Metals, Arsenic, and Sulfur in the Aue and Eibenstock Granites, Erzgebirge

Vikt. L. Barsukov, N. T. Sokolova[†], and O. M. Ivanitskii

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 119991 Russia
e-mail: geokhi@ru
Received December 27, 2004

Abstract—Average concentrations of Pb, Zn, Cu, and other metals, as well as S and As, were calculated for the Aue granitic cupola, the contact aureole of which hosts the large vein-type uranium deposit of Schlema–Alberoda and the Schneeberg uranium–base metal deposit (Erzgebirge, Germany). The cupola was exposed by mine workings and boreholes, which provided an opportunity to evaluate variations in the abundances of metals in the granites over a vertical interval of more than 2.5 km and estimate their losses in the upper oxidized part of the investigated volume of the cupola (coefficient of iron oxidation, KO_{Fe}, increases in the granites from bottom to top from 7 to 70%) compared with the lower unaltered and unoxidized part (with a KO_{Fe} plateau at about 5%). The average concentrations of metals in the upper part of the cupola are lower than those in the lower part by a factor of 2.5 for Pb, 1.56 for Zn, 1.45 for Cu, 1.3 for Co, etc. A similar decrease in the abundances of ore elements along the vertical section associating with the relative epigenetic alteration and oxidation of the granite was previously described by us for U and Th and for the components of high-temperature ores, W, Sn, and Mo. The removal of ore elements from the granite was accompanied by a decrease in the bulk contents of sulfur and arsenic by a factor of 1.35 and 1.65, respectively. The leaching of trace metals from the granites of the upper part of the Aue cupola was followed by their partial redeposition above the cupola in the ore veins of the Schlema and Schneeberg deposits.

DOI: 10.1134/S0016702906090059

INTRODUCTION

The Aue granitic cupola has attracted considerable interest, because its contact aureole hosts the large vein-type uranium deposit of Schlema, and the Schneeberg base metal–uranium deposit, which has been known since the Middle Ages, is confined to its southwestern continuation. The cupola of the giant Erzgebirge pluton is composed of granites of the main phase of the early (330–320 Ma) Gebirge intrusive complex (OG) [1]. The Aue cupola has been exposed by mine workings and penetrated by boreholes to depths of about 2.5 km.[1] This allowed us to obtain samples from various hypsometric levels. Our previous papers were related to the concentrations of radioelements, U, Th, and K, in the Aue cupola [2], and W, Sn, and Mo, which

are typical of the high-temperature veins of Schlema and the whole region [3]. This paper focuses on the average concentrations of base metals (Pb, Zn, Cu, Ni, Co, Ag, and Bi) in the granites of the Aue cupola. These data are important for the understanding of the formation conditions of numerous quartz–sulfide veins of Schlema and Schneeberg, which were formed relatively close in time to the beginning of uranium mineralization compared with the early quartz veins (part of which also contain sulfides and W, Sn, and Mo mineralization). Moreover, the uranium ore veins of Schlema always contain Pb, Zn, Cu, and Bi sulfides [4], and the post-uranium veins bear Ni, Co, Bi, and Ag [5]. Since these metals are typical thiophile elements, their concentrations are evaluated together with the contents of sulfur and arsenic, which were also analyzed by us in the Aue granites. Similar to our previous studies, the obtained data are compared with the available evidence on the concentrations of metals in the Eibenstock massif, which is composed of the YG rocks of the young (305–295 Ma) Erzgebirge intrusive complex [1].

The Aue cupola is made up of typical hypabyssal granites showing coarse-grained subhedral and occasionally porphyritic textures. Their unaltered varieties are composed of orthoclase (24–29%), zoned andesine (36–38%), quartz (27–30%), and biotite (6–12%). The mineral and chemical compositions of granites from

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[†]Deceased.

[1]Depths in the Schlema–Alberoda deposit (and, correspondingly, the levels of granite sampling) are given relative to the conventional zero level coinciding with the bottom of the Marx–Semmler (MS) ancient drainage gallery in the Schneeberg deposit, near its mouth (330 m above sea level). The horizons of granite sampling are hereafter referred to as positive numbers (e.g., 1305), omitting the minus signs and "m" (meters) after the numerals. In the above case, "1305" denotes the depth in meters from the zero level, i.e., –1305 m relative to MS.

various levels (depths) were described in [1, 2] and other publications and are not reiterated here in detail. However, since our first publication on the Aue granites [2], the differences between the lower and upper parts (halves of the volume studied) of the Aue cupola have been comprehensively described [6], and it is reasonable to discuss them in more detail.

Although the texture of granite remains unchanged, there is an upward increase in the degree of epigenetic hydrothermal alterations. The average content of quartz (from ~29 to ~34 wt %) and secondary sheet silicates (muscovite and chlorite) increases somewhat at the expense of a corresponding decrease in the fraction of feldspars and biotite. Plagioclase becomes more albitic: it is represented by andesine no. 30 in the lower part of the cupola and is partly replaced by oligoclase and albite no. 5–8 in the upper levels. The ferroan end-member annite is predominant in the composition of dark brown biotite from the lower part of the Aue cupola, whereas the lighter greenish biotite that survived chloritization in the upper part of the cupola has lost most of its iron and is dominated by the Mg end-member phlogopite. According to F radiography, the major sources of fission tracks in the granites of the lower part of the cupola are accessory minerals confined mainly to Fe-biotite. Both the number of fission-track centers in Mg-biotite and the intensity of their decay decrease abruptly in the upper part of the cupola. In contrast, such centers appeared in the newly formed minerals (chlorite, muscovite, Fe oxides, etc.) and at grain boundaries and microscopic fractures. The granite of the lower part of the Aue cupola is light gray, and dispersed hematite pigment appearing in the upper part of the cupola imparts a pinkish color to the granite. The boundary between the lower relatively unaltered and upper altered parts of the cupola is drawn at the horizon of 1260, which will be substantiated below.

The chemical composition of granite shows minor variations with decreasing depth. We noted previously [2] that there is no functional relation between the average (average for a particular horizon) contents of major elements and depth. This is not quite correct, because the arithmetic mean values of concentrations vary from horizon to horizon. This is inevitable, when some horizons are represented by 1–3 silicate analyses and others by 10–15 analyses. Therefore, a horizon-based comparison is not plausible and does not reveal true tendencies. However, a comparison of the weighted mean concentrations of components in larger taxa (three horizons below level 1260 [2, Table 3, analyses 12–14] and five horizons above it [2, Table 3, analyses 7–11]) reveals significant variations in the vertical section [6]. They are shown in Table 1. It can be seen from this table that there is a slight decrease from bottom to top in SiO_2 content (despite the increase in the fraction of quartz), Na_2O, and K_2O, and a similarly slight increase (more precisely, relative preservation) in the concentrations of CaO, MgO, FeO, and Al_2O_3.

Table 1. Differences between the weighted average major-element compositions of granites from the lower and upper parts of the Aue cupola after [5, Table 3]

Component	Lower*	Upper**
SiO_2	71.25	70.98
Al_2O_3	13.39	13.72
Fe_2O_3	0.16	0.73
FeO	2.46	2.68
MgO	0.52	0.68
CaO	1.19	1.23
Na_2O	3.38	3.22
K_2O	5.06	4.62
H_2O	0.66	0.33–0.70

*Weighted average composition based on 22 analyses of granite from horizons –1710, –1620, and –1305 m relative to MS.

**Weighted average composition based on 35 analyses of granite from horizons –1125, –945, –820, –540, and –120 m relative to MS. An average H_2O content of 0.70% (26 analyses) was given in [5] (Table 3, no. 3) for the granite of the upper part of the Aue cupola.

There is a considerable (more than fivefold) increase in the concentration of Fe_2O_3, which resulted in an upward increase in the coefficient of iron oxidation in the granite from 3.6–5.7% to 30–40% in our samples, and even up to 45.4–69.3% in the silicate analyses by Pietzsch [7].[2]

Such slight mineral and chemical changes in the granites of the upper part of the Aue cupola, which did not disturb the texture of rocks but caused an increase in silica solubility, were aptly named the dispersed muscovitization of granite by Zaraiskii [8]. These epigenetic alterations of granite (by definition occurring after granite crystallization) caused by its reactions with thermal aqueous solutions are not to be confused with supergene alterations. The concentration of thermal anomalies above the OG cupolas (later YG) of the emplaced and cooling Erzgebirge pluton 330–295 Ma ago caused intense infiltration of thermal waters through and above them and prolonged washing of these cupolas with water, especially their apical parts long before the denudation-related exposure of granites on the surface. The dispersed muscovitization of the granite was related to such an ancient interaction with thermal waters: its lower boundary is now observed 1.5 km from the present-day surface (correspondingly, it occurred much deeper during granite cooling), obviously outside the current zone of hypergenesis. The character of mineral transformations (one plagioclase replacing another, removal of Fe from biotite with the

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[2] The coefficient of oxidation is calculated from the contents of ferric and ferrous iron in the rock by the formula KO_{Fe} (%) = $[Fe_2O_3] \times 100/[Fe_2O_3] + [FeO]$ or from similar relations for elemental Fe(III) and Fe(II).

Table 2. Published data on the average concentrations of Pb, Zn, Cu, and S (ppm) in the Erzgebirge granites

Intrusive phase, massif	Index	Pb	Zn	Cu	S
Early intrusive complex (Gebirge granites), 330–320 Ma					
Main phase	OG-1	21 [16], 33 [12, 13], 34 [1], 36 [11, 14], 43 [15]	47 [15], 50 [12–14], 69 [16]	5 [1], 5.6 [14]	800 [1], 400 [14]
Aue	OG-1	15 [11], 15–20 [10]		2 [1]	
Kirchberg	OG-1	25–30 [10], 29 [11], 33 [12]	50 [12]	6 [20]	
Bergen	OG-1	9 [15], 17 [11], 20–25 [10]	25 [15]		
Zobes	OG-1	19 [11]			
Phase not specified	OG	22 [11], 32 [1]		2 [1]	500 [1]
Late intrusive complex (Erzgebirge granites), 305–295 Ma					
Main phase	YG-1	6 [1], 8 [11], 17 [12–14], 20 [1]	43 [12–14], 47 [15]	2 [1], 6.9 [14]	400 [1], 500 [14]
Eibenstock	YG-1	5 [15], 7 [10]	68 [15]		400 [1]
Ehrenfriedersdorf	YG-1	2 [15], 5 [11], 14 [1], 25 [10]	44 [15]	2 [1]	
Geyer	YG-1	11 [15], 14 [1], 15 [10]	56 [15]		
Altenberg	YG-1	14 [11], 15–20 [10]			
Popershau	YG-1	18 [15]	75 [15]		
Phase not specified	YG	5 [11], 14–18 [1]		2 [1]	500 [1]

retention of Mg-biotite, etc.) suggests that they occurred under relatively high *T–P* conditions.

The mineral and chemical compositions of granite change gradually, and there is of course no sharp boundary between the relatively unaltered lower part and the altered upper part of the Aue cupola. The boundary between the lower and upper zones can be arbitrarily placed using a measurable characteristic of the granite. For this purpose, we used the coefficient of iron oxidation in granite, KO_{Fe}, which is a calculated geochemical indicator of redox conditions in the Aue cupola. In all the horizons below 1260, i.e., over a vertical interval of more than 1 km (to a depth of 2270), the KO_{Fe} values of granite form a plateau at about 5%. We accepted this value as an initial value for the OG of the Aue massif, and the granites with such KO_{Fe} values were assigned to the lower part of the cupola almost unaffected by epigenetic processes (unoxidized). The horizons between 1260 and the surface show an upward increase in the KO_{Fe} value of granite from 7.2 to 30–70% and were assigned to the upper relatively altered (oxidized or affected by oxidation) half of the cupola.

As a result, the goal of our study was expanded to include both the calculation of the average contents of metal, sulfur, and arsenic using new analyses and the estimation of the difference between the average contents of these elements in the upper and lower halves of the explored part of this cupola. In other words, this study was aimed at assessing the extent of changes in the concentration of trace elements in granite during its dispersed muscovitization and oxidation in the upper part of the Aue cupola. In addition to the analysis of numerical data, we performed a computer simulation of thermodynamic equilibria between the Aue granite and its pore solutions in the course of a *T–P* decrease, including the simulation of changes in the release of ore elements from the granite into the equilibrium water phase [6]. Some results of this modeling are used in this paper.

PREVIOUS WORK

A wealth of data were published in the second half of the 20th century on the abundances of trace metals, S, and As in various granitic massifs of the Erzgebirge, including the Aue granites. Table 2 gives an overview of data for the most important elements, Pb, Zn, Cu, and S.

According to Vinogradov [9], the average abundance of lead in crustal granites is 20 ppm.[3] The available estimates of the average concentrations of Pb in the Gebirge (OG) granites of the main phase from various exposures of the Erzgebirge pluton [1, 11–20] vary by a factor of almost 3, from 15 [11] to 43 ppm [1, 12]. It was suggested [11, 13] that the average concentration of Pb in the Aue granites is 15–20 ppm, which is slightly lower than in other exposures of the Gebirge granites and in the OG on the whole. In other words, these rocks are supposed to be slightly depleted in Pb compared with the global background value for felsic

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[3] There are more recent estimates for the background element contents in rocks [10]. They are somewhat different from those of [9] for Co, Bi, and S and almost identical for all other elements considered here. However, in our opinion, new data from the official manual [10], even if they are more accurate, need to be acknowledged by leading geological centers of all countries. The estimates of Vinogradov have long been approved by the geological community and we prefer to use these values.

rocks. Even lower Pb contents were reported for the younger granites (YG), from 5 to 18 ppm [12–15].

The background concentration of zinc in granitic rocks is 60 ppm [9]. The available measurements for the Gebirge granites (OG) show a lower average Zn content ranging from 25 ppm for the Bergen massif [12] to 50 ppm for the granites of the main phase (OG-1) [14, 15]. Forster [17] reported a higher value of 69 ppm. The YG samples show average Zn concentrations of 43–52 ppm [13–15] and are in general practically indistinguishable in this parameter from the OG; however, higher concentrations of 68 and 75 ppm were obtained for the Eibenstock and Popershau massifs, respectively [15].

According to Vinagradov [9], the average concentration of copper in felsic igneous rocks is 20 ppm. The available data for Cu concentrations in the OG rocks, including the granites of the Aue cupola are 3–10 times lower, 2.0–6.6 ppm [12]. The young granites of the main phase (YG) also showed low Cu concentrations, from 1 [13] to 6.9 ppm [15].

Only a few estimates were reported for the concentrations of the less abundant metals nickel, cobalt, silver, and bismuth in the OG rocks, including the Aue cupola. In particular, Tischendorf et al. [13, 15] estimated 7.2 ± 3.5 ppm Ni, 6.9 ± 3.2 ppm Co, and 0.05 ppm Ag for the Gebirge granites. Brauer [12] reported a higher Ni concentration of 10 ppm and a lower Co concentration of 3 ppm. There is no data on the average concentration of Bi in the OG rocks, and its background abundance in granitoids is 1×10^{-4} ppm [9].

The average content of sulfur in felsic igneous rocks is 400 ppm [9]. Its bulk content in the Erzgebirge granites was estimated by a few authors, who reported differing values. Lange et al. [1] estimated the bulk S content of the OG of the main phase on the basis of 12 samples at 800 ppm, which is twice as high. Tischendorf et al. [15] later obtained a lower value of 400 ppm using only six samples. The average S content of the YG rocks was estimated at 400–500 ppm from a limited number of analyses [1, 12]. To our knowledge, there is only one estimate of arsenic content in the OG of 4.4 ± 1.6 ppm [15].

A common feature of all the estimates of metal, sulfur, and arsenic contents in the OG and YG rocks is that they were obtained using samples from granite massifs collected on the present surface or in shallow workings. No attempts were undertaken to correlate the scatter in the determinations obtained from studies of particular granite outcrops with fine differences in the compositions of the granites, procedures of sample treatment, and analytical methods. Therefore, the most reliable and comprehensive data on the concentrations of the whole series of trace metals in the Erzgebirge granites can be found not in publications focusing on particular granite outcrops but in the generalizations by Kovalenko et al. [18], Kozlov [19–21], and Tischendorf et al. [15, 22], who compared these granites with rare-

metal granites from other regions (Mongolia, Transbaikalia, and Chukchi Peninsula).

METALS, ARSENIC, AND SULFUR IN THE GRANITE OF THE AUE CUPOLA

Sampling of the Aue Granite

Vlasov [5] showed that the total thickness of fracture veins at Schlema increases toward the granite (which is clearly illustrated by the oblique section constructed by him), and most vein fractures penetrated the boundary zone of the Aue cupola and most likely drained it during ore formation. However, the uranium mineralization of the Schlema veins hardly extends beyond the productive sequence of metamorphic rocks,[4] which has a high reducing capacity and comprises more than 90% of uranium vein ores. Only very rare and low-grade ore lenses were found in some veins among the granites (cross section of such a vein, R-20, was previously published by us [24]). This is why the mine workings of all horizons entered the barren granites only when it was necessary for operational purposes and to relatively small distances from the contacts. This predefined the character of granite sampling: most granite samples were collected in workings not far from the contact of the cupola, up to 60 m in plan view (horizons 810, 945, and 1620) and 108 m in horizon 1620. Only in horizons 1305 and 1170 were samples obtained up to 305 and 968 m from the contact, respectively. The distance between sampling sites varied from a few meters to 30–50 m, most commonly 10 m. We obtained 200 samples for metals and arsenic and 44 samples for sulfur in such mine workings. Thus, our samples characterized in fact the concentrations of these elements in the granite of the Aue cupola only at various levels of its border zone with an average thickness of 120–250 m. This fact will not be pointed out further, but it should be kept in mind that in this paper the Aue cupola always refers to the portion sampled by us. In addition to the samples from mine workings and boreholes, 21 samples for Pb (Co and As were also determined, as well as Zn in two samples and S in one sample) were collected from a granite outcrop at the Aue Quarry.

The maximum number of samples (126–128) represented horizon 1170, where long (726 m) cross-cut no. 1611 cut the granite from SE to NW, and the sampling interval was extended by borehole no. 287 (242 m long). Unfortunately, this cross-cut exposed a wide zone of heterogeneous granite (almost from its mouth over 720 m along the cross-cut), which is characterized by frequent changes in rock texture, either in grain size (from coarse- to fine-grained) or in appearance–disappearance of porphyritic fabric (with orthoclase meta-

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[4] A sequence of large strongly flattened lenses and interbeds of carbonaceous schists, carbon-bearing siliceous shales, carbon-bearing hornfels, metadiabases, skarns, skarnoids, and quartz–mica schists [23].

blasts up to 7 cm in size) and large schlieren enriched in biotite and other mafic minerals (probably granitized country-rock xenoliths). More importantly, this zone exhibits extensive epigenetic alterations in the granite. These processes resulted in the development of microcline or albite in some intervals and, more frequently, the strong silicification and muscovitization of the granite and appearance of quartz and carbonate stringers and veins. Several short drifts were even run along some of these veins during exploration operations. The general character of the epigenetic alteration of granite in this zone corresponds to the maximum of dispersed muscovitization [6, 8], which is typical of the uppermost levels of the Aue cupola. These alterations caused a significant depletion of all ore elements in the granite of this zone [2, 3]. We supposed [2] that this cross-cut penetrated a zone of large postgranitic dislocations (continuation of long-lived faults of the Loessnitz–Zwoenitz tectonic zone), along which epigenetic changes extended to deeper levels than in the granite outside this zone. Taking into account these considerations, the samples taken in this cross-cut were used for the computation of average concentrations for the upper part of the Aue cupola, because the low concentrations measured in them correspond to much shallower levels (their average metal concentrations are similar to those observed in horizons 810–540 and even shallower).

Analytical Methods

Granite samples were analyzed for Pb, Zn, Cu, Ni, Co, Ag, Bi, and As at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (samples of Aue granites), and mainly at the laboratory of SGAO Vismut (some Aue granite samples and all samples from the Eibenstock massif) by arc atomic emission spectroscopy. The detection limits for particular elements were 10 ppm Zn; 1 ppm Pb, Cu, Ni, Co, and As; and 0.1 ppm Bi and Ag. The mean square deviation was 8–10%. Control analyses did not reveal any significant systematic discrepancies between the analytical results obtained at the Vernadsky Institute of Geochemistry and Analytical Chemistry and SGAO Vismut. This allowed us to use the analytical data of both laboratories together.

Bulk sulfur content was determined in 44 granite samples from the Aue granite using an AUS-7844 analyzer. The method is based on the combustion of a rock charge in an oxygen flow with subsequent absorption of the produced SO_2 by appropriate solutions and their coulometric titration on the basis of pH value. The temperature of combustion was 1200–1300°C. The error and detection limit were 5 ppm (each result is an average of 3–5 measurements).

The histograms of the concentrations of trace elements in the Aue granite exhibit a left-sided asymmetry (Fig. 1), which is not quite distinct only for silver, probably because of the small number of samples. They show several peaks and are polymodal (consist of two or more subsets with different average values) and in general correspond to a lognormal distribution. These features suggest that the average concentrations of metals calculated by us for the whole Aue massif are the results (algebraic sums) of several factors. Since the obtained values are close to the lognormal distribution, geometric means must be calculated for the characterization of concentration sets for each trace element and each depth level (at each horizon) [24]. Hereafter, we operate mainly with the geometric mean estimates of the concentrations of base metals and arsenic. However, in order to facilitate the comparison of new data for the Aue granites with previous estimates for this and other massifs (which ignored the lognormal distribution), both geometric and arithmetic means (by definition, the latter are higher) are given below for all elements.

Concentrations of Metals and Sulfur in the Granite and Their Vertical Variations

It would be impossible to present tables with all the analyses in this paper; moreover, the raw data are not very informative to the reader. Therefore, Table 3 gives the initial geometric means of element concentrations for each sampled horizon. Table 4 shows general characteristics of the mean concentrations. A comparison of the values of concentrations in particular horizons is not useful to detect regular variations in the vertical section because of the different sizes of data sets, lengths of sampled intervals, and distances between sampling sites. The situation with trace metals and sulfur is thus similar to that with the average contents of major components in particular horizons of the granite, which was discussed above. Therefore, the calculated geometric mean concentrations of metals were compared between higher rank units, the whole lower part of the Aue cupola (below horizon 1260) and the whole upper part of the cupola (above horizon 1260), which provided better insight into the vertical variations (Table 5).

Lead. The concentration of Pb in the granite samples ranged from 3 to 70 ppm. The lowest average value of 8.43 ppm was obtained for horizon 540, and the maximum value of 37.80 ppm was measured in horizon 1710 (Table 3). The arithmetic and geometric mean concentrations for the whole data set (194 analyses representing the whole cupola) are 19.8 and 16.18 ppm, respectively (Table 4). Both values are close to the average Pb concentration in crustal granites, 20 ppm [9].

However, the concentration of Pb in the upper part of the Aue cupola (Table 5) is only 40.6% of that in its lower part. The geometric mean of Pb concentration in the lower unaltered part of the cupola is 31.86 ppm (49 analyses), which is more that 1.5 times higher than the background value for granites. This implies that the initial OG preserved in the lower part of the Aue cupola is enriched rather than depleted in Pb, which was assumed on the basis of data for the whole cupola and
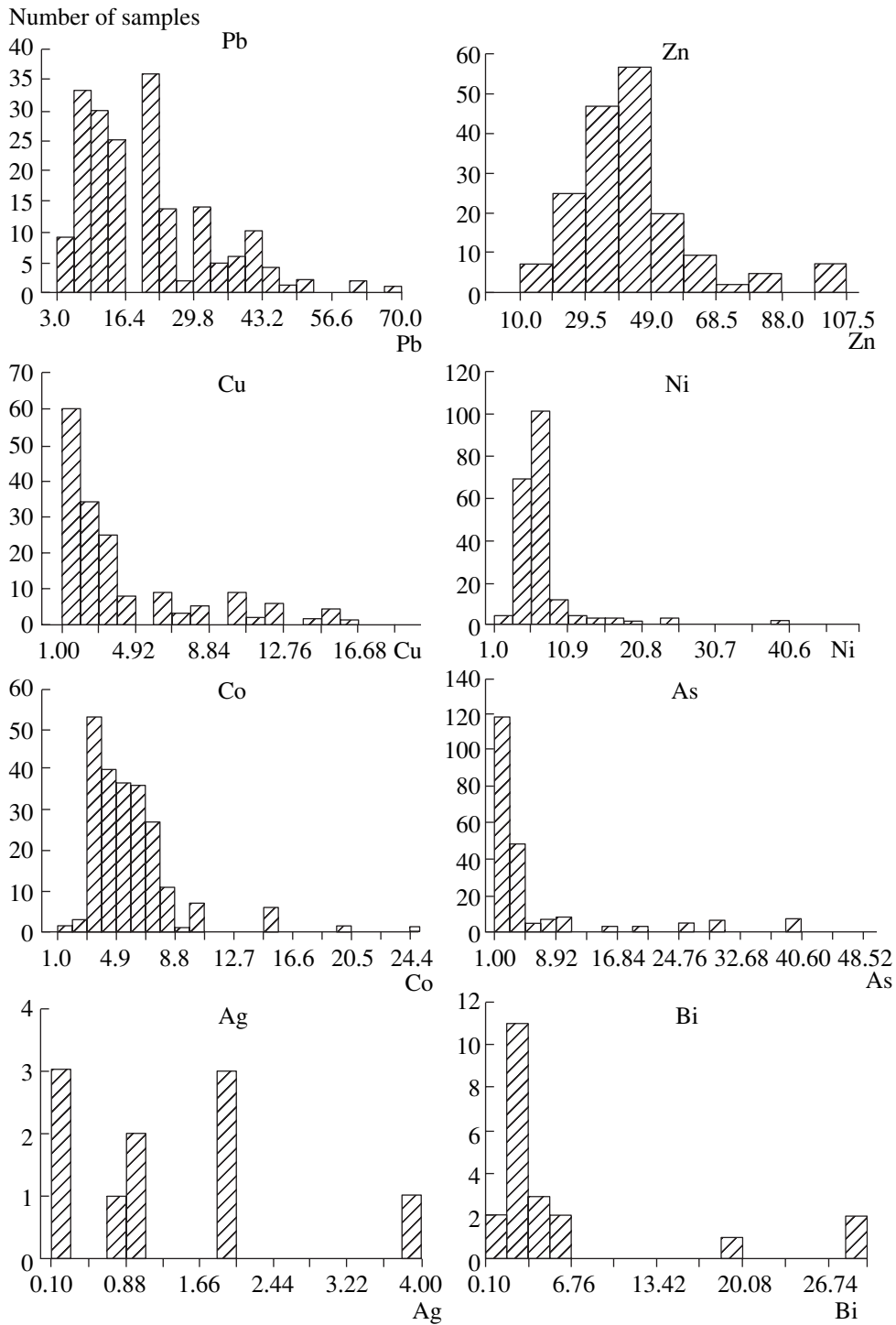
Number of samples

Fig. 1. Histograms for the concentrations of Pb, Zn, Cu, Ni, Co, As, Ag, and Bi in the granites of the Aue cupola.

the majority of previous estimates for these rocks and for the Gebirge granites as a whole. In the relatively altered upper part of the cupola, the average Pb concentration is only 12.945 ppm for 167 samples (ranging from 11 to 31.7 ppm for particular horizons), which is lower by a factor of 1.3 than the background value. The average Pb concentration of the massif is an algebraic sum of these two subsets of values (the same is true of other metals and sulfur, which will be shown below). Since the number of samples from the upper part of the Aue cupola is larger by a factor of 3.4 than the number of samples from the unaltered lower part, they dominate in the average value obtained for the whole cupola.

Table 3. Geometric mean concentrations of base metals, arsenic, and sulfur in the granites of the Aue cupola at various depth levels (various horizons relative to MS) of the Schlema deposit

Horizon	Pb ppm	Pb n	Zn ppm	Zn n	Cu ppm	Cu n	Ni ppm	Ni n	Co ppm	Co n	Bi ppm	Bi n	Ag ppm	Ag n	As ppm	As n	S ppm	S n
540	8.43	3	84.34	3	4.16	3	7.83	3	6.35	25	1.06	3	0.74	31	40	22	261.0	11
810	26.15	9	17.37	9	11.04	9	9.19	8	6.187	8	0.5	8			–	–	240.2	11
945	28.84	3	104.2	3	5.08	6	6.85	6	4.80	6	24.49	6			50.40	14	342.0	3
1125	–	–	–	–	–	–	–	–	–	–	–	–			–	–	445.0	1
1170	11.99	128	34.79	128	2.12	126	6.05	120	4.39	135	2.73	14			2.06	129	340.0	1
1305	37.12	13	81.76	12	5.02	13	10.92	12	6.89	12	–	–	–	–	5.07	12	498.0	5
1395	24.92	6	83.65	6	3.32	6	6.77	9	4.53	8	–	–	–	–	3.68	10	–	–
1620	37.80	5	–	–	13.11	5	4.57	5	3.23	6	–	–	–	–	7.10	–	227.6	5
1710	30.67	23	39.56	23	1.77	23	8.07	4	5.52	21	–	–	–	–	2.85	21	336.7	3
2270	–	–	85.0	2	11.5	2	5.72	–	6.40	–	–	–	–	–	3.92	–	–	–
Average for granites [9]	20		60		20		8		5		0.01		0.05		1.5		400	

Table 4. Characteristics of the average concentrations of metals and sulfur in the OG rocks of the Aue cupola

Element	Number of samples, n	Average, ppm	Geometric mean, ppm	min, ppm	max, ppm	Student's t factor
U	150	15.23	14.0	4.31	37	–
Th	150	24.21	21.1	3.64	51	–
W	54	16.88889	14.63668	4.0	50.0	9.43671
Sn	193	8.66368	7.56883	1.0	40.0	5.04782
Mo	188	6.64362	3.86950	1.0	150.0	16.48677
Pb	194	19.79897	16.17740	3.0	70.0	12.67408
Zn	187	46.57754	39.14895	10.0	400.0	39.86601
Cu	175	4.78857	2.74321	1.0	50.0	6.73091
Ni	205	7.97561	6.57246	1.0	100.0	10.07007
Co	225	5.59111	4.94623	1.0	40.0	3.72035
As	207	6.77295	3.01167	1.0	100.0	13.53391
Ag	10	1.32000	0.74289	0.1	4.0	1.21454
Bi	23	12.78696	4.46231	0.1	100.0	23.58675
S	44	301.8	262.566	190	498.9	–

Table 5. Comparison of the average abundances of metals and sulfur for felsic rocks in general (ppm) with geometric mean concentrations (ppm) in the granites of the Aue cupola in general, C(av); in the granites of the upper (above horizon –1260 m) and lower (below horizon –1260 m) parts of the cupola, C(u) and C(l), respectively; and their differences, C(l) – C(u), C(l)/C(u), and C(u)/C(l)

Average for granites [9]	U	Th	W	Sn	Mo	Pb	Zn	Cu	Ni	Co	As	Bi	Ag	S
	3.5	18	15	3	1	20	60	20	8	5	1.5	0.01	0.05	40
C(av), ppm	14.0	21.1	14.6	7.6	3.9	16.2	39.1	2.7	6.6	4.9	3.0	4.5	0.7	262
C(u), ppm	12.2	19.4	13.6	7.4	3.8	12.9	35.5	2.5	6.2	4.5	2.5	4.5	0.7	233
C(l), ppm	16.4	21.4	17.0	8.2	4.2	31.9	56.4	3.6	7.4	5.8	4.1	–	–	314
C(l) – C(u), ppm	4.2	2	3.4	0.8	0.4	9.0	10.9	1.1	1.2	1.3	1.6	–	–	41
C(l)/C(u)	1.34	1.1	1.25	1.12	1.10	2.47	1.56	1.45	1.18	1.28	1.65	–	–	1.35
C(u)/C(l)	0.74	0.91	0.80	0.90	0.90	0.40	0.63	0.69	0.84	0.76	0.61	–	–	0.74

The speciation of Pb in the granite of the Aue cupola was never studied. Tauson [25, 26] showed that the major portion of Pb in granites, from 61.91 to 95.5%, usually occurs in feldspars. The same can be inferred from the data by Brauer [12], if his average Pb concentrations in the major minerals of the Gebirge granites are recalculated to the proportions of minerals in the Aue granite. Such recalculations suggest that about 83% Pb occur in feldspars in the Aue granites (~49% in orthoclase and ~34% in plagioclase), whereas the remaining 17% are distributed among mafic minerals, quartz, muscovite, and accessory phases. According to the thermodynamic modeling of granite equilibrium with aqueous solutions at high T and P [6], Pb released from feldspars during even a slight epigenetic replacement by muscovite and quartz in the presence of water (pore solution) and pyrite (source of sulfide sulfur) must take away S(II) from the latter and be fixed in the most stable Pb phase under these conditions, galena.

The presence of galena constrains the total solubility of granitic Pb in aqueous (pore) solution. According to the same models, part of the galena from the oxidized granite of the upper part of the cupola is rapidly replaced by cerussite at temperatures of <240–230°C, which increases the bulk solubility of Pb.

Zinc. The concentration of Zn in our samples ranges from the minimum detection limit of 10 ppm to very high values of about 400 ppm. The latter are related to epigenetic, obviously superimposed sulfide stringers (they also show extremely high sulfur contents). The average values for particular horizons vary by a factor of 6, from 17.4 ppm in horizon 810 to 104.2 ppm in horizon 945 (Table 3). The arithmetic and geometric means of Zn concentration in the whole data set (187 analyses) are 42.58 and 39.15 ppm, respectively (Table 4), which is about 1.5 times lower than the average global estimate for granitoids [9].

The geometric mean of Zn concentration seems to change irregularly in the vertical section from one horizon to another (Table 3). However, in the relatively fresh lower part of the cupola, the geometric mean for 42 analyses is 55.43 ppm (arithmetic mean is even 61.7 ppm), which is close to the granite background (or even higher), contrary to the opinion on the depletion of Zn in the OG rocks. Zn concentration decreases in the weakly altered and oxidized granites of the upper part of the cupola by a factor of 1.6 (to 35.5 ppm, 148 analyses), i.e., to half the background value, which provides a misleading impression of Zn deficit in the OG rocks in general (Table 5). The bulk value for the cupola is also an algebraic sum of values for the two subsets; owing to the much more extensive sampling of the upper part of the cupola, this value appeared to be lower than the global average Zn concentration for felsic intrusions.

According to Tauson [25, 26], Zn initially occurs mainly in mafic minerals of granite (biotite, hornblende, and magnetite); these minerals usually contain 48–82% of the bulk metal, whereas feldspars comprise only 13–38%. Similar to Pb, the thermodynamically stable phase of Zn in the relatively unaltered granite of the lower part of the Aue cupola in contact with aqueous (pore) solution in the presence of pyrite is sulfide (sphalerite), and part of the Zn must be transferred into this phase from major minerals [6]. The presence of sphalerite controls the total solubility of Zn in this zone. In the oxidized upper part of the cupola, other secondary Zn phases, such as smithsonite and zincite, become stable and replace in part sphalerite (and control zinc release into the solution).

Copper. The concentrations of Cu in the samples of Aue granite ranged from below the detection limit (<1 ppm) to 50 ppm. The horizon average values varied from 1.77 for horizon 1710 to 13.11 ppm for horizon 1620 (Table 3). The arithmetic and geometric means for the whole Aue cupola (193 analyses) are 4.79 and 2.74 ppm, respectively (Table 4). These values are much lower (by a factor of 4–5) than the average concentration for granites, 20 ppm [9].

The geometric mean concentration of Cu in the Aue granite is also an algebraic sum of two subsets, representing the Cu richer relatively unaltered lower part of the cupola (3.64 ppm for 49 analyses) and the oxidized upper part of the cupola showing a lower average Cu abundance (2.51 ppm for 144 samples). Thus, although the concentrations of Cu in the granites from the two parts of the Aue cupola are much lower than the global average value for felsic rocks, the upper part retains only 68.9% of Cu occurring in the lower part of the cupola (Table 5).

Ryabchikov [27] argued that Cu may initially occur in sulfides in fresh granites. The results of thermodynamic modeling [6] also suggest that chalcopyrite is the most stable Cu phase in the Aue granite. During the weak alteration of granite in the upper part of the Aue cupola, part of the chalcopyrite is replaced at relatively low temperatures initially by bornite, then by chalcocite and, occasionally, cuprite.

Nickel. The average Ni concentrations in particular horizons range from 4.57 for horizon 1620 to 10.91 ppm for horizon 1305 (Table 3). The arithmetic mean for the whole sampled interval (from MS to horizon 2270) of the Aue cupola (205 analyses) is 7.98 ppm, which is practically identical to the average abundance in granites (8 ppm [9]). The geometric mean is slightly lower than the background value, 6.57 ppm (Table 4). Similar to the previous elements, the average concentration in the upper part of the cupola (6.25 ppm) is lower than that of the lower part (7.41 ppm).

Cobalt. Cobalt was analyzed in all levels where sampling was conducted. The geometric mean of Co concentration in particular horizons varied in a relatively narrow range, from 3.23 (horizon 1620) to 6.87 ppm (horizon 1305) (Table 3). For the whole Aue cupola (from MS to horizon 2270), the arithmetic mean of Co concentration for 225 analyses is 5.59 ppm, which is practically identical to the average Co abundance in crustal granites estimated by Vinogradov [9]. The geometric mean value for the whole data set is 4.95 ppm (Table 4). The average Co concentration in the granites of the upper part of the Aue cupola is 1.3 times lower than in the lower part.

Bismuth and silver. These metals were analyzed only in granites from selected horizons of the upper part of the Aue cupola, and the number of samples was much lower than for other metals. The arithmetic and geometric means of Bi concentration in this part of the cupola calculated for 43 samples are 12.7 and 4.46 ppm, respectively, and the mean Ag concentrations for 10 samples are 1.32 and 0.74 ppm, respectively (Tables 3, 4). The geometric means of Bi and Ag concentrations are much higher than the average abundances of these metals in granites estimated by Vinogradov [9], 0.05 and 0.01 ppm, respectively.

Arsenic. The concentration of As in particular samples varied by two orders of magnitude, from 1 (detection limit) to 101 ppm. The average concentration in particular horizons ranged from 2.06 ppm in horizon 1170 to 50.4 ppm in horizon 945 (Table 3). The arithmetic mean of As concentration in the granite of the whole Aue cupola calculated for 207 samples from eight depth levels is 6.77 ppm. The geometric mean is more than two times lower, 3.01 ppm (Table 4). Both values are significantly higher than the average abundance of this element in crustal granites (1.5 ppm [9]). There is a significant difference between the concentrations in various depth levels of the Aue cupola: 4.14 ppm As in the lower part of the cupola and 2.505 ppm (1.65 times lower) in the upper part (Table 5).

Sulfur. The average bulk content of sulfur was determined for 44 granite samples. Most of them (38 samples) were collected in the border zone (up to 100 m from the contact), and only six samples were taken far

from the contact (one sample from horizon 1170 was taken at a distance of 680 m from the contact). The S content of granite samples varies considerably from 40 to 609 ppm. Four samples showed much higher contents of 1400–3000 ppm, and these samples were rejected during the calculation of average contents (they contain sulfide veinlets and are also enriched in metals, especially in Zn). The arithmetic mean of S content in the whole data set, except for the four aforementioned samples with extremely high S contents, is 301.8 ppm, which is somewhat lower than the previous estimates of the average S content in the OG rocks, including the granites of the Aue cupola, and lower than the average S abundance for granitoids reported by Vinogradov [9]. However, this value is identical to the background S content proposed in the manual of IMGRE [10]. The geometric mean value is of course lower, 265.6 ppm (Tables 3, 4). The contents of S in various depth levels of the Aue cupola differ by a factor of 1.35, 314 ppm in the lower part and 233 ppm in the upper part.

Similar to other granitoids [28], the major portion of S occurs in the unaltered granite of the Aue cupola as iron sulfides, primarily pyrite, occasionally troilite, pyrrhotite, and iron arsenosulfide (arsenopyrite). However, Ricke [29] demonstrated in 1960 that sulfate sulfur may initially occur in igneous rocks. There is a limited isomorphic substitution of sulfate sulfur for silicon–oxygen tetrahedra in silicates (owing to the charge difference, probably through phosphate ions: $SO_4^{2-} \longrightarrow$ $PO_4^{3-} \longrightarrow SiO_4^{4-}$) [28]. It is possible that the initial Aue granite contained a certain amount of sulfates, and they could be more abundant in the more oxidized upper part of the cupola. According to thermodynamic models [6, 30], the epigenetic alteration of granite under the influence of aqueous thermal solutions results in the formation of small amounts of anhydrite, although sulfate was never observed in thin sections. Nonetheless, a gradual increase in the degree of S oxidation from the deep to shallow parts of the Aue cupola is very probable, taking into account the observed sharp oxidation of Fe.

In order to obtain qualitative constraints on the relations of sulfide (pyrite) and sulfate sulfur in the Aue granite, we undertook their phase analysis. With the kind assistance of I.N. Volkov (Shirshov Institute of Oceanology, Russian Academy of Sciences), T.P. Demidova conducted such a pilot analysis in 2001 for four of our samples that were collected in various depth levels of the Aue cupola 30–40 years ago. The results of phase analysis are shown in Table 6a. We were aware that during the prolonged storage of the samples in contact with atmospheric oxygen and moisture, sulfur could be partly oxidized, $S(II) \longrightarrow S(VI)$, and the initial proportions of sulfur species that existed in the granite during its sampling must be somewhat shifted toward a higher sulfate content. Judging from the high contents of S(VI) in the four samples, this was probably the case. However, another observation attracted our attention: the total content of various sulfur species, S(II) + S(II)pyr + S(VI), determined by phase analysis appeared to be significantly different from the bulk sulfur content analyzed with a higher accuracy in the same samples by the combustion of charges in an O_2 flow (standard error of ±5 ppm, and each value is the average of 3–5 measurements). The total sulfur content of two samples from the upper part of the Aue cupola was 1.2 times higher than the sum of various sulfur phases, and two samples from the lower part of the cupola yielded a difference by a factor of 1.7–1.9. This discrepancy can probably be attributed to the fact that the method of phase analysis [31] that was designed for marine sediments and proved successful for fresh silts probably detects only part of the crystalline pyrite and arsenopyrite, which are the main repositories of sulfur in the granite samples. If this is the case, the difference between S_{bulk} and bulk S in phase analysis (Table 6a) is most likely due to the underestimation of the mass of pyrite and arsenopyrite sulfur. In our opinion, more plausible estimates can be obtained by adding this difference to S(II)pyr, even despite the systematic error related to the overestimation of S(VI) content relative to the value in the initial granite resulting from the oxidation of the stored samples. In such a case, the total content of S(II), including pyrite–arsenopyrite sulfur, decreases in the granite from bottom to top (Table 6b; from 73.1 to 41.7 wt % of the bulk S content in each sample), and the total content of sulfate sulfur increases correspondingly (from 26.9 to 58.3 wt %). Since the

Table 6a. Comparison of the bulk sulfur contents with the analyses of sulfur species in the granites of the Aue cupola obtained by various methods

Sample no.	Horizon	Bulk S, ppm*	S (ppm) according to phase analysis				% of total S according to phase analysis		
			S(II)	S(II)pyr	S(VI)	Total	S(II)	S(II)pyr	S(VI)
275/66	810	395	50	40	230	320	15.6	12.5	71.9
282/20	1170	386	60	119	150	329	18.2	36.2	45.6
40/72	1620	240	10	35	80	125	8	28.0	64.0
1710/79	1710	372	70	46	100	216	32.4	21.3	46.3

* Results of the analysis of S in samples by the method of sample combustion in an O_2 flow.

Table 6b. Inferred proportions of the contents of sulfide and sulfate sulfur in four granite samples from various horizons of the Aue cupola

Sample no.	Depth from MS	% in total S	
		S(II)	S(VI)
275	810	41.7	58.3
282	1170	61.1	38.9
40	1620	66.7	33.3
1710	1710	73.1	26.9

oxidation state of our samples appeared to introduce an additional uncertainty to the phase analysis of sulfur, no attempts were made to continue this work after four preliminary tests.

Thus, in this and previous studies [2, 3], we obtained new average concentrations of 14 trace elements using large data sets for the granites of the Aue cupola, which are typical OG rocks of this region. The elements studied are characteristic of Erzgebirge deposits in general and of the Schlema and Schneeberg deposits in particular. The arithmetic means of the concentrations of some metals (Pb, Co, Ni) in the granites of the whole Aue cupola appeared to be close to their average abundances in crustal granitoids [9], whereas the arithmetic means for other elements were either lower (Zn, Cu, S) or higher (U, Th, Sn, W, Mo, Bi, and As) than the background granitic concentrations. The available data sets allowed us to establish lognormal distributions for each of these elements. Taking into account such a statistical distribution of particular analyses, geometric mean values were accepted as estimates for element concentrations (Table 4).

The most important result obtained from our data is the detection of significant differences in arithmetic and geometric means of metal and sulfur concentrations between the granites of the lower and upper parts of the Aue cupola. In addition to the elements considered in this paper, similar differences were previously detected for uranium, thorium [2], tungsten, tin, and molybdenum [3].

BASE METALS AND SULFUR
IN THE EIBENSTOCK GRANITE MASSIF

Similar to our previous studies [2, 3], the concentrations of metals and arsenic in the granites of the Aue cupola are compared with those in the younger granites (YG) of the Eibenstock massif, where these granites are not exposed on the surface. Our investigations were restricted to the Schwarzenberg region, where the northeastern contact of this granite massif plunges at a low angle beneath the Cambrian–Ordovician gneiss–schist sequence. The roof of the massif was penetrated at this site by 35 boreholes at depths of 550–1000 m from the present-day surface. After encountering the contact, the boreholes were drilled from a few tens to a few hundreds of meters (up to 250 m) below the roof of the granite massif. About 100 YG samples were collected from drill cores recovered at various distances from the contact of the massif. They were analyzed for Pb, Zn, Cu, Ni, Co, Bi, As, and sometimes Ag by arc atomic emission spectrometry at the laboratory of the former SGAO Vismut.

The YG massif is composed at the sampling site of coarse-grained, sometimes turning into porphyritic granite varieties. The granite is composed of (wt %) 30 quartz, 27 orthoclase, 40 plagioclase, 4.2 biotite, and 3 muscovite after biotite. There is no ore mineralization in the granites and country rocks, and only a slight increase in the degree of granite muscovitization was noted in the border zone.

The available published data on the average concentrations of Pb, Zn, and Cu in the YG and Eibenstock rocks are shown in Table 2. The analyses of drill cores performed for this study are listed for 10-m intervals from the gently sloping contact of the granite (Table 7). The arithmetic means of Pb, Zn, and Cu concentrations are similar to previous estimates. The value for Pb (9.0 ppm) is close to the lower limit of the previous estimates (Table 2), the concentration of Zn (40.8 ppm) is slightly lower than the previous lower limit, and that of Cu (9.8 ppm) is higher than the average for the YG. The depth interval of sampling in this massif is much smaller than the explored vertical section of the Aue granite, and it is not reasonable to make direct comparisons with the significant vertical variations of ore elements in the Aue cupola. Nonetheless, even the data from these shallow boreholes provided evidence for variations in the average concentrations of metals and arsenic in the Eibenstock massif. There are slight changes downward from the gently sloping contact of the granite with the overlying gneisses and schists, and the distribution of samples relative to the contact probably also influences the investigation of trace element systematics in the YG rocks.

We did not determine sulfur contents at various depths in this segment of the Eibenstock massif. There are some measurements in the literature. According to Lange et al. [1], the sulfur content of the Erzgebirge granites is 400 ppm, and the same average content was accepted by these authors for the Eibenstock massif. Tischendorf et al. [15] estimated the average content of sulfur in the main intrusive phase of YG as 500 ppm.

Thus, variations in the average concentrations of metals are clearly manifested along the vertical section of OG in the Aue cupola but are much less pronounced at the Schwarzenberg region, which is probably related to an order of magnitude difference in the depth interval of sampling. However, there are some indications for the existence of such variations, and more reliable evidence can be gained if deeper zones of the Eibenstock massif become accessible for sampling. This feature is

Table 7. Arithmetic mean concentrations of metals and arsenic (ppm) in drill-core YG samples from the northeastern slope of the Eibenstock massif (region of Schwarzenberg Mt.) at various depth levels relative to the gently sloping contact of granites

Depth interval, m	Pb	Zn	Cu	Ni	Co	Bi	Ag	As
0–10	6.8	41.4	11.6	8.19	5.33	7.68	1.13	2.25
11–20	7.4	39.7	10.3	10.5	4.67	8.0	1.0	2.33
21–30	6.4	41.9	9.0	5.8	3.8	12.1	1.0	1.29
31–40	7.2	48.3	9.3	5.25	5.0	3.33	–	1.25
41–50	8.3	36.7	7.7	6.5	4.5	2.75	–	1.5
51–60	8.7	33.3	5.0	5.0	4.0	3.0	–	1.0
61–70	5.0	30.0	12.7	5.33	4.33	–	1.0	–
71–80	6.4	31.0	8.2	5.6	4.6	5.0	1.0	1.5
81–90	7.14	34.3	7.0	5.0	5.0	–	–	–
91–100	7.0	40.0	4.0	4.0	3.0	1.0	–	1.0
101–110	8.6	55.0	7.5	7.0	5.5	1.0	–	1.0
111–120	10.0	55.9	8.5	7.0	10.0	1.0	–	1.0
121–130	10.0	55.0	7.0	7.5	6.0	3.0	–	1.5
131–140	10.0	54.0	6.0	8.5	6.0	1.5	–	1.0
Average, ppm	9.0	40.8	9.8	7.1	4.9	6.57	1.07	1.7
Number of samples	92	83	77	65	65	53	14	49

common for the Erzgebirge granites and, probably, for granites in general, and it would be interesting to search for its manifestation in other granite massifs.

DISCUSSION AND CONCLUSIONS

This is the final publication presenting our investigations of the distribution of 13 trace ore components, U, Th, W, Sn, Mo, Pb, Zn, Cu, Ni, Co, As, Bi, Ag, and S in the vertical section of the Aue granitic cupola and in a segment of the Eibenstock massif, which were launched in 1996. Compared with previous studies, we used a much more extensive data set (~150–225 samples for ten elements, ~50 samples for W and S, and 10–23 samples for Ag and Bi), which allowed us to refine the average concentrations of these components in the whole Aue granite massif and also reveal their regular variations along the vertical section. Therefore, the following discussion is based on both the new data on base metals, arsenic, and sulfur and previous results for U, Th, W, Sn, and Mo [2, 3].

(1) The sampling of the Aue cupola over a depth interval of almost 2.5 km from the present-day surface and the granites of the Eibenstock to depths of about 1 km allowed us to estimate for the first time the concentrations of metals at various hypsometric levels, including the deep zones of OG and YG, i.e., at the levels of the minimum influence of ancient epigenetic alterations and recent supergene processes. In other

words, we had an opportunity to sample such depth levels where the granites remained similar to the pristine composition. Such data were not previously reported, and they significantly changed our understanding of the behavior and distribution of trace components in the granites of the Erzgebirge. The concentrations of all metals, arsenic, and sulfur are significantly higher at great depths (over a vertical distance of >1 km, from horizon 1260 to horizon 2270 in the Aue cupola) than the average concentrations calculated for both massifs on the whole and much higher than many of the previously published estimates for these elements in the granites of the western Erzgebirge. Moreover, the overwhelming majority of the metals considered in this and previous papers [2, 3] (U, Th, W, Sn, Mo, Pb, Zn, Ni, Co, and As) are enriched, often strongly enriched, relative to the average abundances of these elements in felsic intrusive rocks in general. Only the average concentrations of Cu in the OG of the Aue massif remain below the background level in the deep horizons of the cupola.

(2) The analysis of metals, sulfur, and arsenic in granite samples (as well as other ore component reported previously) provided a means to observe and estimate a very important geochemical phenomenon. The weak epigenetic alterations of the upper part of the Aue cupola, so-called dispersed muscovitization [8, 6] and its red coloration with a hematite pigment (iron oxidation), did not disturb the rock texture and had minor

effects on the major-element composition of the granites. However, these processes produced much stronger transformations in the accessory component of the rocks [6] and were accompanied by the extensive removal of trace ore components dispersed in the granite. While the differences in the concentrations of major minerals and their chemical components between the upper and lower parts of the Aue cupola are limited to a few percent (Table 1), the concentrations of trace elements in the unaltered and altered granites differ by factors of 1.1–2.47 (Table 6). In principle, the phenomenon of trace metal leaching from a rock without any significant disturbance in its mineral composition has long been experimentally reproduced, when geochemists, following Tauson [25], attempted to detect the so-called free form of elements in igneous rocks. Numerous publications of the 1950s–1960s described the selective extraction of uranium and other metals from rocks by very dilute soda or soda–chloride ammonium solutions, which did not destroy (!) rock-forming minerals. These studies carefully controlled the negligible discharge into the solution of potassium and sodium (preservation of feldspars) and divalent bases (preservation of other major phases). It should be noted that the addition of small amounts of an oxidizer (e.g., H_2O_2) to the ammonium solution was necessary for the dissolution of "free" uranium and other "free" metals in these experiments. In essence, both in nature and in our models, a similar situation was reproduced without the direct addition of an external oxidizer to the initial aqueous phase but with the varying intensity of rock (Aue granite) oxidation under the influence of solution percolating through it.

A slight change in the average concentration of metals along the vertical section of the Eibenstock granite could also be related to barely discernible epigenetic transformations in the apical zone (increasing muscovitization described in the literature), although this suggestion requires additional investigations.

This phenomenon must be accounted for during the investigation of the trace-element geochemistry of granites: very slight, almost imperceptible (without special robust statistical comparisons) epigenetic alterations of the major-element composition of granites may cause much more extensive perturbations in the concentrations and speciation of trace elements in these granites.

(3) Based on the results of our investigations, trace elements were characterized for the first time by three groups (subsets) of values. One of them is the average concentrations of metals, arsenic, and sulfur for the OG rocks of the whole Aue cupola, irrespective of the position of the sampling site in the vertical section and the extent of epigenetic transformation of the rock. The second group includes the first data on the average concentrations of the same elements in the apparently unaltered (unoxidized) granites from deep horizons below 1.5 km relative to the present-day surface, which can

evidently be regarded as initial characteristics for other OG occurrences. The third group of values characterizes trace element concentrations in the apparently altered (oxidized) granites of the upper part of the Aue cupola, between 0 and 1.0–1.5 km from the present-day surface. The first group of values, i.e., the concentrations of trace elements in the cupola on the whole, is an algebraic sum of the second and third subsets. By the example of the Aue granites, we showed that the concentrations of elements in the second and third groups may be significantly different, and the values for the massif on the whole are strongly dependent on the relationships between the second and third subsets. The higher the fraction of second-group analyses in the complete set, the closer the latter to the initial trace-element composition of the granite. The smaller this fraction, the stronger the disturbance of the initial concentrations of components in the granite estimated on the basis of the complete set. Therefore, it is important to distinguish between the values corresponding to the two subsets, representing relatively unaltered and altered rocks.

(4) The above considerations led us to the following conclusion. If even a small difference of the major-element composition of granite from its initial state provokes considerable changes in the concentration of trace components exemplified by the Aue cupola, such minor differences must be accounted for during a comparison of different granite exposures. What is a reliable indicator for the initial (unaltered) state of granites? We propose to use the degree of iron oxidation for the interpretation of the trace-element systematics of granites. The coefficient of iron oxidation is readily calculated from any silicate analysis or from a phase analysis for iron. In the lowermost kilometer (horizons 2270–1260) of the Aue cupola, KO_{Fe} forms a plateau at about 5% (with a scatter of horizon average values from 3.58 to 5.73% and a weighted mean value of 4.8% for 25 analyses). It is reasonable to use the same value of 5% as an indicator of unaltered compositions of granites from other OG exposures. If deep levels are inaccessible in other exposures, and it is impossible to compare granites from various depth levels, it is instructive at least to correlate the estimates of trace element concentrations in samples from these exposures with KO_{Fe} values and compare various massifs and sites in them taking into account this indicator of redox conditions in the granites.

(5) The results obtained here suggest that tremendous amounts of ore components were removed from the upper part of the Aue cupola. The data of Table 6 can be used to calculate the losses of ore elements from the slightly altered (oxidized) upper part of the Aue cupola compared with its unaltered lower part. In order to eliminate the uncertainty in the position of the boundary of the cupola in plan view, the calculations were performed for a single sector (Fig. 2) bounded to the SW by the Roter Kamm fault dipping to the NE at
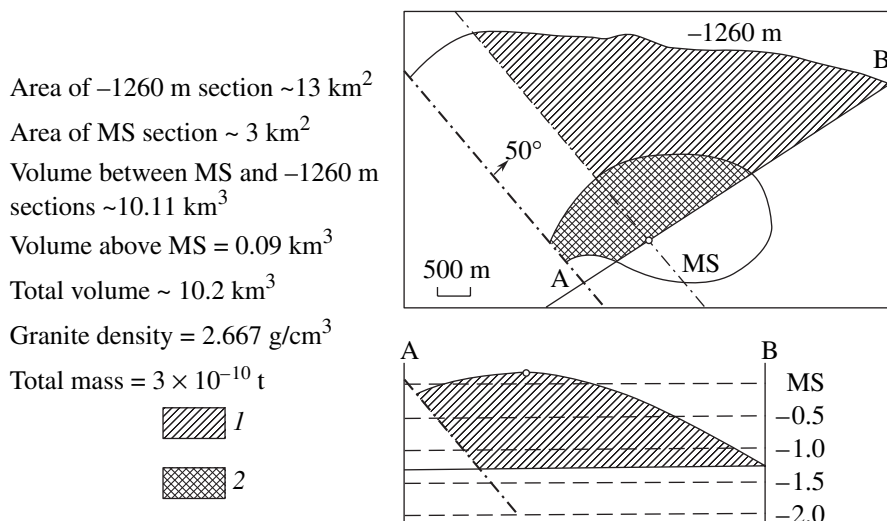
Area of –1260 m section ~13 km^2

Area of MS section ~ 3 km^2

Volume between MS and –1260 m sections ~10.11 km^3

Volume above MS = 0.09 km^3

Total volume ~ 10.2 km^3

Granite density = 2.667 g/cm^3

Total mass = 3 × 10^{-10} t

Fig. 2. Sketch of the calculated sector of the upper part of the Aue granite cupola bounded to the southwest by the Roter Kamm fault (dipping to the NW at 50°) and to the southeast by a vertical plane passing through the center of the granite outcrop (Aue Quarry) along the 60° NE azimuth parallel to the Loessnitz–Zwoenitz syncline and the projection of this sector onto the vertical plane. (*1*) Area of the section of the sector at a depth of 1260 m from the MS level accepted as the boundary between the lower and upper parts of the cupola and (*2*) area of the section of the sector at the MS depth.

50° and to the SE by a vertical plane passing through the center of the granite outcrop (Aue Quarry) parallel to the axis of the Loessnitz–Zwoenitz syncline (azimuth 60° NE). The contour of this sector at a depth of 1260 m below the MS, at the boundary between the lower and upper halves of the cupola, was constructed by the interpolation between the isohypses of –1000 and –1500 m relative to sea level on the map of the surface relief of the Erzgebirge pluton [32, 33]. It was taken into account that the trace of the Roter Kamm fault is shifted at this level to the NE by 1225 m relative to its surface trace and that the conventional zero level (MS) of the Schlema deposit occurs 330 m above sea level. The total volume of the upper part of the Aue cupola in this sector is more than 10 km^3 (calculated using the formula for a truncated pyramid, ignoring the concavity of the massif).[5] Given an average density of the granite of 2.667 g/cm^3 [34], the mass of granite in the sector is >2.67 × 10^{10} t. Multiplying this mass by the losses of metal and sulfur contents from the upper part of the cupola compared with its lower part, $C(l) - C(u)$ in Table 5, we obtain the minimum values for the masses of ore elements, arsenic, and sulfur exported from the upper part of this single deliberately limited sector (probably about one-fourth) of the Aue cupola accompanying the weak epigenetic alteration of gran-

ite. As can be seen from Table 8, the mass of each of the characteristic elements of the Schlema and Schneeberg deposits extracted from this sector is tens to hundreds of thousands of tons (only the mass of extracted Mo is ten thousand tons). Consequently, the scales of metal release from the upper part of the Aue cupola, including its Gleisberg outcrop (near Schneeberg), are much higher than their resources in the ores of the Schlema and Schneeberg deposits. It is obvious that there is a causal link between the extraction of these components from the upper part of the Aue cupola and the deposition of part of these components in the hydrothermal veins of the deposits above the Aue cupola.

(6) The low average concentrations of metals (in particular, Zn and Pb) in some granite exposures, the most probable reason for which was examined by the example of the Aue granites, were used as a basis for

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[5] The section area of the sector at a depth of 1260 m below MS is S_1 ~ 14 km^2, the section area at MS is S_2 ~ 3 km^2, and the height is h = 1.26 km. The volume of the truncated pyramid between these planes is $V = 1/3h(S_1 + \sqrt{S_1 S_2} + S_2) = 0.42 \times (14 + 6.5 + 3) = 9.87$ km^3. The top of the cupola above the MS level is 0.09 km^3 in volume. Rounding gives about 10 km^3.

Table 8. Magnitudes of the removal of metals and sulfur from the upper (above horizon –1260 m relative to MS) part of the northeastern sector of the Aue cupola related to the slight alteration (dispersed muscovitization) of OG

Element	Loss, 10^3 t	Element	Loss, 10^3 t
U	112.1	Pb	240.3
Th	53.0	Zn	291.0
W	90.8	Cu	29.4
Sn	21.4	Ni	32.0
Mo	10.7	Co	34.7
As	42.7	S	2163

the suggestion of the deficit of chlacophile elements in the Erzgebirge granites. This suggestion can hardly be admitted. As was noted above, the initial average concentrations of Zn, Pb, and other metals, except for Cu, in the unaltered Gebirge OG (probably not only in the Aue cupola) are not lower and are often higher than the average abundances of these elements in felsic rocks. Indeed, the sampling of the surface exposures of these granites, the upper zones of which were slightly affected (oxidized) by epigenetic processes, yielded low concentrations for a number of metals. However, the tremendous export of Pb, Zn, and other trace ore components from the cupolas of Gebirge granites accompanying their very minor epigenetic alterations probably provided both the decrease in the average concentrations of metals in accessible outcrops and formation of giant and high-grade uranium, rare metal, and base metal deposits above these massifs in Germany, the Czech Republic, and Slovakia. This supports the geochemically anomalous character of the OG with respect to U, W, Sn, and chalcophile elements. The situation with Cu is different: all the granites, both unaltered (primary) and altered are depleted in Cu. However, the Erzgebirge has never been regarded as a copper province, and there are no significant copper deposits in this region. Thus, Cu is the only chalcophile element depleted in the OG rocks.

ACKNOWLEDGMENTS

REFERENCES

1. H. Lange, G. Tischendorf, W. Palchen, et al., "Zur Petrographie und Geochemie der Granite des Erzgebirges," Geologie **21**, 457–489 (1972).

2. Vikt. L. Barsukov, N. T. Sokolova, and O. M. Ivanitskii, "Distribution of U, Th, and K in Granites of the Aue and Eibenstock Massifs, Erzgebirge, Germany," Geokhimiya, No. 12, 1157–1174 (1996) [Geochem. Int. **34**, 1041–1056 (1996)].

3. N. T. Sokolova and O. M. Ivanitskii, "Distribution of Sn, W and Mo in the Aue and Eibtnstock Granitik Massifs, Erzgebirge, Germany," Geochem. Int. **39** (Suppl. 2), 219–225 (2001).

4. Vikt. L. Barsukov, "Quartz–Calcite–Pitchblende Veins of the Erzgebirge and Position of Coffinite in Them," in *Problems of Applied Radiogeology*, Ed. by D. Ya. Surazhskii (Atomizdat, Moscow, 1967), pp. 150–194 [in Russian].

5. B. P. Vlasov, L. V. Matyushin, and G. B. Naumov, "Schlema–Alberoda Vein Uranium Deposit, Erzgebirge" Geol. Rudn. Mest. **35** (3), 205–221 (1993).

6. Vikt. L. Barsukov, "Modeling of Geochemical Processes during Formation of the Schlema Deposit (Erzgebirge). I. Processes in the Aue Granites," Geokhimiya (in press).

7. K. Pietzsch, *Geologie von Sachsen* (Verl. Wissenschaft, Berlin, 1963).

8. G. P. Zaraiskii, "The Conditions of the Nonequilibrium Silicification of Rocks and Quartz Vein Formation during Acidic Metasomatism," Geol. Rudn. Mest., No. 4, 294–307 (1999) [Geol. Ore Dep. **41**, 262–275 (1999)].

9. A. P. Vinogradov, "Clarkes of Chemical Elements in the Major Types of Igneous Rocks of the Earth's Crust," Geokhimiya, No. 7, 555–571 (1962).

10. *Average Concentrations of Chemical Elements in the Major Types of Igneous Rocks, Soils, and Earth's Crust (Requirements to the Execution and Results of Multipurpose Geochemical Mapping. Scale 1 : 1000000. Appendix 3.25)* (IMGRE, Moscow, 1999) [in Russian].

11. H. von Moenke, "Spurenelemente in Variskischen und Praevariskischen Deutschen Graniten," Chem. Erde. **20**, 227–301 (1960).

12. H. Brauer, "Spureneelementgehalte in granitichhen Gesteinen des Thuringer Waldes und des Erzgebirrges," Freib. Forschhf. **259**, 85–139 (1970).

13. G. Tishendorf and F. K. Schust, "Geochemical Specialization of Erzgebirge Granites," Geol. Geofiz., No. 2, 27–36 (1980).

14. G. Just, "Trace Element Studies in Granitic Rock. Sequences Southern Part of the GDR—On the Existence of A-Type Granitic Melts," Gerlands Beitrag. Geophysik **94**, 381–408 (1985).

15. G. Tischendorf, M. Geisler, H. Gerstenberger, et al., "Geochemistry of Variscan Granites of Westerzgebirge–Vogtland Region—An Example of Tin Deposit-Generating Granites," Chem. Erde **46**, 213–234 (1987).

16. W. Irber, "The Lanthanide Tetrad Effect and Its Correlation with K/Pb, Eu/Eu*, Sr/Eu, Y/Ho and Zr/Hf of Evolving Peraluminous Granite Suites," Geochim. Cosmochim. Acta **63**, 489–508 (1999).

17. H. I. Forster, "Cerite (Ce) and Thorian Synchysite (Ce) from the Niederbobritzsch Granite, Erzgebirge, Germany. Implications for the Differential Mobility of the LREE and Th during Alteration," Can. Mineral. **38**, 67–79 (2000).

18. V. I. Kovalenko, G. Tishendorf, V. S. Antipin, et al., "Geochemical Comparison of Rare-Metal Granites from the German Democratic Republic and People's Republic of Mongolia," Geokhimiya, No. 12, 1845–1856 (1976).

19. V. D. Kozlov, *Geochemistry and Ore Potential of Granitoids in Rare Metal Provinces* (Nauka, Moscow, 1985) [in Russian].

20. V. D. Kozlov, "Comparative Geological–Geochemical Estimation of the Ore Potential of Granitoids and the Productivity of W–Sn Mineralization (Central Europe, Transbaikalia, Chukchi Peninsula)," Geol. Geofiz. **41**, 857–875 (2000).

21. V. D. Kozlov, "Geochemical Evolution of the Variscan Granitoid Magmatism as Related to the Metallogeny of the Bohemian Massif" Geol. Rudn. Mest., No. 5, 459–475 (2000) [Geol. Ore Dep. **42**, 414–428 (2000)]

22. G. Tischendorf, "Zur geochemischen Spezialisirung der Granite des Westerzgebirgischen Teilplutons," Geologie **19**, 25–40 (1970).

23. V. I. Velichkin and B. P. Vlasov, "Geologic Factors Controlling the Scales of Vein Uranium Deposits in the Northern Part of the Bohemian Massif," Geol. Rudn. Mest., No. 5, 400–412 (1994).

24. W. C. Krumbein and F. A. Graybill, *An Introduction to Statistical Models in Geology*, (McGraw-Hill, New York, 1965; Mir, Moscow, 1969).

25. L. V. Tauson, *Geochemistry of Trace Elements in Granitoids* (AN SSSR, Moscow, 1961) [in Russian].

26. L. V. Tauson, *Geochemical Types and Ore Potential of Granitoids* (Nauka, Moscow, 1977) [in Russian].

27. I. D. Ryabchikov, *Thermodynamics of the Fluid Phase of Granitoid Magmas* (Nauka, Moscow, 1975) [in Russian].

28. V. V. Shcherbina, "Geochemistry of Sulfide Sulfur," in *Geochemistry and Mineralogy of Sulfur* (Nauka, Moscow, 1972), pp. 9–15 [in Russian].

29. W. Ricke, "Ein Beitrag zur Geochemie des Schwefels," Geochim. Cosmochim. Acta **21**, 35–80 (1960).

30. Vikt. L. Barsukov and N. T. Sokolova, "Hydrothermal Alteration of Host Rocks at the Schlema Uranium Deposit, Erzgebirge, Germany. I. Principal Geochemical Characteristics," No. 1, 55–77 (2000) [Geochem. Int. **38**, 49–68 (2000)].

31. N. N. Zhabina, *New Methods of Sulfur Determination in Marine Sediments* (Inst. Okeanol. AN SSSR, Moscow, 1985) [in Russian].

32. *Metallogenetische Karte Erzgebirges*, Ed. by J. Wasternack, G. Tischendorf, K. Posmorny, and M. Stemprok (1974).

33. G. Tischendorf, J. Wasternack, H. Bolduan, and E. Bein, "Zur Lage der Granitoberflache im Erzgebirge und Fogtland," Z. Angew. Geologie **11**, 410–425 (1965).

34. *Short Reference Book on Geochemistry*, Ed. by G. V. Voitkevich (Nedra, Moscow, 1977) [in Russian].