Tauson V.L. Experimental approaches to separation of trace element binding forms in minerals (exemplified with gold in pyrite)

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A method is proposed for separating binding forms of trace elements in minerals based on the analysis of microquantities of a substance (individual crystals) and statistical treatment of analytical data obtained. The method is applied to the problem of "invisible" gold in pyrite. The samples from Au-Ag deposits of Russia North-East reveal a sorption nature of "invisible" gold rather than incorporation of gold into the mineral structure. The structurally bound Au contents are not higher than 0.1-0.3 ppm.

Introduction: Widely used in geochemistry, bulk element content represents a thing in itself especially for trace elements which speciation is commonly unclear. The most important information about mineral-forming conditions and mineral-trace element correlations originates from the distribution of structurally bound constituent of a trace element. This type of binding form strictly follows the interphase distribution law and so allowed reliable reconstructions of the fluid phase composition based on the corresponding data for coexisting mineral phases. Nevertheless, the structurally bound form often amounts only a minor part of the total trace element content. Its separation represents a complicated problem of analytical geochemistry. This communication reports on a version of the solution based upon the experimental approaches [1,2], the possibilities are exemplified with the problem of "invisible" gold in pyrite, i.e. disseminated, locally or completely evenly distributed gold with particle sizes beyond detection limit of optical microscopy (including lattice gold distributed uniformly at atomic level).

Background: The analysis of mineral substance microquantities (namely, small single crystals) is used to obtain the rank-scaled statistical samples of analytical data. Physically, this mean that any representative assemblage of single crystals contains at least several crystals which are free from active centers or defects responsible for the presence of binding forms other than the structurally bound one. Since all these forms only can rise the total content of the element, it seems reasonable to obtain a statistical sample of single crystals with lowest but significant contents. The schematic pathway of analytical data treatment is shown in Table 1. The main features of this scheme are the following. The statistical sample n_1 of the lowest contents is transformed to the sample n_2 (with average Au content $\overline{x}_2$) by imposing the condition reflecting empirical data on the behavior of structurally bound form [2,3]: the coefficient of variation in the sample should be not higher than 30% (including 10% reproducibility error of analytical method, AAS GF).

Therefore, the distribution of Au concentrations between individual crystals in n_2 is the same as if only structurally bound gold is present. Next is the separation of the part of evenly distributed Au camouflaging the structurally bound form and originating from the sorption of the element and its compounds at crystal surfaces. To put it in another way, it is necessary to separate the part proportional to specific surface area of a crystal. For this purpose, the average crystal mass $\overline{m}$ is determined for the sample n_2, crystal shape is approximated with a true polyhedron and finally, the specific surface area of average crystal is estimated. Such method was worked out using synthetic Au-containing pyrite crystals for which the gold solubility has been determined [1,3]. It is shown that the proportion of evenly distributed adsorbed constituent varies from 0 to 80% with the specific surface. The surface enrichment effect is considered to be negligible only when $\overline{S}_{spec} \cong 7$ sm^{2}g^{-1}. Thus, the structurally bound constituent of Au concentration could be found out by extrapolation of $\overline{x}_2$ - $\overline{S}_{spec}$ functions obtained for different crystal size fractions.

Results and Discussion: The method proposed is approved on naturally occurring pyrites from Au-Ag deposits of North-East Russia (thanks are due to Dr.R.G.Kravtzova for placing samples at my disposal). Only three cases are found to be appropriate for data extrapolation to the region of low $\overline{S}_{spec}$ values (Table 2). Unfortunately, only in one case (K-24, Oroch deposit) the representative set of data for different crystal size fractions is obtained. Otherwise, the coarse crystal fractions (>1mm) were absent or represented by anhedral grains. A further feature of note is that the method proposed depends heavily upon both the size and shape of crystals. Anhedral grains and incompletely facetted crystal pieces are not recommended to use because the sizes of their precursors are unknown. In each size fraction the crystals of a prevailing habit form are selected. The correlation between experimental and natural data shows that the crystals with $\overline{S}_{spec} \cong 20 - 40$ sm^{2}g^{-1} commonly observed for studied natural pyrites can contain ~ 15-70 ppm of evenly distributed gold and such values of $\overline{x}_2$ are actually observed. This allowed to ensure that one and the same mechanism of gold uptake operates in experimental and natural conditions associated with an active role of crystal surfaces. Extrapolation of natural data to $\overline{S}_{spec} = 7$ sm^{2}g^{-1} (Table 2) makes possible the estimation of lattice gold contents (~0.12-0.34 ppm). So, the structurally bound gold constitutes the minor portion of the total content of evenly distributed Au. Following the paper [3], the gold contents in ore-forming solutions can be estimated as ~2-6 ppm, in accordance with Au concentrations in liquid phase of fluid inclusions trapped by minerals of gold ore deposits [4,5]. Almost all evenly distributed constituent of gold admixture to pyrite ("invisible" gold) is owe to sorption and its consequences rather than the incorporation of gold into the mineral structure as have been admitted earlier [6,7]. This is also true for arsenian pyrites because As content affects only the slope of $\overline{x}_2$ - $\overline{S}_{spec}$ dependences. This supports our recent conclusion that As is not involved to crystal-chemical mechanism of gold incorporation [1,3]. Arsenic plays another role elevating gold content in fluid phase and increasing sorption onto pyrite crystal surface [8]. This may be conceived as a main reason of high "invisible" gold contents in arsenian pyrites.

Table 1. Analytical data treatment for evaluation of Au content distributed evenly and average crystal specific surface area

Assemblage of N single-crystals (N $\geq$ 20)

$\Downarrow$

N_1 ($C_{Au} > 3$ MDL=0.6 ppb)

$\Downarrow$

$n_1 = 1/3$ N_1 - the sample of least values, average $\overline{X}_1$

$\Downarrow$

$$n_2 = n_1 \left\{ \begin{array}{l} + n_i(\overline{x}_i \leq 0.3\overline{x}_1) \\ - n_i(\overline{x}_i > 0.3\overline{x}_1) \end{array} \right\}$$

$\Downarrow$

$\overline{x}_2 \pm \sigma$
(average concentration of evenly distributed Au, for which the distribution character is the same as for structurally bound form)

$\Downarrow$

$\overline{m}$
(average mass of crystal in the sample n_2)

$\Downarrow$

$\overline{r}$
(average crystal size)

$\Downarrow$

$$\overline{S}_{spec} = k\overline{r}^2 / \overline{m}$$

(average specific surface area)

Table 2. Extrapolation estimate of structural gold constituent in pyrite crystals from Au-Ag deposits of North-East Russia

Sample No.	Deposit	Equation	Structurally bound Au (ppm)
K-24	Oroch	$\overline{x}_2 = 0.01645\overline{S}_{spec.}^2 - 0.00376\overline{S}_{spec.} - 0.54247$	0.24
B-4835	Dalnee	$\overline{x}_2 = 0.11586 \cdot \exp(0.15413\overline{S}_{spec.})$	0.34
P-1953	Dalnee	$\overline{x}_2 = 9.0567 \cdot 10^{-5} \cdot \overline{S}_{spec.}^{3.70766}$	0.12

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