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Zn and Cd Distribution Updip of the Ore Veins of the Dzhimidon Base-Metal Deposit in Northern Ossetia, Russia

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Abstract—The analysis of the bulk samples of ore veins from the Dzhimidon base-metal deposit in Northern Ossetia, Russia, has revealed the vertical zoning of Cd and Zn distribution: the average (Cd/Zn) × 1000 ratio is 1.64 ± 0.17 at the lower level (1520 m, adit no. 49), 4.23 ± 0.16, at the intermediate level (1640 m, adit no. 47), and 7.0 ± 0.3, at the upper level (1680 m, adit no. 3). The average value of the (Cd/Zn) × 1000 ratio in the total sampling is 4.1 ± 0.2. The decrease in temperature up the dip of ore veins is a possible cause of the established zoning.

Keywords: Cd/Zn-ratio in ores, vertical zonality, base-metal vein deposits.

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INTRODUCTION

The zoning of ore deposition, i.e., the regular variation in proportions between two or several components of mineralization along the strike, dip, and thickness of an ore zone, is quite important for the development of methods for searching for geochemicals (Solovov, 1985). The data on vertical zoning of orebodies play a great role not only in searching geochemistry (the forecast of mineralization at depth and determination of the depth of erosion) but in the solution of genetic problems and verification of the results of thermodynamic modeling of ore formation. The data presented in this paper are part of a study whose target is a reconstruction of physico-chemical parameters, material sources, and formation of the orebodies and halos of vein hydrothermal deposits. The investigations were conducted by geochemical (the study of element distribution in orebodies and host rocks) and thermodynamic (construction and analysis of equilibrium–dynamic models of vein formation) methods (Borisov, 2000, 2003; Borisov et al., 2006).

The Pb–Zn deposits of the Sadon ore district in Northern Ossetia, Russia, are the objects for the study of vein ore formation. The aim of this work is to present the data on the variation in the Cd/Zn ratio updip of base metal ore veins based on the example of the Dzhimidon deposit and to interpret this variation.

BRIEF CHARACTERISTICS OF THE DEPOSITS FROM THE SADON DISTRICT

Middle to Late Paleozoic granites are the major host rocks of the high-angle veins of deposits from the Sadon ore district. The outcrops of granites are surrounded by a wide band of Lower and Middle Jurassic tuffs, fine-clastic tuff breccia, lavas of andesite–dacitic porphyrites, and sedimentary rocks (sandstones, claystones, and siltstones). The Jurassic volcanic and sedimentary host rocks are less significant in comparison with granites (Nekrasov, 1980, 2007). A channel role for the near-latitudinal Sadono–Unal deep normal fault, which limits the area of the development of the vein deposits from the south, is commonly accepted. The main deposits of the district are controlled by northwestern and northeastern splay shear fractures and tension cracks restricted to the reclined limb of the normal fault. The ore processes occurred in the Middle Jurassic, before the Callovian. The vein thickness varies from 0.1 to 5 m and more. The veins were excavated for more than 1100 m updip (Verkhnii Zgid) and for 1000 m along the strike. The major ore minerals are sphalerite, galena, pyrite, chalcopyrite, and pyrrhotite; arsenopyrite is less abundant. The gangue minerals include quartz, carbonates, chlorite, and others.

The metasomatic processes after the host granites include silicification, chloritization, sericitization, and carbonatization. Based on thermobarogeochemical data (Lyakhov et al., 1994), the temperatures of ore formation are 415–65°C and pressures are 230–0.011 MPa. The gradients updip of the vein bodies could attain 35–40°C and 25 MPa for 100 m. A productive quartz–galena–sphalerite assemblage was formed at 345–120°C. The ore-forming hydrothermal fluids were chloride–carbonate with more than 50% chlorides. The paleodepth of the formation of the deposits from the lower structural level (Precambrian metamorphic rocks, Paleozoic granites, and Early Jurassic volcanic rocks) is estimated at 2.5–3 km (Nekrasov, 1980), i.e., a pressure close to the lithostatic one should be about 80–100 MPa at this depth.

In comparison with most deposits of the district (Zgid, Sadon, Arkhon, and Kholstin), which are hosted by Middle to Late Paleozoic granites of the Sadon type and volcanic rocks of the Early Jurassic Ossetin Formation, the host rocks of the Dzhimidon deposit are crystal schists and amphibolites of the Neoproterozoic–Lower Paleozoic Buron Formation. In recent years, we have been conducting works at the Dzhimidon deposit, which is the only explored deposit in the district. Three northeastern ore zones from east to west—East-Dzhimidon, Tsagarsar, and Bozang—were revealed at the deposit (Groznova et al., 2006). The ore zones are exposed by series of adits: no. 8 (1760 m in altitude), no. 3 (1680 m), no. 47 (1640 m), no. 45 (1560 m), and no. 49 (1520 m). Adits nos. 8 and 45 were excavated a long time ago and have been inaccessible for more than 15 years. We began our study in 1999–2000 when adit no. 3 worked and adit no. 47 was established (the infrastructure of the Bozang ore zone was constructed before 2003). The excavations in adit no. 49 have operated from 2008 until the present through the Bozang and Tsagarsar ore zones. Adits no. 3 and 47 became almost inaccessible in 2009. We sampled the material from ore veins of the Dzhimidon deposit consecutively during the advancement of exploration works from adit no. 3 to adit no. 49.

METHODS OF FIELD AND LABORATORY WORK

The sampling was carried out using our own method. Massive bands of the oriented vein monoliths (from one contact to another) were sampled at the various horizons of the excavations along the transverse sections of the vein orebodies. The lengths of such sections can reach 1.5 m and more, depending on vein thickness. At the field camp, the oriented monoliths were described and cut on plates–samples and separated samples (the sampling step is 2–5 cm, their weight is up to 5 kg). After this, the samples were crushed, quartered, and powdered. The weight of the final samples was 100–200 g. We collected data on 17 transverse vein sections at three horizons of the deposit (135 samples). Some of these include series of samples that describe the complete vein section from one contact to another (13 sections with 4 to 29 samples in each) and several samples, bulk combined sample (4 samples).

The Fe, Zn, Pb, Cu, Cd, As, Mn, and Ca contents in the bulk samples from ore veins were determined on a RLP 3 X-ray fluorescent energy dispersive portable analyzer (Mo anode), at an acceleration voltage of 15, 20, 30, and 38 kV (38 kV during analysis), a current intensity of 30–400 mcA (100 mcA in our case), and a time of analysis of 5 min (Department of Geochemistry, Moscow State University). The Ag and Sb contents were determined using a AI-1024-95-16 multichannel impulse analyzer with a radioactive isotope (^{241}Am) as an excitation source (20 min exposure).

RESULTS OF THE STUDY

Statistical processing of the analytical results was conducted for all 135 ore samples: Tsagarsar orebody (adit no. 49, 1520 m, 5 sections, 28 samples) and veins and apophyses of the Bozang ore zone (adit no. 47, 1640 m, 10 sections, 91 samples, and adit no. 3, 1680 m, 2 sections, and 16 samples). The data on the Tsagarsar orebody obtained in 2010 widened the sampling from 10 to 28 samples for the horizon of adit no. 49. This allowed us to compare the distribution of several elements updip of the veins for the entire deposit. Statistically reliable results were obtained only for the Cd/Zn ratio (the standard errors and deviations, sampling dispersion, and Student's test were analyzed). The Zn and Cd contents in the studied samples vary from 0.11 to 39.6% and 0.003 to 0.15%, respectively. These contents in the bulk samples are governed by the amount of sphalerite, so it is expedient to use the concentration ratios but not the absolute values.

Fig. 1 demonstrates the distribution of the sample amounts by single intervals of the Cd/Zn ratios for three elevation levels. It is evident that maximums of the frequency occurrence are regularly shifted relative the values of the Cd/Zn ratio (from $(1–2) \times 10^{-3}$ to $(6–7) \times 10^{-3}$) updip of the orebodies. At the lower horizon (adit no. 49), the average value of the (Cd/Zn) × 1000 ratio is 1.64 ± 0.17 (71% of the samples have values from 1 to 2), at the intermediate horizon (adit no. 47), this was 4.23 ± 0.16 (78% of the samples have values from 2 to 5), and the upper horizon (adit no. 3) is characterized by 7.0 ± 0.3 value (75% of the samples have values from 5 to 8). The standard deviation was 0.83, 1.51, and 1.19 for the samples from adits no. 49, 47, and 3, respectively. The significance of the discrepancies in average values of the Cd/Zn ratio was confirmed by the Student's test: t was 8.2 for the samplings from adits no. 3 and 47 and 11.1 for the samplings from adits no. 47 and 49, at the critical value of the Student's test of about 2 at the 95%-level of the confident probability. Fig. 2 displays the values of the Cd/Zn ratio in all samples from the orebodies of the Dzhimidon deposit depending on the true altitude. The average value of the Cd/Zn ratio in the entire sampling is 4.1 ± 0.2.

The use of other elemental proportions from our database showed no reliable and regular results. This is probably related to the fact that Zn and Cd are a pair of elements from the same mineral, sphalerite. Therefore, even a small amount of sphalerite makes it possible to correctly determine the Cd/Zn ratio, even in a small number of the bulk samples. It should be noted that sphalerite generations could be unevenly distributed in ores. Three generations of sphalerite were described at the Dzhimidon deposit (Groznova et al., 2006). Sphalerite of the first generation is characterized by a higher Fe content (up to 10–15%) and the lowest Cd contents. Sphalerite of the second and third generations has lower Fe content and increased Zn

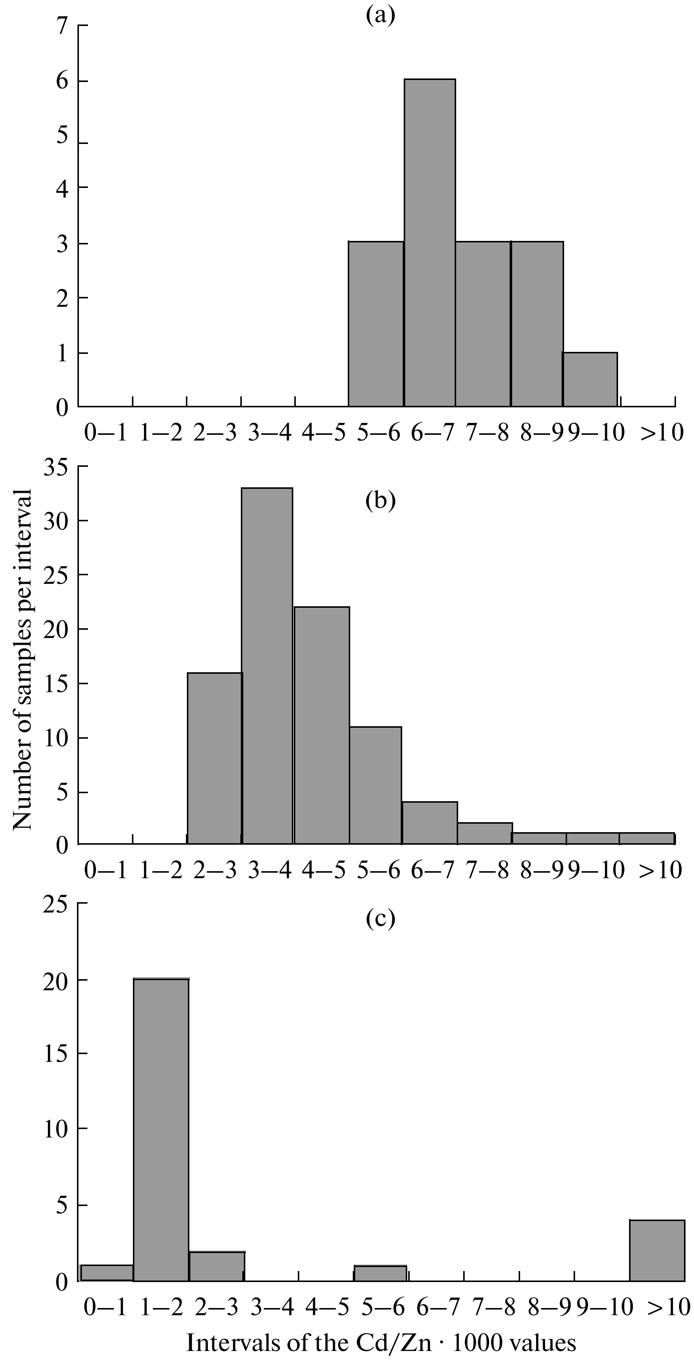

Fig. 1. Distribution of the samples over the single intervals of the Cd/Zn ratio for the three elevation levels from the Dzhimidon deposit. (a) 16 samples (Bozang ore zone, adit no. 3, 1680 m), (b) 91 samples (Bozang ore zone, adit no. 47, 1640 m, (c) 28 samples (Tsagarsar ore zone, adit no. 49, 1520 m).

and Cd concentrations. The variable amount of these sphalerite generations in the bulk ore samples can influence an unstable Cd/Zn ratio, which is probably reflected on histograms (Fig. 1) and in the mean accuracy of this ratio at the different elevation levels.

The variations in the other contents of elements (Fe, Zn, Pb, Cu, Mn, As, and Sb) depend on the amount of different host minerals in the studied sample, which varies both in separate sections and along the vein strike. The choice of the sampling location in the continuous section through the veins was random and was due to sampling convenience, i.e., by the possibility of sampling large oriented monoliths through the vein section in the underground excavations; therefore, the samples could have been unrepresentative for the mentioned elements. In addition, Fe, Cu, Mn, As, and Sb could simultaneously occur in several host minerals, for example, in pyrrhotite, pyrite, sphalerite, chalcopyrite, arsenopyrite, manganosiderite, and fahlore. The main problem of the Ag–Pb pair and its major host mineral, galena, is related to the low Ag content in the bulk samples at Pb concentration of less than 1% (in many samples it was close to the lower detection limit of the X-ray fluorescent analysis).

DISCUSSION

It is known that the Cd/Zn ratio in the Earth's crust is 2.63×10^{-3}, varying from 1.2×10^{-3} in ultramafic rocks to 3.3×10^{-3} in acidic rocks and clays (Ivanov, 1997; Grichuk, 2005). The average Cd/Zn ratio in the sphalerite of the various deposits was 4.02×10^{-3} (massive sulfide base metal, 3.04; stringer, 3.65; Pb–Zn stratiform, 4.17; Pb–Zn skarn, 7.03, etc.). The average Cd/Zn ratio in the bulk ore samples from the Dzhimidon deposit agrees well with the given values. However, no reliable data on vertical zoning of Cd and Zn distribution in ores from the base-metal stringer deposit are found in the literature.

Let us review the possible explanations for the variable Cd/Zn ratios during hydrothermal ore formation.

1. The evolution of the ore-bearing fluid source. The average value of the Cd/Zn ratio in condensates of the volcanic gases from 12 studied volcanoes was 67×10^{-3}. Such a high value is related to the fact that in volcanic exhalations Cd, in contrast to Zn, is transported in a high-temperature form—Cd^0 (Grichuk, 2005). This leads to the most intense Cd transport by endogenic fluids that entered the hydrothermal system at certain stages and it could produce an increase in the Cd/Zn ratio in ores. Our data (the average value of the Cd/Zn ratio at the surveyed deposit and low values in the lower horizons) indicate that this hydrothermal system developed without a significant contribution of endogenic fluid, in spite of the presence of the Middle Jurassic granite–porphyritic stock, whose influence on the temperature of the hydrothermal system formation was probably decisive.

2. Changes in the composition of the ore-bearing fluid during the deposition of sphalerite or its exhaustion of Cd. The Cd distribution in sphalerite is governed by the partition coefficient (K_D) between sphalerite and fluid. The estimation of its value for this system (Kase and Horiuchi, 1996) shows that it is more than 1 at 600–150°C. In this case, the decrease in Cd concentration in the fluid (an exhaustion) during deposition of sphalerite updip of the veins should lead to a decrease in the Cd/Zn ratio.

3. Heterogeneous formation conditions related to the decrease in temperature of mineral formation updip of the ore veins. High values of the temperature gradient updip of the veins (up to 35–40°C per 100 m) were reported from many deposits of the region (Lyakhov et al., 1994) and this may have been the main factor of ore deposition. From their research on the min-

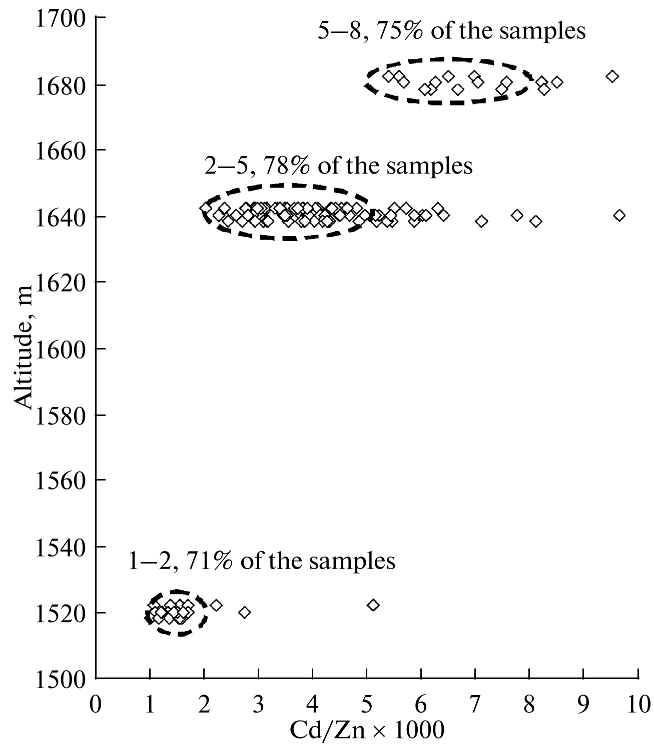

Fig. 2. Cd/Zn ratio variation in Pb–Zn veins from the Dzhimidon deposit depending on altitude.

eralogical and geochemical features of the Dzhimidon deposit, workers from the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences (IGEM RAS) have drawn the conclusion that cooling of the hydrothermal fluid is the main cause of ore formation (Groznova et al., 2006; Groznova, 2010). Differences in the thermodynamic features of the Zn and Cd chloride complexes and the properties of the ZnS–CdS solid solution with a decrease in temperature could lead to an increase in the Cd molar fraction in sphalerite, which was confirmed by E.F. Bazarkina (Bazarkina, 2010; Bazarkina et al., 2010). These works describe the results of an experimental study of the constants of Cd chloride complexes in aqueous solutions at various *T*–*P*-parameters and show that the Cd content and Cd/Zn ratio in sphalerite increase upon a decrease in temperature from 400 to 250°C (100 MPa). Thus, it may be assumed that most probable cause of zoning is related to a decrease in temperature of ore formation updip of the veins.

It is important to link the variation in the Cd/Zn ratio upon a decrease in temperature with the real distribution of mineralization updip of the veins but geochemical data obtained is not enough for this estimation. This can be considered from the results of thermodynamic modeling and their correlation with the parameters of natural objects (Borisov et al., 2006). The vein level up the dip in thermodynamic models is described through the decrease in temperature of ore formation. It is typical of all models that the maximum content of sphalerite in ore occurs at 150–160°C and an increase in bulk pyrite content and decrease in sphalerite concentration occur toward the deeper level (200–210°C). A decrease in sphalerite content is noted in models at temperatures less than 150°C. Comparison of the values of the bulk pyrite and sphalerite contents in the main orebodies of the deposit with the results of modeling allows us to relate the maximum of sphalerite deposition to veins at the level of adit no. 47 (1640 m). These data show that the sphalerite content regularly decreases to the horizon of adit no. 49 (1520 m). Thus, a value of the (Cd/Zn) × 1000 ratio of less than 2 points indicates that the maximum of ore deposition should occur higher and the amount of sphalerite (and galena) will only decrease down the dip of the orebodies. This is a preliminary conclusion, which will be specified in models after the creation of a thermodynamic supply for the description of the ZnS–CdS solid solution.

CONCLUSIONS

1. The vertical zoning of the Cd and Zn distribution in ore veins from the Dzhimidon base-metal deposit, Northern Ossetia was established. The (Cd/Zn) × 1000 ratio varies from 1.64 ± 0.17 (the horizon of adit no. 49, 1520 m) to 4.23 ± 0.16 (the horizon of adit no. 47, 1640 m) and 7.0 ± 0.3 (the horizon of adit no. 3, 1680 m).

2. The probable cause of the zoning is related to a decrease in the temperature of ore formation updip of the veins.

REFERENCES

1. Bazarkina, E.F., Cd and Zn Transport in Hydrothermal Fluids: Experiment and Physico-Chemical Modeling, *Extended Abstract of Cand. Sci.* (Geol.-Min.) Dissertation, IGEM RAS, Moscow, 2010.
2. Bazarkina, E.F., Zotov, A.V., and Akinfiev, N.N., Pressure-Dependent Stability of Cadmium Chloride Complexes: Potentiometric Measurements at 1–1000 bar and 25°C, *Geol. Rudn. Mest.*, 2010, vol. 52, no. 2, pp. 167–178 [*Geol. Ore Dep.* (Engl. Transl.), 2010, vol. 52, no. 2, pp. 167–178].
3. Borisov, M.V., *Geochimicheskie i termodinamicheskie modeli zhil'nogo gidrotermal'nogo rudoobrazobaniya* (Geochemical and Thermodynamic Models of the Hydrothermal Vein Ore Formation), Moscow: Nauchn. Mir, 2000.
4. Borisov, M.V., Geochemical and Thermodynamic Models for the Genesis of Low- and Medium-Temperature Vein Mineralization and Metasomatism in the Wall Rocks, *Geochem. Inter.*, (Engl. Transl.), 2003, vol. 41, suppl. 2, pp. 145–312.
5. Borisov, M.V., Bychkov, D.A., and Shvarov, Yu.V., Geochemical Structures of Base-Metal Filling Veins and Parameters of Hydrothermal Ore Formation, *Geokhimiya*, 2006, vol. 11, pp. 1218–1239 [*Geochem. Intern.* (Engl. Transl.), 2006, vol. 11, pp. 1129–1147].
6. Grichuk, D.V., Cd/Zn Ratio as Indicator of Endogenic Fluid Contribution into Hydrothermal Systems, *Materialy VII mezhdunarodnoi conferentsii "Novye idei v naukakh o Zemle* (Abstracts of the VII Int. Conf. "New Ideas in the Earth Sciences"), Moscow, 2005, vol. 2, p. 83.
7. Groznova, E.O., Mineralogical and Geochemical Features and Formation Conditions of Lead–Zinc Ore at the Dzhimidon Deposit, Northern Ossetia, *Extended Abstract of Cand. Sci.* (Geol.-Min.) Dissertation, IGEM RAS, Moscow, 2010.
8. Groznova, E.O., Dobrovol'skaya, M.G., Kovalenker, V.A., et al., Mineralogy and PT Formation Conditions of Lead–Zinc Ore at the Dzhimidon Deposit, Northern Ossetia *Geol. Rudn. Mest.*, 2006, vol. 48, no. 2, pp. 126–154 [*Geol. Ore Dep.* (Engl. Transl.), 2006, vol. 48, no. 2, pp. 108–134].
9. Ivanov, V.V., *Ekologicheskaya geokhimiya elementov* (Ecological Geochemistry of Elements), Moscow: Ecologiya, 1997. Book 5.
10. Kase, K. and Horiuchi, Y., Cadmium, Manganese, and Cobalt Contents of Sphalerite from the Kieslager-type Copper Deposits, Japan, *Resource Geol.*, 1996, vol. 46, no. 3, pp. 137–150.
11. Lyakhov, Yu.V., Pozdeev, K.M., Tibilov, S.M., et al., Thermodynamic Model of Ore Zoning and Estimation of Prospects of the Sadon Lead–Zinc District, *Rudy i Metally*, 1994, vol. 2, pp. 45–54.
12. Nekrasov, E.M., *Strukturnye usloviya lokalizatsii zhil'nykh svintsovo–tsinkovykh mestorozhdenii* (Structural Conditions of Localization of Vein-Type Lead-Zinc Deposits), Moscow: Nedra, 1980.
13. Nekrasov, E.M., Geology and Structural Features of Vein-Type Lead and Zinc Deposits, *Geol. Rudn. Mest.*, 2007, vol. 49, no. 6, pp. 559–570 [*Geol. Ore Dep.* (Engl. Transl.), 2007, vol. 49, no. 6, pp. 487–496].
14. Solovov, A.P., *Geokhimicheskii metody poiskov mestorozhdenii poleznykh iskopaemykh* (Geochemical Methods of Searching of Mineral Deposits), Moscow: Nedra, 1985.