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On the Possibility of Analytical Determination of Structurally Bound Gold in Sulfide Minerals

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Abstract—The idea of a statistical analysis of the distribution of hydrothermally synthesized single sulfide crystals using their gold contents is developed specifically to distinguish the structurally bound gold component. Mercury was taken as a model example. Similar to gold, mercury shows reduction-aided chemisorption on sulfides, but its speciation can be directly determined by thermal atomic absorption analysis. It was ascertained that the structurally bound component is best characterized by a set of the lowest values of element concentrations with a variation coefficient no higher than 20% (not accounting for the random error of determination). Proceeding from this result and from previous data on Au distribution, a scheme was elaborated to process the analytical results for individual crystals in order to characterize the structurally bound Au component. The main requirement for the analytical method—a combination of a low detection limit and high accuracy—is met by atomic absorption spectrometry with electrothermal atomization of liquid or solid samples. The optimum conditions of analysis were determined for sulfide minerals (pyrite, galena, and greenockite). Some modifications of the method were compared, which demonstrated a reasonable agreement for both low and high Au contents. The application of the method of direct Au determination in solid samples revealed difficulties in the determination of the structurally bound Au component at high Au concentrations close to the saturation limit, and it was necessary to analyze fragments of crystalline individuals. A more promising variant of the experimental procedure includes the investigation of phase correspondence in gold-bearing systems with Au-under-saturated minerals. The perspectives of the direct determination of Au speciation by the method of a stepwise increase of atomization temperature of solid samples are discussed.

INTRODUCTION

The discrimination of the structurally bound admixture of a trace element is the most complicated and important stage in any experimental study of microisomorphism or endocrypty [1]. Noble metals, especially gold, are typical trace elements, and this issue relates to them, because the structurally bound form often accounts for a small fraction of the total concentration. As a consequence, there is not yet any reliable evidence on the limits and speciation of gold even in the most important mineral-carriers [2].

This study is based on the assumption that the hydrothermal synthesis of gold-bearing sulfide minerals may produce crystals with a certain gold form predominating. At high-pressure and high-temperature hydrothermal conditions, only strongly sorbed forms of the element connected with surface defects can be retained on the surface of a growing crystal [3]. Only these species can be incorporated as volume defects into the volume of the crystal during its progressive growth. The lowest Au contents must be characteristic of conventionally "ideal" crystals, in which structurally bound gold is predominant. The term conventionally ideal crystals is used for crystals free of defects appro-

priate for the nonstructural forms of Au, although in other respects they could be far from perfect. In other words, we believe that in the products of any experiment, a series of crystals can be distinguished that are free or almost free of active centers or defects (without specifying for the moment their particular types) responsible for the presence of nonstructural gold species. In this paper, we characterize the methodic realization of such an approach to the investigation of Au incorporation into sulfide minerals.

SYNTHESIS OF GOLD-BEARING SULFIDES

Sulfide minerals were obtained under conditions approaching equilibrium, which was attained using a small temperature gradient (consequently, a low oversaturation in the growth zone), a relatively high temperature (500°C), and the preliminary isothermal homogenization of the system [4]. In order to vary the Au content in fluid and, consequently, in crystallizing sulfides, we added small amounts of As or Se, which are known as gold "conveyors" [4]. In this study, crystals of galena, greenockite, and pyrite were investigated in the associations $\text{FeS}_2 + \text{CdS}$ and $\text{PbS} + \text{CdS}$ in order to determine the limits of Au incorporation into pyrite and

galena. The synthesis was carried out in 10% ammonium chloride solution at a pressure of 100 MPa. The experimental procedure was described in detail in our previous publications [2, 4, 5].

Gold was analyzed in the experimental products that met special requirements [2], namely, the spontaneous formation and growth of at least several hundred crystals to a final size of 1–3 mm. No less than 15 of the most perfectly faced crystals were selected for analysis. The crystals were 1–2 mm in size and displayed smooth clean faces completely free of surface contamination from fine-grained crystalline quench phases or surface ingrowths.

ANALYTICAL METHODS

General Premises and a Model Example

In order to divide up a set of individual crystal analyses into classes corresponding to particular forms of element occurrence, it is necessary to define the number of classes and boundary conditions in order to assign each analytical point to an appropriate class. Cluster analysis provides an algorithm for the solution of similar problems [6], but in our case, it was difficult to eliminate the superposition of empirical conditions characteristic of particular forms. Let us begin with the number of classes. The application of autoradiography [5], X-ray spectral microanalysis [4], and thermal atomic adsorption spectrometry [7, 8] to hydrothermally synthesized sulfides and magnetite with minor Au, Hg, or Cd allowed three basic forms of trace element occurrence to be distinguished: structural, sorption, and mineral proper. This is generally similar to the well-known geochemical classification of trace element forms by Shaw [9]. In the case of gold, particles and films (islands) of native gold formed through reduction-driven adsorption on the surface of sulfides can be classified as an "intermediate" form in a certain sense [10–15]. It is known that such a process takes place even if the solutions are undersaturated in gold [16]. However, experiments demonstrated that Au⁰ particles may be rather large and be confined to macroscopic defects on the surface or in the volume of crystals (cracks, growth steps, macroblock boundaries, etching pits, etc.). They also may be smaller, and, in that case, they will disguise other forms, including the structural one. Nonetheless, gold that passed from fluid into the crystal both through chemisorption with the participation of element conveyors as chemical compounds [4] and by reduction-driven adsorption on electrochemically active centers must be distributed less homogeneously in comparison with the structurally bound gold, because the distribution of sorption forms is strongly affected by contingent factors (surface defects, position of the face with respect to parent solution, local oversaturation at the crystal–fluid interface, etc.). The role of singular centers on the surface was repeatedly pointed out. For instance, Khachatryan and Lunina [17] studied the

stability of hydrous sols of metals and observed the coagulation of fine dispersed metallic particles only at certain areas on the surface of large oxide grains (with the highest defect density?).

Nowadays, there is no data allowing a strictly quantitative treatment of this problem with application to gold. However, some insight can be gained using mercury as a model example, because it also shows reduction-driven chemisorption on sulfides under hydrothermal growth conditions [18]. The study of mercury is of special interest, because in this case, it is possible to separate isomorphic and sorption forms and examine the distribution of each form separately in a set of individual crystals under investigation. Such a discrimination can be made most precisely with galena, which shows single-mode easily resolved thermal peaks of the release of sorption and isomorphic mercury. This allows the use of Hg-bearing galena for the calibration of an apparatus for the thermal atomic absorption analysis (TAA) of mercury speciation [7].

In order to obtain the statistical parameters of the distribution of mercury forms from a set of individual crystals, we synthesized crystals of coexisting galena and sphalerite with small amounts of mercury sulfide in the system. The standard procedure of hydrothermal synthesis in titanium containers was employed with 10% NH₄Cl solution, a temperature of 450°C, a temperature gradient of ~0.4°C/cm, and a total pressure of 100 MPa [18]. When possible, mercury was analyzed in euhedral galena crystals, 1–2 mm in size, showing smooth clear faces. If there were few individual crystals, small intergrowths of 2–3 individuals with a predominant development of one crystal were used. It was not necessary to carefully remove sphalerite, because the segments of isomorphic mercury release from galena and sphalerite do not overlap in TAA, and the amount of sorption mercury in sphalerite is lower than that in galena. Thus, a small admixture of the former do not interfere with the analysis of the latter. We decided to work with a two-mineral association for several reasons. First, the strong fractionation of isomorphic mercury into sphalerite enabled us to obtain a wide spectrum of Hg contents in galena without the formation of a mercury phase, because the excess Hg was always consumed by sphalerite. Second, it was possible to calculate the content of isomorphic mercury in galena from its content in sphalerite and the well-known value of the partition coefficient [18]. The analyses were carried out on a TAA device, which was described in detail elsewhere [7]. Every crystal or intergrowth was ground under ethanol to a grain size of ~0.01–0.05 mm, and a microscopic charge was placed into a platinum boat. As the boat was heated at a rate of ~7°C/s, the absorption signal from the spectrometer and sample temperature were registered simultaneously in an analytical experiment. The thermal peaks of mercury discharge were recorded by a two-coordinate potentiometer. The area under the discharge curves was calculated by an automatic integrator, which allowed us to determine the

Table 1. Results of Hg determination for two occurring forms (sorption and isomorphic) in monocrystals and small intergrowths of galena synthesized in the system PbS–ZnS–HgS–NH₄Cl–H₂O at 450°C and 100 MPa

No.	Charge, mg	Hg, ppm			
		sorption	isomorphic	Σ**	
				total population	set of minimum values
1	0.355	9.6	N. d.	11.9	
2	0.72	3.2	2.7	5.9	5.9
3	1.435	7.0	N. d.	9.3	
4	1.015	1.6	3.4	5.0	5.0
5	0.29	16.9	N. d.	19.2	
6	0.34	21.5	N. d.	23.8	
7	0.36	5.6	N. d.	7.9	7.9
8	2.65	6.3	1.6	7.9	7.9
9	1.30	9.5	N. d.	11.8	
10	1.615	8.8	N. d.	11.1	
11	1.335	10.9	1.6	12.5	
12	1.360	12.6	3.0	15.6	
13	2.665	6.0	1.6	7.6	7.6
14	0.415	17.1	N. d.	19.4	
15	4.82	4.6	0.9	5.5	5.5
16	1.46	8.8	N. d.	11.1	
17	1.96	7.9	N. d.	10.2	
18	1.145	10.7	2.0	12.7	
19	0.785	8.4	N. d.	10.7	
20*	3.325	3.8	2.6	6.4	6.4
21*	6.38	9.9	2.4	12.3	
22*	3.19	19.0	N. d.	21.3	
23*	5.125	14.5	3.2	17.7	
24*	5.055	3.2	3.0	6.2	6.2
25*	4.19	22.8	2.3	25.1	
\bar{x}		10.0	2.3	12.3	6.6
S^2		33.43	0.56	33.66	1.02
$V_x, \%$		58	32	47	15

* Intergrowths.

** If Hg_{isom} was not determined (N. d.), the sum Hg_{sorp} + \bar{x}_{isom} was used.

Hg concentration in each form using the calibration curve [7].

Of course, the distribution of mercury species is not fully analogous to that of gold. There is a significant difference in that Hg is easily sorbed physically from a fluid containing Hg_{aq}⁰; i.e., every crystal contained some sorbed mercury. In contrast, there was a negligible amount of Au_{aq}⁰, and the chemical adsorption that is characteristic of gold is more selective and sensitive to

crystal defects. Thus, the model example of Hg only allows us to develop general approaches to the distribution of Au species, such as the choice of the best algorithm for the classification and determination of the admissible intervals of the statistical characteristics of distribution of the sorption and isomorphic forms of the element. Let us consider Table 1 as an example. It presents the analyses of 19 individual crystals and six small intergrowths of galena obtained in a single experiment. This example was selected, because, in this case, the contents of isomorphic Hg were ~2–3 ppm, and

both forms amounted to 5–25 ppm. Thus, the problem that was formulated in the introduction has been solved, namely, the ability to distinguish the structurally bound form of an element on the background of its other, more abundant, form. Table 1 shows that the content of isomorphous mercury could not be determined in some instances. This was related to its wide and sometimes diffuse thermal peak, which prevented the calculation of the peak area by the automatic integrator. The “sorption” peak is normally more distinct although often asymmetrical.

The data in Table 1 lead us to the following inferences. First, isomorphous mercury is distributed more homogeneously in galena than its sorption form and the total concentration of both forms. It should be taken into account that for such low concentrations, the error of determination increases considerably and is no lower than 10% [7]. Consequently, the variation coefficient determined for isomorphous Hg is probably the upper limit for this form. The elimination of random error yields 22%, which is very close to a value of 20%, which was proposed previously for the structurally bound gold [5] on the basis of the combined data of the quantitative analytical methods and autoradiographic investigations of crystals. Thus, the example of mercury confirms that the value of the variation coefficient for the concentration of structurally bound gold can be assessed as 20%, and higher heterogeneities can be ascribed to the presence of other forms. Second, taking a sample of the lowest contents of total Hg and limiting it by the aforementioned condition of 20% maximum

deviation from the sample mean $\left(\frac{x_i - \bar{x}}{\bar{x}} \leq 0.2\right)$, we can

obtain an approximate estimate for the true concentration of the isomorphous form. This procedure requires a consideration of the uncertainties and the peculiarities of mercury behavior, which makes it not quite similar to gold and many other elements, and that sorption mercury occurs in all crystals without exceptions and its concentration under experimental conditions is never lower than 2–3 ppm (Table 1). Thus, the model example of mercury shows that the structurally bound portion of a trace element can be estimated as a first approximation from a sample of the minimum values of bulk concentrations obtained from the analysis of a sufficiently large number of individual crystals from each experiment. However, in the case of Au, the procedure of processing analytical data should be refined. There are various recommendations on the volume of the sample of minimum values [6], but we believe that the most reasonable is the utilization of the experience directly related to the behavior of gold in hydrothermal sulfide systems. Autoradiography and electron microprobe analyses [4, 5] demonstrated that about four-fifths of the crystals do not bear inclusions of gold-bearing phases, which could have been detected by these methods (the best spatial resolution of both methods is about tenths of a micrometer). Furthermore, the analysis of

great bodies of data obtained for the system FeS₂–CdS–Au [2], and, recently, CdS–PbS–Au, demonstrated that the final sample, which was correlated with the structurally bound form of Au, contained from one-third to half of the initial values. This allows us to propose the following tentative scheme of data processing. The identification of the structural form begins from a sample of minimum values (n_1) comprising one-third of the total population, for which the sample mean is determined, \bar{x}_1 . Then, the sample is supplemented by values, which could be assigned to the structural form on the basis of the 20% criterion (see above) and 10% error in the reproducibility of determination (n_2). Thus, the sample is expanded on the expense of values differing from \bar{x}_1 by no more than 30%. Then, we determine the new mean value \bar{x}_2 and the error of reproducibility, which is regarded as an analytical error of the method of determination of the structurally bound Au admixture. Note that n_2 can be both larger and smaller than n_1 ; i.e., not only expansion but also reduction of the sample is possible if some values do not meet the applied criterion.

Analytical Techniques

Tauson *et al.* [2] studied the distribution of Au forms in sulfide systems and found that the best results were provided by a set of 15–20 crystals, ~1–2 mm in size. It should be kept in mind that if the crystals are smaller and more numerous, then it is, in principle, more likely that “ideal” individuals containing only the structurally bound Au will be found. However, the mass of an individual crystal may not be sufficient to provide an Au content higher than the analytical detection limit. This is especially important if, in order to lower the fraction of crystals contaminated by other Au forms, the growth experiment is carried out in a region far from the potential saturation of the system in gold (at low abundances of element conveyors). Thus, the main requirement for the analytical method must be a low detection limit in combination with high accuracy. This requirement is met by the method of atomic absorption spectrometry in its electrothermal variant with a graphite furnace-atomizer (AAS ETA). Two modifications of this method were utilized in this study: with the preliminary acid decomposition of crystals and Au determination in liquid solution (AAS ETAL) and without decomposition, i.e., direct determination in a solid specimen (AAS ETAS). The latter has two obvious advantages. First, the determination of trace elements directly in mineral grains allows the elimination of contamination from chemical reagents used in the analytical procedure (which is not very important for gold). Second, the lack of the dilution effect, which is inevitable upon using solutions, allows the determination of very low element concentrations even in small crystals, grains, or their fragments (<1 mm). Unfortunately, these advantages have the reverse effect: at relatively high Au contents

(>50 ppm), even small charges (<50 µg) yield very high absorption values, which do not allow quantitative analysis and require the addition of a special diluting powder. This introduces problems related to the purity of the powder and its homogeneous distribution.

The measurements by AAS ETAL were carried out at the Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences, and those by AAS ETAS, at the Institute of Environmental Geochemistry, Heidelberg University. The results are presented and compared in the following section. Here, we consider in more detail the techniques of the analytical experiment.

The analysis of Au by the AAS ETAL method was performed using hydrochloric solutions. Greenockite crystals were dissolved in HCl; galena, in diluted HNO₃; and pyrite, in HCl + KClO₃; heating was applied in all cases. We used a Perkin-Elmer M 503 atomic absorption spectrometer equipped with a deuterium corrector of background absorption and a graphite atomizer (HGA-72, -74). The analysis was carried out in an Ar flow, and the amplitude of signal change was registered by a Hitachi 056 potentiometric recorder. A lamp with a hollow cathode (Russia) was used as a source of radiation. Standard gold chloride solutions were used for calibration. They were prepared by the dilution of a basic solution with a concentration of 1000 µg/l. The scheme of analysis included four steps (temperature in °C and step duration in seconds are shown in parentheses): drying (105, 25), pyrolysis (300, 25), atomization (2500, 5), and annealing (2700, 2). The gas regime was at maximum at all steps, except the atomization step, which was performed in a regime of gas halting. The detection limit for Au was 0.2 ppb at an accuracy of ±10% [2].

The determination of Au in solid specimens by AAS ETAS was performed on an Analytik (Jena) AAS EA5 device which was combined with a Sartorius analytical balance (measurement error of ±5 µg) and equipped with a special system for loading solid particles into the graphite furnace. It consisted of a metal holder on slides, in whose clamp a specimen carrier (a boat of heat-resistant graphite) was fixed. The charge was loaded into the boat, which was fixed by the holder and inserted into the graphite pipe (furnace), where pyrolysis and atomization of the specimen occurred in sequence. Temperatures below 1000°C were determined from the voltage, which was automatically selected on the basis of the value prescribed in the program. Above 1000°C, temperature was corrected on the basis of the intensity of the infrared radiation of the graphite heater: a special IR sensor recorded the value of the radiation intensity and delivered a command to increase or decrease the voltage, which was set in the program for the attainment of the target temperature. The analytical procedure corresponded in general to the scheme used for solutions and included the following main steps: drying and elimination of adsorbed water

from the specimen; pyrolysis, when organic contaminants were burned out, volatile admixtures were removed, and partial decomposition of the specimen material took place; the autozero step, when thermal equilibrium was attained in the graphite furnace; atomization and transition of the element studied into the state of atomic vapor; and "purification" or annealing, when, owing to an increase in the temperature and gas flow rate, the volume of the furnace and specimen carrier were purified from the remains of the specimen. The concentrations were calculated automatically in the selected mode of either "Peak height" or "Peak area." The later parameter is preferable in many cases [19] but not always. As will be shown, at low Au contents (in the region of the linear dependence of absorption on the number of atoms), Au concentrations in galena and greenockite calculated from the peak height show better convergence with values obtained by AAS ETAL. On the other hand, in the case of solid sulfide specimens, there are a number of features that must be accounted for in the thermal scheme of the analytical experiment. The most important of them is an intense background, which often completely suppresses the valuable signal. The background signal is yielded by sulfur released from sulfides under the influence of the high temperature necessary for the decomposition of minerals. This effect is especially strong for pyrite. The reaction with the graphite of the atomizer and atmospheric oxygen (the furnace is not a closed system) results in the appearance of smoke and a significant unspecific absorption of the radiation of the cathode lamp. In order to reduce this effect, we increased the temperature of the pyrolysis stage, which was aimed at removing the sulfur from the graphite pipe before the beginning of the measurement stage of analysis. The stable removal of sulfur was attained when two sequential pyrolysis phases at temperatures of 1250 and 1700°C were introduced. The first stage corresponded presumably to the transformation of pyrite into pyrrhotite ($\text{FeS}_2 \rightarrow \text{FeS}$, the first release of excess sulfur), and the second, to pyrrhotite decomposition (the release of residual sulfur). For the same purpose, i.e., to attain stable sulfur removal, the maximum regime of gas flow was applied at the autozero stage and the minimum regime (instead of the recommended regime of gas halting) was used at the stage of atomization. This allowed us to eliminate the unfavorable influence of the background signal. The investigations of gold-bearing pyrite showed that the extensive transition of gold into the atomic state began at 2100°C and continued up to 2800–2830°C. Three main temperature regions of absorption were distinguished: 2200–2400, 2500–2600, and 2650–2800°C. The relatively high gold contents in the pyrite studied often prevented the formation of distinct peaks, which overlapped with one another forming broad plateaulike absorption patterns. We think that the character of this Au behavior could be related to the diversity of its forms occurring in pyrite, but this question requires an additional detailed study.

It is not clear, what happens to the various gold forms during the thermal transformations $\text{FeS}_2 \rightarrow \text{FeS} \rightarrow \text{Fe}$ at high temperatures and heating rates. The extended temperature interval of gold transition from pyrite into an atomic state hampers the choice of an optimum temperature program, and the high contents of nonstructural gold result in the appearance of the aforementioned wide absorption peaks. Furthermore, nonstructural gold released from pyrite is probably capable of reacting with graphite on the surface of the sample carrier. After the analysis of crystals containing more than 100 ppm of Au, there was no complete purification of the surface of the sample carrier, which required additional annealing (often 4–5 cycles). No traces of the initial crystal were visually observed on the sample carrier. The total mass of removed gold was 0.4–0.7 ng or 3–5% of the total gold determined in the specimen. It is obvious that under high-temperature conditions (>2400°C) and for a high content of nonstructural Au, some gold is retained on the graphite surface. Correct measurements are possible if gold concentration in pyrite is no higher than 10–15 ppm. Therefore, the data on pyrite in this paper are presented fragmentally.

The assessment of the optimum parameters of the atomization program for greenockite and galena was carried out using the same scheme as for pyrite. Individual crystals of the minerals were placed into the furnace, and the changes in the value of absorption were observed in the course of a stepwise increase of atomization temperature. The conditions of sulfur removal from the volume of the graphite furnace were determined preliminary by the method of selecting the pyrolysis temperature: 1300 and 1200°C for galena and greenockite, respectively. In order to eliminate completely the possible influence of residual sulfur, the regime of gas flow was set to maximum at the autozero stage and to minimum at the atomization stage. In the course of investigations, it was found that the extensive transition of Au into an atomic state began at 2000 (greenockite) and 2200°C (galena), and the maximum values of absorption were observed at 2200 and 2300°C, respectively. At these temperatures, the mineral grains were completely evaporated. Because of this, the further temperature increase up to 2400°C resulted in a sharp decrease in the value of absorption. In contrast to pyrite analysis, no contamination phenomena of the surface of the sample carrier were observed in this case. The Gaussian shape of the peaks and the ratio of the peak height to its area at temperatures of the maximum Au release suggest that the described atomization conditions were optimum. In contrast to pyrite, gold atomization from greenockite and galena occurred in a narrower interval and was not accompanied by the appearance of a series of absorption peaks. This allows us to suggest that the analysis of these sulfides for Au and the determination of structurally bound gold can be performed with a degree of reliability no worse than at the use of solutions. Note that the detection limit for Au in the AAS ETAS method is

about 0.1 ppm. The AAS ETAL method is inferior in sensitivity owing to at least a thousandfold dilution at the use of very small charges (≥ 0.2 ppm, depending on the real dilution). Moreover, as was mentioned above, the analysis of solid specimens shows a number of advantages: rapidity (the sample decomposition operation is missing); lack of contamination by chemical reagents; and the possibility to analyze heterogeneities in the distribution of the element even within a single grain owing to the very small amount of matter necessary for the analysis, from 0.1 to 2–3 mg. The main drawback of the method is the small concentration interval appropriate for direct quantitative measurements (0.1–50 ppm); the analysis of higher contents requires the use of a special diluting powder, and, at very small values of charges, it is very difficult to provide the homogeneity of the mingled materials. It is obvious that for the analysis of crystals with high gold contents (>50 ppm), the AAS ETAL method is preferable, because the necessary solution concentration is easily attained by dilution. On the other hand, AAS ETAS is more adequate for the investigation of very small crystals (<0.5 mg) and crystals with low Au contents (~ 1 ppm). Thus, the compared methods can efficiently supplement each other.

RESULTS AND DISCUSSION

Tauson *et al.* [2] determined the saturation limit of Au in hydrothermally synthesized pyrite at 500°C and 100 MPa as 3 ± 1 ppm and demonstrated that all higher Au contents reported in previous publications were related to nonstructural forms. Our AAS ETAS analyses support this conclusion. The described procedure of polyphase atomization allowed us to establish that even at the highest bulk Au contents (>200 ppm), there were grains in the specimens (although rare) containing only 2–5 ppm Au. The data obtained also allowed us to distinguish grains with different characters and shapes of absorption peaks. About one-third of the crystals showed a plateaulike peak, and the Au contents calculated from the peak area were from ~ 100 to ~ 300 ppm. Another third of the grains showed several modes of the absorption curve (2–3) and slightly lower Au contents. Finally, the remaining grains are conspicuous in having a single peak and the lowest Au contents (<50 ppm), which suggests the lowest fraction of nonstructural Au in these grains. Unfortunately, we do not yet know if a particular sequence of peaks can be directly correlated with a certain form of element occurrence. Such a relationship probably exists for pyrite. However, it is necessary to explain why Au of various forms is transformed into an atomic state at different temperatures, which requires special experiments. Nonetheless, our data obtained from the investigation of pyrite crystals support the feasibility of the proposed approach based on the statistical processing of grains with the lowest Au contents.

Table 2. Comparison of analytical results for structurally bound Au in hydrothermally synthesized sulfide crystals (CdS–PbS–Au system) obtained by the methods of solution analysis after acid decomposition of the crystals (L) and direct determination in solid specimens (S)

Specimen no.	Method*	Sample volume**	Set of minimum values, n_2	$\bar{x}_2 \pm \sigma$
MA9-4 galena	L	$N = 19, n_1 = 6; n_2 = 8$	5.6; 3.7; 4.3; 5.5; 2.4; 5.7; 5.7; 5.7	4.8 ± 1.0
	S_a	$N = 17, n_1 = 6; n_2 = 9$	6.6; 10.1; 7.9; 7.1; 8.3; 10.3; 10.7; 10.8	9.2 ± 1.3
	S_h	$N = 17, n_1 = 6; n_2 = 5$	4.5; 4.8; 3.6; 4.2; 6.0	4.6 ± 1.3
MA9-4 greenockite	L	$N = 15, n_1 = 5; n_2 = 4$	1.0; 2.9; 1.5; 2.8	2.0 ± 1.4
	S_a	$N = 9, n_1 = 3; n_2 = 3$	0.3; 0.7; 0.6	0.5 ± 0.5
	S_h	$N = 9, n_1 = 3; n_2 = 3$	0.8; 0.6; 1.3	0.9 ± 0.9
MA9-6 galena	L	$N = 20, n_1 = 7; n_2 = 5$	1.2; 1.8; 5.0; 5.2; 4.0	3.4 ± 2.3
	S_a	$N = 18, n_1 = 6; n_2 = 4$	1.0; 0.4; 0.2; 1.4	0.8 ± 0.9
	S_h	$N = 18, n_1 = 6; n_2 = 4$	0.6; 0.2; 1.7; 2.0	1.1 ± 1.4
MA9-6 greenockite	L	$N = 19, n_1 = 6; n_2 = 5$	0.8; 1.4; 1.2; 1.5; 1.1	1.2 ± 0.3
	S_a	$N = 7, n_1 = 2; n_2 = 2$	0.6; 1.4	$1.0 \pm 2.5^{***}$
	S_h	$N = 7, n_1 = 2; n_2 = 3$	1.4; 1.5; 1.5	1.5 ± 0.5

* L, solution; S_a , solid specimens, calculation from peak area; and S_h , solid specimens, calculation from peak height.

** N is the total population; n_1 and n_2 are the first and second sets of minimum values.

*** For a confidence limit of 90%, in other cases, 95%.

More detailed data were obtained for galena and greenockite. In those cases, it was possible to comprehensively compare the "solution" and "solid-phase" variants of the method. The most interesting region is that of low Au contents where Au determination does not require dilution by blank material. Such crystals were obtained owing to the presence of excess lead in the system. The conditions of structurally bound gold determination and the statistical parameters of the samples are shown in Table 2; the calculations were carried out using the procedure described above. It can be seen that independent analyses yield similar results, especially if the concentrations in solid specimens are calculated from peak height. This suggests that the optimum conditions of element atomization were applied. The difference between the estimates of concentration from the parameters "Peak height" and "Peak area" results from the fact that absorption peaks are broader during the analysis of minerals compared with the calibration solutions, because the discharge of gold atoms from minerals is more extended in time. The data on greenockite are somewhat more ambiguous, which is related to the behavior of CdS grains at "thermal impact": they were often cracked and lost from the furnace volume before the beginning of the measurement stage. Because of this, the set of greenockite analyses is not sufficiently representative. The strength of this effect was diminished by the correction of the gas flow (reduction) and slower specimen heating up to the pyrolysis stage. The situation was additionally complicated by the scarcity of good crystals for measurement, which resulted in the statistical unrepresentativeness of the greenockite data. However, the results on Au speci-

ation obtained by different variants of the method were compatible in the majority of cases and consistent within the error of reproducibility (Table 2). Finally, the results of the investigation of the standard greenockite sample are instructive. This sample showed the highest content of structurally bound gold for its synthesis conditions, 50 ± 10 ppm [2, 5]. Every crystal was split into several fragments, and three of them were analyzed. Table 3 shows that a concentration lower than 50 ppm was found only once. This supports the supposition that part of the Au, namely its structurally bound component, is rather uniformly distributed in each grain ($V_x = 20\%$, Table 3). This is the main feature of structurally bound gold, which makes it different from other forms. However, the data obtained (\bar{x}_i is often significantly higher than \bar{x}_2 ; Table 3) suggest that in the region of crystal oversaturation in gold (owing to nonstructural forms), it is difficult to distinguish the structural component. This requires a representative set of analyses of fragments from individual crystals. In principle, the AAS ETAS method allows this problem to be solved, because it is valid for very small amounts of material. It is obvious that this method can, at least, be used for the analysis of the heterogeneity of mineral grains with respect to gold content. Nevertheless, the variant of the experimental method based on the investigation of phase correspondence in the gold-undersaturated region seems to be more promising for the estimation of the limits of Au incorporation into minerals [2].

Considering the problem of the analytical determination of structurally bound gold as a whole, it should be pointed out that we discussed here only the possibil-

Table 3. Analytical results obtained by the AAS ETAS method for fragments of greenockite (CdS) grains with the highest possible content of structurally bound gold (50 ± 10 ppm)

Grain no.	Au, ppm*	\bar{x}_i **	Set volume	Set of minimum values, n_2	$\bar{x}_2 \pm \sigma$
1	66.1	60.6	N = 18 $n_1 = 6$ $n_2 = 9$	66.1; 65.1; 50.6; 64.2; 58.8; 52.2; 58.3; 29.4; 56.3	55.7 \pm 8.6
	65.1				
	50.6				
2	90.3	79.8			
	70.1				
	79.1				
3	82.6	74.0			
	64.2				
	75.1				
4	78.3	63.1			
	58.8				
	52.2				
5	58.3	52.9			
	70.9				
	29.4				
6	67.2	65.2			
	56.3				
	72.1				

* Determined from peak area.

** $i = 1-6$.

geochemistry owing to the possibility of studying the speciation of trace elements and, in particular, the characterization of the structurally bound component of the noble metal admixture. The poor representativeness of this method due to the small mass of matter analyzed is usually considered as its fundamental shortcoming, but this is not true for a solution of the problem under consideration. In contrast, it provides an opportunity to study heterogeneous gold distribution within small grains and monocrystals. The methods of experimental geochemistry allow the conditions for the synthesis of crystals to be optimized; some of these crystals contain only structurally bound Au. Analytical data for individual crystals in both variants of the AAS ETA method (the analysis of liquid and solid specimens) allow the determination of the statistical parameters of distribution of structurally bound Au and its discrimination from other forms, which are related to higher gold contents. However, the precise characterization of the structural form requires special experimental investigations or direct analytical methods. A promising direction for future research would be to evaluate the possibility of direct characterization of Au speciation by the AAS ETAS method using the procedure of a stepwise increase in atomization temperature.

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CONCLUSION

The development of high-sensitivity analytical methods, which undoubtedly includes atomic absorption spectrometry with electrothermal atomization of elements from solid samples (AAS ETAS), provides new opportunities for experimental mineralogy and

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