Distribution of Iridium in Hydrothermal Synthesized Sulphides Fe, Cu, Zn, Pb Using Radioisotope [192]Ir

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Introduction

Considerable amount of the information about high concentration of elements of platinum group (EPG) in low-temperature formations has appeared in the last years. The formation of EPG is happened as a result of hydrothermal and sedimentation processes. The mining concentration of platinoid is detected in rocks and ores of blackschist formation, hydrothermal deposits of gold, oceanic hydrothermal ores and ferromanganese concretions. The high mobility of EPG is established also during process of weathering of soil (Laverov et al., 1997; Rudashevsky et al., 1995; Korobeynikov et al., 1998; Peucker-Ehrebrink et al., 2000; Kucha et al., 1999; Baturin 1993). Thus in many cases it is underlined that concentrators of EPG in ores and rocks are sulphide minerals, but the form of their presence is not established more often. The iridium always is presented at a structure of EPG minerals of ores of listed types of deposits and so can be selected as the indicator of geochemical behavior of EPG.

Experiments

We have made experiments on hydrothermal synthesis of iridium containing sulphides of -Fe, -Cu, -Pb and -Zn with usage of a radiotracers method. The isotope ^{192}Ir was used as radioactive «label». Autoradiography was used as a method of registration of isotope ^{192}Ir in the synthesized minerals. The experiments are built in steel autoclaves with titanium ampoules V=55 см³, at P = 500 bars, which was set on PTX diagram for aqueous solutions NH_4Cl. Temperature of a hydrothermal crystallization was set by VRT-3 with accuracy ±3°C and was equaled to 400 °C and 500 °C (two series of experiments). A gradient of temperature between the upper zone and lower was 14 °C. Time of experiments was from 100 till 1000 hours. Three experimental systems were generated with the purpose of synthesis of pairs of sulphides: Fe-Pb, Fe-Cu and Fe-Zn. The mixture made from elements of the mark especially pure in stoichiometric proportions, typical for pyrite, galena, chalcopyrite and sphalerite. Solution of chloride of ammonium 2,06 M was the working solution.
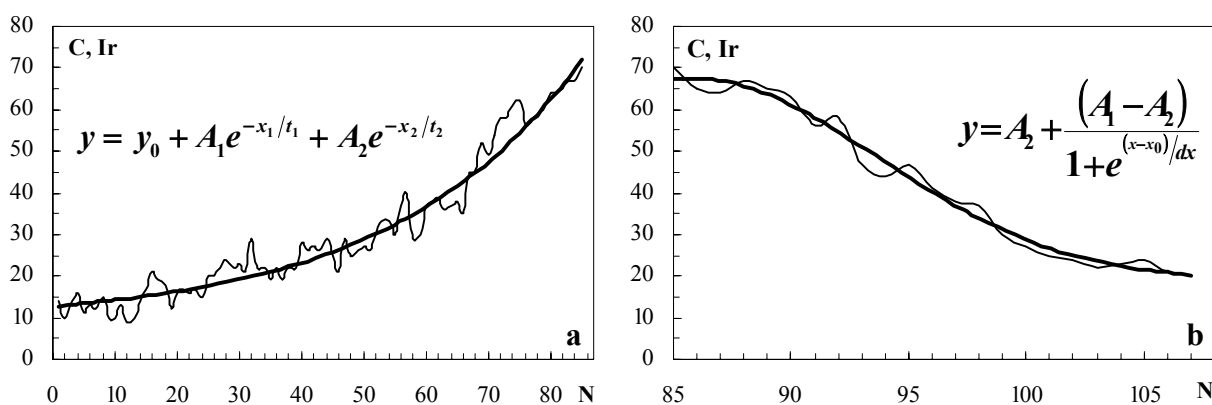

In figure a:
$$y = y_0 + A_1 e^{-x_1/t_1} + A_2 e^{-x_2/t_2}$$

In figure b:
$$y = A_2 + \frac{(A_1 - A_2)}{1 + e^{(x-x_0)/dx}}$$

Figure 2. *Results of data approximation of modification of concentration iridium (C_{Ir}=d) in synthesized sulphides. a - external surface of sulphide (from the solution part) — boundary zone, b - boundary zone — near-surface of sulphides. N — the length of the profile.*
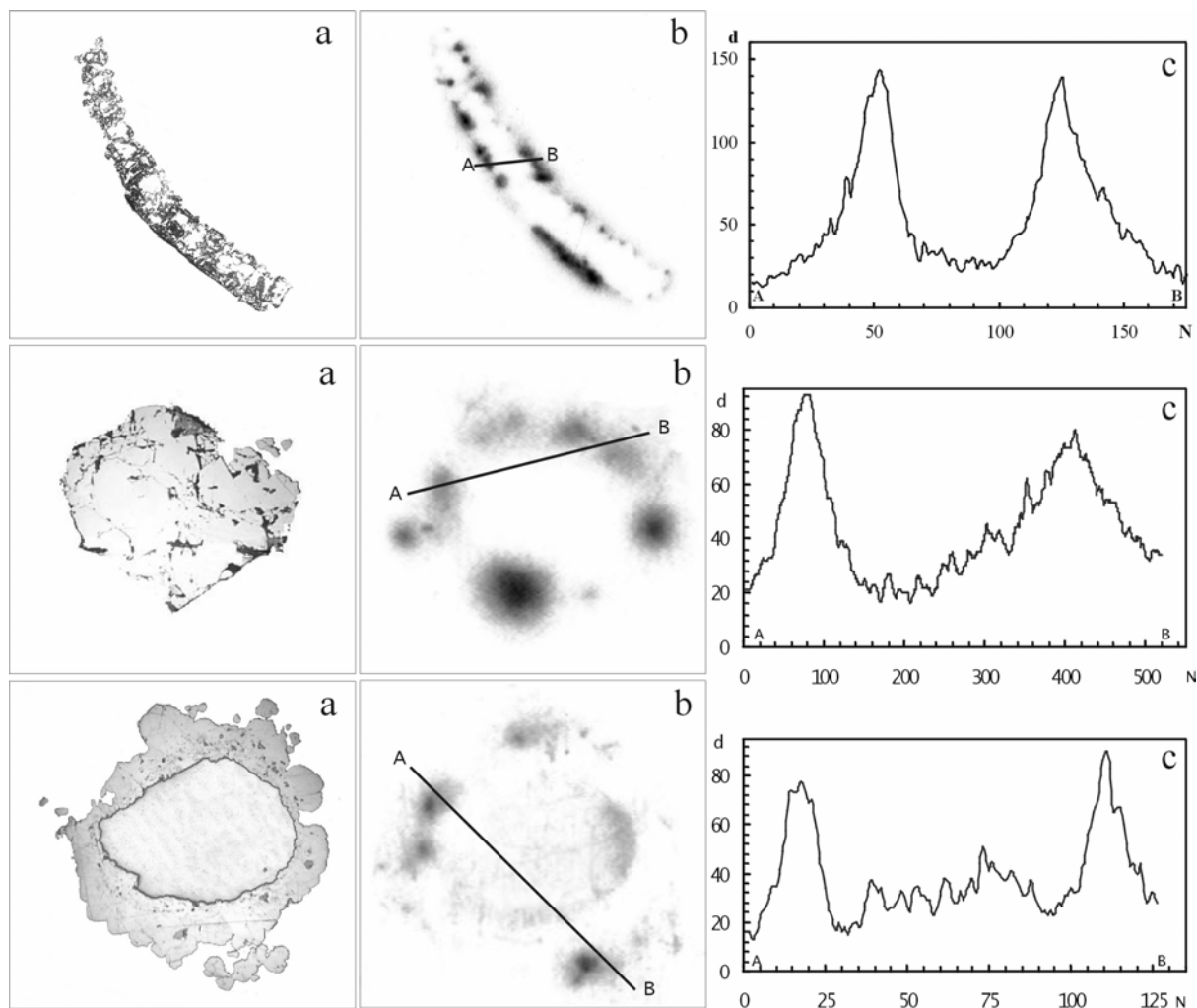
Figure 1. *Photographs of sulphides (a), autoradiograms (b), fixing of spatial distribution of iridium (by ^{192}Ir) and relational concentrations of iridium in profiles (c), delineated in density of blackening «d». Maximal density of blackening of autoradiograms corresponds to maximal concentration of iridium. Upper row is chalcopyrite; middle row is pyrite; lower row is sphalerite. There is 10 hours of exposition. Nuclear emulsion is AF. There is the number of points on axis of abscissa.*

Quantity of entered iridium varied from 11 ppm up to 74 ppm concerning an initial hinge of fitting of a blend (P=10 g) and was added in a blend as hydrochloride solution $Na_2^2[IrCl_6]^2$ c Ph=3,5. Water-soluble compound of iridium was received by a method of chlorination of metallic Ir, previously «marked» by a radionuclide ^{192}Ir on reaction [190]Ir (n,γ) [192]Ir. A plate of iridium was irradiated in a channel of a nuclear reactor with resonant neutrons. The radionuclide ^{192}Ir is also beta emitter that has allowed to using a method of a beta-autoradiography for determination of a spatial distribution and forms of presence of iridium in the synthesized minerals. The registration of a beta-radiation was made with usage of an emulsion for nuclear researches such as MR and film for an autoradiography such as AF.

Results end discussions

As a result of experiments the crystals and polycrystallic aggregates of pyrite, pyrrhotite and galena were obtained for Fe-Pb system; pyrite, chalcopyrite, bornite, chalcosine and pyrrhotine were obtained for Fe-Cu system; pyrite, pyrrhotite, ferriferous sphalerite and kleiophan were obtained for Fe-Zn system. The fragments of mineral aggregates and crystals were filled up by epoxy and then cemented preparations were made, which then were opened by abrasion and were polished on diamond pastas for autoradiographic and

mineralgraphic analysis. After experiments the measuring a gamma-activity of solution (with usage of the measurement standards), synthesized sulphides and titanium ampoules on the apparatus for an activation analysis «Intertechnique» were made.

It was determined, that all quantity of iridium, introduced in experimental systems, concentrates in the synthesized sulphides. The solutions and titanium ampoules did not contain iridium. The polished preparation with fragments of synthesized mineral sulphide aggregates and crystals, beta - authoradiography, fixing distribution of iridium in them and profiles reflecting changes of concentration of iridium in sulphide aggregates are shown in a fig. 1. The enrichment by iridium of external surface of separate large crystals or polycrystallic aggregates is character of a spatial distribution of iridium in the synthesized sulphides. The internal parts of crystals and aggregates of sulphides do not contain iridium. And such type of distribution is marked as a matter of fact for all sulphide minerals: pyrite, chalcopyrite, bornite, pyrrhotite, galena, sphalerite. Own minerals of iridium in the synthesized sulphides are not detected, as by the data of an autoradiography (the points of maximum blackening on nuclear emulsions are missed), and as at analyzing on a scanning electron microscope. In infrequent cases the ultra dispersible inclusion - concentrators of iridium, which structure did not manage to be established, are marked.

Lowering concentration of iridium in sulphides to final stages of experiment in process of extract of iridium by sulphides in incipient states and reduction of its concentration in solution is definitely determined. In many cases the crystals of sulphides, derivate at the end of experiment, did not contain iridium practically.

As a result of the made experiments is established, that the iridium is not included in structure of any of the synthesized minerals, but it is concentrated on a surface of growing crystals and polycrystallic aggregates, that is on the crystal - solution boundary. The similar character of a spatial distribution of iridium between sulphides and solution corresponds to adsorption equilibrium. For the evidence of this supposition the type of iridium distribution in a layer on boundary sulphide-solution on the part of solution and on the part of a crystal was analyzed. Is established, that the distribution curves of iridium on boundary sulphide - solution (site 1) have asymmetry: more flat gradual increase of iridium concentration from solution to a sulphide surface, in comparison with

(site 2) a surface of sulphide - near-surface part of a crystal. Curves of concentration distribution of iridium on sites a surface of a crystal - solution (fig. 2a) and surface of a crystal - near-surface area of a crystal (fig. 2b) were built by the method of approximating. Is established, that on a site 1 changing of iridium concentration is described by an equation with a square of cross correlation (R^2) 0.966:

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} \qquad (1)$$

According to the Hall theory (Kreger 1969; Hall 1953), the effective value of a coefficient of distribution depends on growth rate and is described by expression, which characterizes distribution of an addition in a growing crystal in case of adsorption equation:

$$k_{eff} = k + (k_{ads} - k)e^{-\upsilon_{sl}/\upsilon}, \qquad (2)$$

Where υ - growth rate, υ_{sl} - rate of transport of impurity atoms between a crystal and melt bordering to it; k_{ads} - coefficient of adsorption, k - coefficient of distribution ($k_{eff}=k$, when $\upsilon_{sl} > \upsilon$, and $k_{eff}=k_{ads}$, when $\upsilon > \upsilon_{sl}$). The dependence k_{eff} from growth rate is explained by formation of an adsorption layer on a boundary surface of phases.

Evidently, that the equations (1) and (2) correlate between themselves. Therefore, according to the theory of the Hall (Kreger, 1969; Hall, 1953), impurity atoms, in this case - iridium, at first are adsorbed on interface and only then are entered into a lattice of a crystal. At low speeds of growth the adsorption layer goes before interface and is supported at the expense of a fast egress of a hard phase of atoms, which originally were adsorbed and are grasped by a growing crystal. It confirms by the analysis of a curve on a site 2 — a surface of a crystal - near-surface area of a crystal (fig. 2 б). Change of concentration of iridium here is described by a sigmoid curve that also corresponds to the theory of the Hall and distribution of concentration of an impurity in solid phase reactions (Tretyakov, 1978).

Conclusion

As a result of the made experiments on hydrothermal synthesis iridium containing of sulphides is established, that the iridium is not included in structure of sulphides Fe, Cu, Pb, Zn. The distribution of iridium between solution and sulphide corresponds to adsorption equilibrium, instead of equilibrium between a volume of a crystal and volume of solution. The growth rate of crystals was enough low - $3 \cdot 10^{-6}$ - $3 \cdot 10^{-9}$ cm/sec in our experiments. The concentration of iridium in sulphide minerals can be distributed enough

uniformly in volume of minerals in the defects of crystal structure in the case of very high growth rate of crystals. It is occurred at the expense of fast overlap of an arising adsorption layer by mineral generating elements of a growing crystal. In case of a closed system it can be zoning forming. Evidently, that the coefficient of distribution (C_s/C_l) of iridium in an experimental system: sulphides Fe, Cu, Pb, Zn - hydrothermal solution is less than 1, but according to adsorption equilibrium in this case it is necessary to use not a coefficient of distribution, but effective coefficient of distribution dependent on coefficient of adsorption equilibrium (Kreger 1969; Hall 1953).

The obtained data also indicate that the conclusions about the forms of presence and coefficients of iridium distribution obtained on the basis of total, instead of local analysis of coexisted phases, cannot correspond to actual values.

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