AT THE MECHANISM OF ALLOCATION OF MINERALS. 2. SULFIDES OF ORE DEPOSITS

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1. Studying sulfides of ore deposits helps to specify conditions of their formation. On isotope matter of S sulfur frequently try to determine sources of sulfur. It is more important to emphasize, that formation of isotope structure S is first of all physical and chemical process. According to experiments (EB) sulfides are divided on groups:

a). Sulfides, in particular, biogenic, isotopic equilibrium to the oxide form of sulfur (SO_4^{-2} and so forth). Negative values are typical for them $\delta^{34}S$ (up to - (30-40) %o), significant ranges of change $\delta^{34}S$ and simplification S with falling T.

b). S, for example, in meteorites, it is isotopicaly equilibrium S connections of kind H_2S, S^{-2} and so forth. For them small limits of fluctuation $\delta^{34}S$ about 0‰ (meteoric standard) and enrichment of sulfur by an isotope ^{34}S with falling T are characteristic. On EB at joint allocation even at very low concerning sulfides concentration of sulfates S of the last takes away overwhelming part heavy S.

Table

Deposit	Region	ПТМ	TPT	Minerals		Ion	$T_{изот}$ °C	
				X	Y		X	Y
Cerro-de-Pasco	Peru			Py	Sph	H_2S	150	160
West Shasta	USA	ПМ	СФ	Py	Q	H_2S	350	300
Broken Hill	Australia	КП	СФ	Gn	Sph	H_2S	200	340
Rex Hill	Tasmania	Sn	ЖЛ	Gn	Sph	H_2S	250-300	300-350
Сардана	Russia	КП	СФ	Gn	Sph	S^{-2}	150-200	300-350
Rosebery	Tasmania	WS	ЖЛ	Gn	Sph	S^{-2}*	170	300
Darwin	USA	КП	ЖЛ	Gn	Sph	S-2*	300	300
Cheonbo	Korea	Au, Ag	ЖЛ	Gn	Sph	S^{-2}	150	360
Смирновское	Russia	ПМ	ЖЛ	Gn	Sph	S^{-2}	150	360
Ruakaka	H. Zealand	ПМ	ЖЛ	Gn	Sph	S^{-2}	250	300
Darwin	USA	КП	СФ	Py	Sph	S^{-2}*	190	300
Левиха	Russia	КП		Py	Sph	S^{-2}	350	240
Филизчай	Russia	КП	СФ	Py	Sph	S^{-2}	200	300
Rosebery	Tasmania	WS	ЖЛ	Py	Sph	S^{-2}*	350	300
Gaspe	Quebec	Cu		Po	Cp	S^{-2}	350	150
Горевское	Russia	ПМ	СФ	Po	Gn	S^{-2}	350	250
Филизчай	Caucasus	КП	СФ	Po	Py	S^{-2}	350	300
Горевское	Russia	ПМ	СФ	Gn	Sph	SO_4^{-2} (?)	150	260
Rex Hill	Tasmania	Sn	ЖЛ	Gn	Sph	SO_4^{-2} (?)	150	340
Lake	Ural	КП	СФ	Gn	Sph	SO_4^{-2} (?)	225	270
Pine Point	Canada	ПМ	СФ	Gn	Sph	SO_4^{-2} (?)	150	270
Broken Hill	Australia	КП	СФ	Gn	Sph	SO_4^{-2} (?)	200	340
Cleveland	Tasmania	Mo	ЖЛ	Po	Sph	SO_4^{-2} (?)	350	220
Rex Hill	Tasmania	Sn	ЖЛ	Gn	Sph	HSO_4^{-1} (?)	350	345
Anvil	Canada	ПМ	СФ	Py	Sph	HSO_4^{-1}*(?)	345	345

The note: ПТМ-industrial type of a deposit. TPT - type of ore body. In columns "Minerals" X and Y are axes of coordinates on which values $\delta^{34}S$ specified in the text of the table of minerals are postponed, and in the column "Temperature" the established T values of formation of these minerals on the isotope data. (*) are values of T are coordinated on several mineral pairs.

2. On the literary data distribution of isotopes S between sulfides from 50 deposits of the former USSR and Foreign countries is investigated on the basis of the analysis of 80 minerals samples: Gn-Sph (43 %), Py-Sph (18), Py-Cp (15), Po-Py (8), Po-Cp (8), Py-Mo (5) in pyritaceous-polymetallic (КП-36 %), polymetallic (ПМ-24), copper (10), gold-silveric (Au-Ag-6), tungsten-tinic (WS-6), tin (Sn-4), uraniumic (2), molybdenumic (Mo-1), rock crystal objects with stratiform body (CF - 51 %, as deposits - 3), interspersed (1 %), vein (ЖЛ-25 %) ore bodies (Gn- galena, Sph- sphalerite, Cp- chalcopyrite, Po- pyrrotite, Py-pyrite, Mo- molibdenite, Q- quartz, Cc-calcite). It is revealed: 1). In ores I type (vein and interspersed) with falling T and distance from an ore body there is a pauperization, 2). In ores of II type (massive) S enrichment by isotope ^{34}S. EB allows to assume, that in ores-II sulfides are equilibrium isotopicaly to substances restored; and in ores-I - oxidized forms S.

3. The technique of an estimation of substance composition (C), isotopic equilibrium to the given mineral (M) is developed on the basis of the theory of new kinds of isotope geothermometers developed by us. The diagram of isothermal distribution of isotopes S in two coexisted M, described by the equation of a direct line of a kind $\delta^{34}S\ (M_1) = s\ [\delta^{34}S\ (M_2)] + S$ is under construction. The angular factor (s) depends from T formations of minerals and a kind substance, equilibrium isotopicaly M_1 and. M_2. On size (s) it is calculated T_{isot} formations of minerals. We believe that the duet «M-C» is a product decomposition of some initial parent substance. Then comparison T_{isot} with established by a method independent reference $T_{эт}$, allows defining composition of substance C (at presence of the known fractionation equations of sulfur isotopes between two minerals).

4. Some results of the analysis are reflected in the table. Sulfides will be equilibrium isotopicaly to ions S^{-2} (50 %), SO_4^{-2} (14), HSO_4^{-1} (12) and H_2S (5) which on a oxidation degree of S are subdivided into groups: restored (H_2S and S^{-2}) and oxidized (HSO_4^{-1} and SO_4^{-2}) S forms; have no 19 address of % выборок. Earlier for the description of distribution of isotopes S the hypothesis of mixture with participation meteoric or biogenic S was used. Finally, because of methodical mistakes this hypothesis has led a problem of a nature of sulfides up a blind alley. At formation of sulfides meteorites appeared not and besides. For paragenesis of M- S^{-2} the following mechanisms of an establishment of these equilibriums are possible on the basis of the following hypothetical reactions:

$$... \rightarrow ... + MeS\ (or\ MeS_2) + H_2S + ... \quad (1)$$

$$... \rightarrow ... + MeS\ (or\ MeS_2) + S^{-2} + ... \quad (2)$$

$$... \rightarrow ... + MeS\ (or\ MeS_2) + SO_4^{-2}\ (or\ HSO_4^{-1}) + ... \quad (3)$$

In connection with reaction (1) in a seal reactions such as $Me\ (HS)_3^{-1} \rightarrow MeS + HS^{-1} + H_2S$ [K.Grejndzher, 1976] or $Me_{+x}(HS)_n x^{-n} \rightarrow MeS + HS^{-1} + H_2S$ [I.L. Chodakovskij, 1966] are usually discussed. Complexes of metals look like $[Zn\ (HS)_3]^{-1}$; $[Pb(HS)_3]^{-1}$; $Zn(HS)_2$ and so forth. But ion HS^{-1} is not established on the isotope data. By Bigeleisen's rule in a chain ($MeS \leftrightarrow HS^{-1} \leftrightarrow H_2S$) an exchange of isotopes ion HS^{-1} should not be fixed, and will be observed isotope equilibrium in association [MeS (or MeS_2) + H_2S]. In conditions of high potential S it corresponds to presence in a hydrothermal solution of polysulfides of a kind $[MeS_2]^{-2}$, $[MeS_4]^{-2}$ etc. [V.V.Scherbina, 1962], soluble in hydrocarbonaten and chloriden solutions [N.I.Govorov etc., 1966].

For low-sulfiden objects for a substantiation of reaction (2) I.G.Ganeeva's hypothesis (1977) is acceptable: in vein deposits minerals are allocated from ansulfiden solutions according to hypothetical reaction of $Pb\ (OH)_4 + 2H_2S \rightarrow [PbS + S^{-2}] + 4H_2O$.

On Kizil-Say U-deposit (S. Kazakhstan) is investigated Py of post-ore Q- and Q-Cc veins. For Py low sizes $\delta^{34}S$ (up to -30‰), reduction $\delta^{34}S$ with falling T (homogenization ГЖВ and Cc isotope) are characteristic. It speaks about influence of oxidized forms S according to reaction (3) on formation Py and formation Py as a result of decomposition of tiosulfate or sulphites on hypothetical reactions (a) $Fe\ (S_2O_3) \rightarrow FeS_2 + 2SO_3$ or (b) $Fe\ (S_2O_3) + H_2O \rightarrow FeS_2 + SO_4^{-2} + H_2$. The opportunity of existence thiosulfates and sulphites in hydrothermal conditions is investigated R.M. Garrels et al (1958), N.G.Tjurinym (1963), V.V.Scherbina (1964), T.M.Sulzhievoj etc. (1982), S.V.Kushnir (1989) and at low concentration of components follows from the analysis of their thermodynamic properties. These reactions are possible at formation Q-Py-of veins. However, their use for analysis Q-Cc- veins is problematic, as in result the sour environment destroying Cc with formation of gypsum or anhydrite can be formed. On an ore field these sulfates are not observed.

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24)'2006
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/izotop-4e.pdf

Published on July, 1, 2006