ISSN 1028-334X, Doklady Earth Sciences, 2006, Vol. 407, No. 2, pp. 339–343. © Pleiades Publishing, Inc., 2006.
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GEOCHEMISTRY

New Mineralogical and Geochemical Data on Lead–Zinc Deposits of the Sadon Ore Field, North Ossetia

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Presented by Academician N. P. Laverov June 27, 2005

Received July 5, 2005

DOI: 10.1134/S1028334X06020425

There are numerous vein Pb–Zn deposits in the northern Caucasus, such as Sadon, Zgid, Arkhon, Kholsta, Verkhnii and Nizhnii Zgid, Dzhimidon, and others. Their geology, structure, ore composition, prospects, and ore potential have been studied for a long time [1–8]. Interest in these deposits was rekindled in the 1970s owing to the discovery and subsequent exploration of the Dzhimidon deposit, prospects of which have been indicated in [9].

The deposits are situated approximately at the same ore-bearing level (1.5–2.5 km), but they occupy different vertical positions (Fig. 1). The host rocks are granites and andesite–dacite porphyrite cover rocks (Verkhnii Zgid, Sadon, Arkhon, and other deposits) and, more rarely, terrigenous rocks (Levoberezhnoe deposit). Buried mineralization of the Dzhimidon deposit is developed in different-aged rock associations, which can be divided into two structural stages. The lower stage consists of metamorphic rocks (hornblende amphibolites and crystalline schists) from the Buron Formation of the pre-Jurassic basement. The metamorphic rocks are overlain by the Lower Jurassic terrigenous rocks of the upper stage. The highest-grade ore bodies are localized among metamorphic rocks [4, 5].

The deposits contain practically the same ore and gangue minerals, proportions of which vary in the individual deposits and certain ore bodies [10]. Pyrite, sphalerite, and galena are the main ore minerals, with subordinate pyrrhotite, magnetite, chalcopyrite, arsenopyrite, arsenopyrite and accessory fahlore, jamesonite, boulangerite, argentite, acanthite, native silver, and silver sulfosalts. Freibergite and dyscrasite were previously described in the ores of the Sadon deposit [11]. Gangue minerals include quartz, calcite, manganocalcite, siderite, sericite, chlorite, and rarer barite, ankerite, K-feldspar, and knebelite.

New mineralogical data have been recently obtained on the Nizhnii Zgid and Dzhimidon deposits. A wide diversity of bismuth minerals was first found and identified in the ores. These are native bismuth, bismuthinite, cosalite, galenobismutite, variable Ag–Pb–Bi–S compounds, Bi-bearing galena, and others (table).

A generalized scheme of the mineral assemblage sequence reflects the same regularities in the ore formation. At all deposits, ore deposition was preceded by and associated with silicification, chloritization, and sericitization of the host rocks. The quartz–arsenopyrite–pyrite assemblage was formed at the first stage. The homogenization temperatures (T_{hom}) of fluid inclusions in quartz I and sphalerite I is 330–240°C (Fig. 2) at the Dzhimidon deposit and 360–270°C at the Sadon deposit. The subsequent (quartz–siderite–magnetite–pyrrhotite–sphalerite) stage is differently manifested at the deposits. In particular, this stage was marked by the formation of the quartz–chalcopyrite–pyrrhotite–sphalerite assemblage at the Sadon, Arkhon, and Dzhimidon deposits and siderite–magnetite assemblage at the Verkhnii Zgid deposits. Carbonate–pyrite–marcasite assemblage, occasionally with magnetite, occur at many deposits. This assemblage is related to disulfidation of early pyrrhotite. The changes in mineral assemblages of the second stage are mainly caused by variations in the sulfur and oxygen regime. T_{hom} of fluid inclusions is 250–200°C in quartz II of the Verkhnii Zgid deposit and 320–200°C in quartz II and sphalerite II of the Dzhimidon deposit (Fig. 2).

The third (quartz–carbonate–sphalerite–galena) stage was responsible for the formation of quartz–arse-

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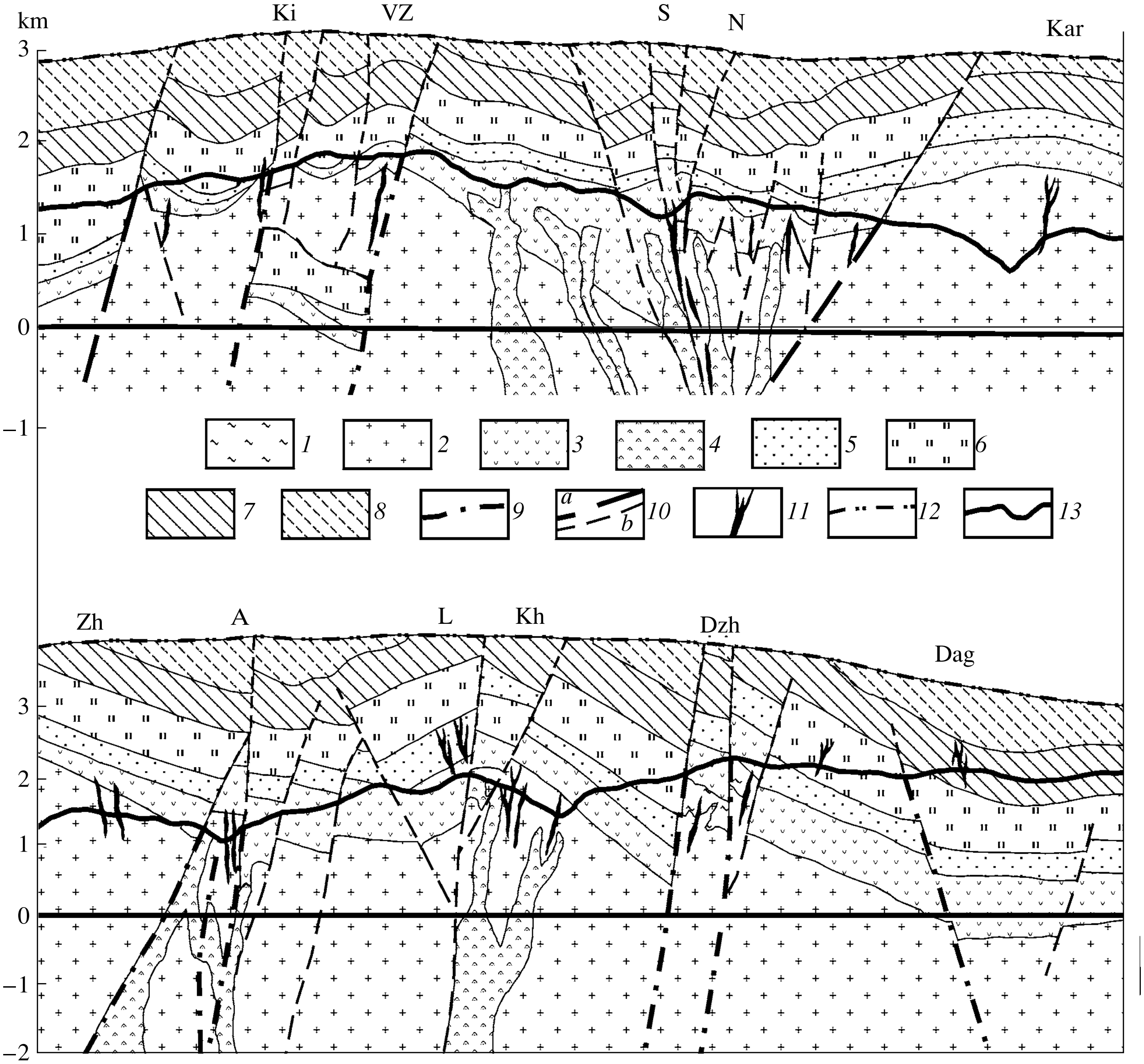

Fig. 1. Longitudinal profile across the Sadon ore belt with reconstructed ancient (premineralization) surface and position of the deposits during ore formation (after Nekrasov, 1980). (*1*) Crystalline schists; (*2*) granites; (*3*) andesite–dacite porphyrite cover; (*4*) subvolcanic bodies of the same rocks; (*5*) sandstones; (*6*) siltstones and mudstones, J_1t_{1+2}; (*7*) siltstones with sandstone interbeds, J_1t_3–al_1; (*8*) mudstones and shales, J_2; (*9*) ore-controlling faults; (*10*): (*a*) large- and (*b*) small-amplitude preore faults; (*11*) ore veins and zones; (*12*) ancient surface existing during ore formation; (*13*) present-day surface. Deposits and large occurrences: (Ki) Kion, (VZ) Verkhnii Zgid, (S) Sadon, (N) Nogkaut, (Kar) Karin, (Zh) Zheltoe, (A) Arkhon, (L) Levoberezhnoe, (Kh) Kholsta, (Dzh) Dzhimidon, (Dag) Dagomys.

nopyrite–pyrite, quartz–calcite–chalcopyrite–sphalerite–galena, and stibnite–sulfosalt assemblages. The latter assemblage varies at different deposits, e.g., silver minerals and Pb–Sb sulfosalts in the ores of the Sadon deposit and Bi-bearing sulfides and Bi–Ag–Pb–S sulfosalts at the Nizhnii Zgid and Dzhimidon deposits. At this stage, the mineral formation temperature was higher (Arkhon, Kholsta, and Dzhimidon deposits). T_{hom} of the fluid inclusions in quartz III and sphalerite III of the Dzhimidon deposit varies widely within 340–120°C. Bismuth minerals of the quartz-bearing assemblage formed at 420°C. T_{hom} of fluid inclusions in quartz III (Sadon and Verkhnii Zgid deposits) is 240–200°C.

Temperature estimates of the third stage determined in the sphalerite–galena pair based on the δ^{34}S geothermometer yielded 320–210°C for the Arkhon deposit, 300°C for the Kholsta deposit, and 230°C for the Verkhnii Zgid deposit. These values are similar to T_{hom} values of fluid inclusions in quartz of this stage, with the exception of quartz III of the Dzhimidon deposit. Relatively good agreement was obtained for temperatures (390–310°C) determined from the coefficient of

Chemical composition of bismuth minerals, wt %

Ord. no.	Mineral	Pb	Bi	S	Fe	Ag	Sb	Se	Zn	Cu	Total
					Dzhimidon						
1	Galena	84.43	1.35	13.37	–	0.46	0.00	0.47	–	0.02	100.10
2	Bi-galena	70.24	14.09	13.91	0.06	0.30	0.00	0.28	0.00	0.07	98.95
3	Bi-galena	68.42	15.10	14.80	–	0.48	0.04	0.57	–	0.11	99.52
4	Hoongarrite	59.06	26.89	11.05	0.34	2.00	0.09	0.26	0.05	0.00	99.74
5	Lillianite	50.86	34.84	13.50	0.09	0.43	0.00	0.23	0.04	0.00	99.99
6	Cosalite	39.33	42.22	16.60	–	0.62	0.00	0.23	–	0.81	99.81
7	Weibullite	33.78	48.04	16.70	–	1.30	0.00	0.10	–	0.00	100.16
8	$Ag_3Pb_8Bi_{11}S_{26}$	32.31	47.76	15.97	–	5.60	0.00	0.10	–	0.40	98.24
9	Galenobismutite	22.18	61.14	15.75	0.03	0.18	0.10	0.11	0.04	0.04	99.57
10	Bismuthinite	0.00	81.06	18.51	0.11	0.00	0.00	0.11	0.00	0.00	99.81
11	Native Bi	0.00	99.56	0.07	0.03	0.00	0.00	0.00	0.02	0.03	99.71
					Nizhnii Zgid						
12	Bismuthinite	3.51	79.89	18.06	–	0.00	–	–	–	–	101.46
13	$Ag_3Pb_6Bi_{10}S_{24}$	25.78	47.66	17.87	–	8.38	–	–	–	–	99.69
14	$Ag_4Pb_7Bi_9S_{24}$	30.82	43.72	17.36	–	9.76	–	–	–	–	101.66

Note: (–) Not analyzed. Minerals were analyzed on a SX-50 microprobe at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (A.I. Tsepin and T.I. Golovanova, analysts).

Cd distribution in the coexisting sphalerite–galena pair (Arkhon deposit).

The last (quartz–carbonate) stage is developed at all deposits. The mineral aggregates of this stage form veinlets cutting both ore bodies and host rocks. T_{hom} of fluid inclusions in carbonate of this stage (Dzhimidon deposit) is 240–220°C (Fig. 2) and less than 200°C at the other deposits.

Sulfur isotopic composition of sulfides together with mineralogical data confirmed the proposed sequence of mineral assemblage precipitation during three ore stages, which is consistent with previous data on sulfur isotopic composition in sulfides of the Zgid deposit [12]. Sulfides of the first stage (pyrite and sphalerite) have the highest positive $\delta^{34}S$ values (+6.7 and 7.6‰, respectively), indicating a crustal sulfur source. Sulfides of the second stage (pyrrhotite, chalcopyrite, and sphalerite) have lower positive $\delta^{34}S$ values (+4, +5, and +3‰, respectively). Sulfides of the third stage have the lightest sulfur isotopic composition (Fig. 3). A regular decrease in $\delta^{34}S$ from early to late sulfides indicates oxidizing conditions of ore formation at the deposits, which led to the formation of barite (Dzhimidon and Verkhnii Zgid deposits) with high $\delta^{34}S$ (from +15 to +24‰).

Thus, the formation of ore bodies was a pulsatory process, with high temperatures (420–360°C) at the beginning of each stage to low temperatures (200–120°C) at the end (Fig. 2), and pressures of no more than 400–300 bar. Solutions, mainly composed of sodium chloride with an admixture of other components, have salinities of 18–0.5 wt % NaCl equiv. The pulsed character of the process is emphasized by an increase in mineral formation temperature at the stage boundaries, changes in solution concentrations, and CO_2 regime. Periodical input of hydrothermal solutions was closely related to the tectonic setting. Repeated delivery of the solutions and their chemical reactions with early mineral aggregates produced different generations of pyrite, sphalerite, quartz, and other minerals. Thus, the mineral assemblages, similar in mineral composition, formed at different mineralization stages was characterized by sulfur isotope fractionation in the early and late sulfides (Fig. 3).

Sulfur activity changed during the formation of mineral assemblages. Geochemistry and iron mole fraction of sphalerite, with allowance for temperature factor, serve as indicators of a sulfur regime during ore formation. Two fields can be distinguished for sphalerite of the Sadon deposits in terms of crystallization conditions. The first field (T = 360–300°C, f_S from 10^{-9} to $10^{-12.5}$) corresponds to the crystallization of the early sphalerite associated with pyrrhotite and pyrite. The second field (T = 290–200°C, f_S from 10^{-12} to $10^{-14.5}$)

corresponds to the crystallization of late sphalerite associated with chalcopyrite and galena. This sphalerite assemblage is typical of many Pb–Zn deposits [13].

In addition to Fe, sphalerite contains traces of Cd, Mn, Co, Hg, In, and other elements. The trace elements vary in their distribution and contents. Mn and Co are typical of early sphalerite, and their contents increase with depth. Cd and Hg are accumulated in late sphalerite, and their contents decrease with depth.

Galena show variable contents of Ag, Bi, and Se. In addition to these elements, the mineral contains Sb, As, Cu, Sn, and Tl. The Ag contents are typically no more than 0.3–0.5%. The Ag-rich galena occurs in the ores in the upper parts of the deposits. In terms of Ag and Bi contents, galena of the Dzhimidon deposit differs from that of other deposits (table). In addition to Ag (up to 0.5%), it contains Bi (up to 15%) and Se (up to 0.6%). The high Bi solubility in galena (13.2 wt %) was experimentally observed at high temperature (600°C and more) and elevated alkalinity (pH 8.5–9) [14]. In the Dzhimidon deposit, the assemblage of Bi-bearing galena and Bi-sulfosalts formed under alkaline conditions, as follows from dissolution and reprecipitation of quartz as metacrysts among calcite, but the temperature was lower (420–400°C). The wide abundance of native bismuth could promote the higher Bi content in galena (as compared to experimental data) [14]. Bismuthinite, cosalite, and other Bi-bearing minerals formed under decreasing temperature. The low-Fe sphalerite and bismuth minerals formed under decreasing sulfur activity.

Spatial distribution of mineral assemblages and geochemical features of the ore minerals reflect vertical zoning of mineralization. Mineralogical and geochemical zonings are interrelated. However, they depend not only on the composition of mineral assemblages, but also on the formation conditions and depths of the deposits located at different vertical levels [10]. A general regularity in mineralogical zoning is expressed in the distribution of high-grade sphalerite–galena ore at the upper and middle horizons of orebodies and deposits, including buried mineralization (Dzhimidon deposit). This deposit also contains Ag, Bi, and Sb minerals atypical of other deposits. Quartz–arsenopyrite–pyrite and sphalerite–pyrrhotite ores mainly occur at the lower horizons of ore veins. The ore veins can bear bismuth mineralization (Nizhnii Zgid and Dzhimidon deposits). The deviations from general regularity in vertical distribution of the early and late mineral assemblages could be caused by a structural factor: namely, the appearance of new fissures crosscutting earlier veins or sharp change in physicochemical conditions.

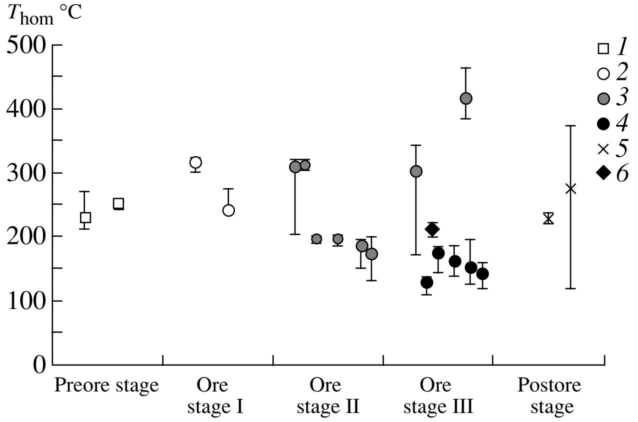

Fig. 2. Homogenization temperatures of fluid inclusions. Minerals of the Dzhimidon deposit: (*1*) quartz of the preore stage; quartz and sphalerite: (*2*) ore stage I, (*3*) ore stage II, (*4*) ore stage III; (*5*) quartz and carbonate of postore stage. (*6*) quartz of ore stage II from the Verkhnii Zgid deposit. Symbols are plotted in the point of average homogenization temperatures.

Geochemical zoning is expressed in the distribution and content of metals (Pb and Zn) in economic-grade ores, as well as trace elements in major ore minerals. Fe, Cu, Co, and Hg can serve as indicators of the affiliation of sphalerite to the early or late assemblages and, hence, to levels of their development. It was established that sphalerites with the highest Fe content (8–14 wt %) and high Co content occur at deep levels and associate with pyrrhotite, pyrite, and manganosiderite. Sphalerite in association with chalcopyrite and galena contains less Fe (2–5 wt %) and occurs in the upper parts of the deposits. According to [11, 15], Hg is a sensitive indicator of mineralization zoning. The Hg content varies from 1.4 ppm at the lower horizons (966 m and less) to 9 ppm at upper horizons (1107–1250 m) to 9 ppm. The Hg content in sphalerite decreases 15 times over the interval of 600 m in the Arkhon deposit and 2.5 times in the Sadon deposit. Galena in the deposits of the Sadon ore field differs in contents of Ag, Bi, Sb, and Hg. With increasing depth, the galena is depleted in Ag, Sb, and Hg and enriched in Bi. In particular, spectral analyses showed that the Ag content in galena from the main vein of the Verkhnii Zgid deposit gradually decreases from 0.4–0.6 to 0.08–0.1% over 600 m, with maximum content found at absolute marks of 1900–1800 m. Ores of the Nizhnii Zgid and Dzhimidon deposits show deviation from a general trend of decrease in Ag content with depth. This is explained by the fact that deep parts of individual orebodies occasionally contain Ag-rich (up to 9.8 wt %) Bi–Pb–Ag–S minerals. Since main carriers of the aforementioned trace elements are sphalerite and galena and the general trend of decrease (or increase) of trace elements with depth is retained, variations in their contents have maximums and minimums which are related to the mineralogical zoning. Hence, both types of vertical zoning are closely related and they indicate the exposure depth of an orebody. Stages of mineral formation and levels of the deposit formation with respect to paleosurface are responsible for these regularities.

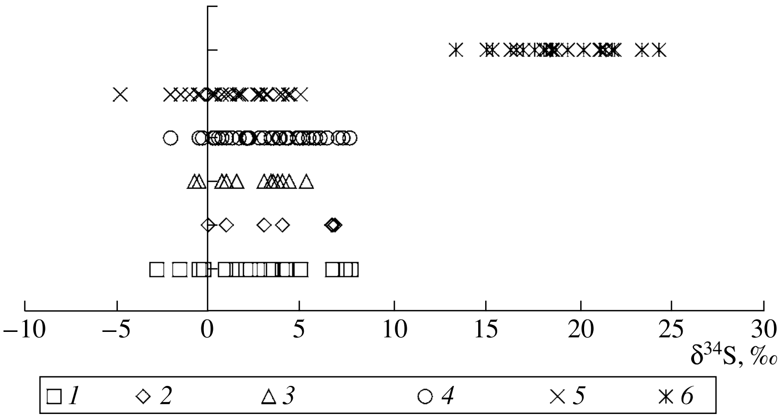

Fig. 3. Sulfur isotope composition of sulfides and barite from the Sadon ore field. (*1*) Pyrite, (*2*) pyrrhotite, (*3*) chalcopyrite, (*4*) sphalerite, (*5*) galena, (*6*) barite.

ACKNOWLEDGMENTS

This work was carried out in the framework of the basic theme of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry ("Composition, structure, and formation conditions of ores of the large endogenous noble and nonferrous metal deposits").

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