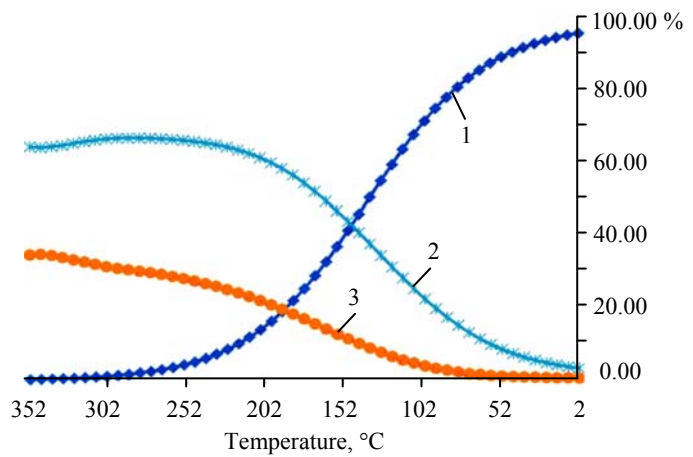


Fig.5. Ratios of the main forms of Mn water migration in the hydrothermal plume varying according to temperature and degree of fluid dilution with sea water
 1 – $MnCl^{2+}$, 2 – $MnCl^+$, 3 – $MnCl_2^0$

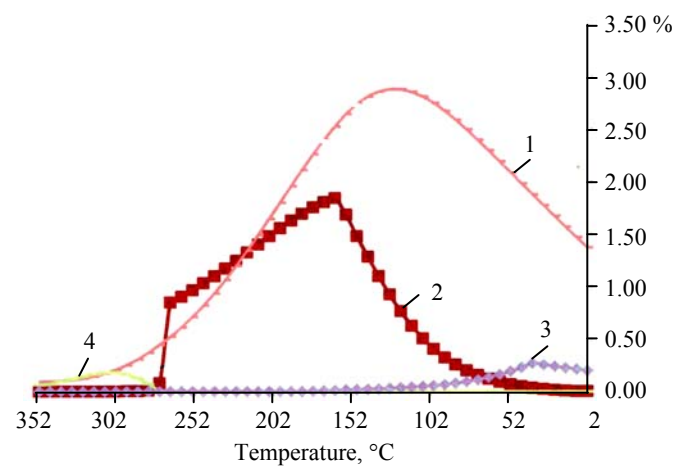


Fig.6. Ratios of secondary forms of Mn water migration in the hydrothermal plume varying according to temperature and degree of fluid dilution with sea water
 1 – $MnSO_4^0$, 2 – $MnOH^+$, 3 – $MnCO_3^0$, 4 – $MnHSO_4^+$

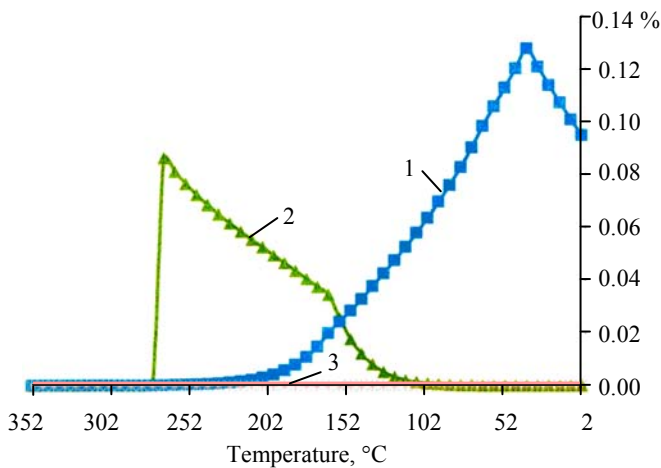


Fig.7. Ratios of insignificant forms of Mn water migration in the hydrothermal plume varying according to temperature and degree of fluid dilution with sea water

1 – MnHCO_3^+ , 2 – MnO^0 , 3 – total content of

MnHCO_3^+ , MnO^0 , MnO_2^{2-} , MnHS^+ , Mn^{3+} , MnO_4^- , MnO_4^{2-}

Verification of thermodynamic model proves its adequacy and allows to make a transition to the next stage of research – examination of geochemical dissipation for key ore components of hydrothermal solutions – Fe, Cu, Zn etc.

Identification of leading migration forms of ore-forming elements is needed to upgrade existing construction of ion selective electrodes, used to examine microcomponent content of near-bottom waters *in situ*. In the process of hydro-geochemical prospecting for hydrothermal sources at the oceanic bottom, ratio of different migration forms in the plume will allow to predetermine location of the discharge zone. In the long view, carried out research can improve efficiency of prospecting for mass concentrations of sulfide ores at the bottom of the Ocean.

Conclusions. The paper reviews the main methods and analyzes modeling results for geochemical processes in the submarine discharge zone of hydrothermal oceanic solutions. Initial data for modeling have been obtained by S.M.Sudarikov and J.-L.Charlou in the course of several expeditions, including collaborative work in the Russian-French expedition *SERPENTINE* on the research vessel «Pourquoi Pas?» (2007).

Results of physical (experimental) modeling of hydrothermal mineralization in the Ocean have been analyzed, along with field observations. Results of field observations, laboratory experiments and theoretical developments are supported by the analysis of regression model of mixing between hydrothermal solutions and sea water in the discharge zone.

Carried out analysis allowed: to verify the model and assess the quality of chemical analysis; to determine the source from which element gets into hydrothermal solution (degree and character of participation of solution components in the hydrothermal process); to calculate end member concentrations – reverse forecasting of element concentration using trend line (regression equation); basing on calculated concentrations of terminal hydrothermal solutions to prepare data for thermodynamic modeling.

Regression model of acid-base properties and chloridity of mineralizing thermal springs confirms adequacy of the model of double-diffusive convection for forming the composition of hydrothermal solutions. Differentiation of solutions according to concentrations of chloride-ion depending on temperature and pH indicator within this model is associated with phase conversions and mixing of fluids from two convection cells, one of which is a zone of brine circulation.

In order to carry out computer thermodynamic modeling of mixing processes between hydrothermal solutions and sea water, hydro-geochemical and physicochemical models of hydrothermal discharge zone have been created. The model has been verified against changes in manganese concentrations in the system: ascending plume – plume with neutral buoyancy. Analysis of obtained results allows to state that prevailing forms of manganese migration in the plume are Mn^{2+} , MnCl^+ , MnCl_2 . Two zones have been identified in the geochemical structure of the plume: 1) high-temperature zone (350-100 °C) with prevalence of chloride complexes; 2) low-temperature zone (100-2 °C), where predominant form of transfer is a free divalent ion.

The first zone can be nominally associated with ascending plume with elevated turbulence, the second one – with lateral plume, within the bounds of which manganese in the form of a free divalent ion can be transferred at the distance of dozens of kilometers. Sulfate complex in insignificant



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Presented results demonstrate practically full correspondence between modeling data and field observations. Verification of thermodynamic model proves its adequacy and allows to make a transition to the next stage of research – examination of geochemical dissipation for key ore components of hydrothermal solutions – Fe, Cu, Zn etc.

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