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## RATIO OF OXIDIZED AND REDUCED FORMS OF NOBLE METALS IN THE AMUR RIVER BASIN

**SUMMARY.** *The noble metals (NM) have an extremely uneven distribution in nature. The oxidation of NM minerals described in the second law of thermodynamics and the Nernst equation occurs on the surface. To determine individual forms of NM both in their oxidized form ( $C_{ox}$ ) characterizing migration and scattering in the environment and reduced form ( $C_{red}$ ) characterizing mineral accumulation is an important task. To determine  $C_{ox}$ , we propose to separate oxidized forms from reduced NM forms by filtration while heating a standard sample up to the boiling point in solution of 3M HCl.  $C_{ox}$  NM forms remain in the filtrate, and  $C_{red}$  NM forms remain in the sediment. The concentrations of the reduced NM forms ( $C_{red}$ ) can also be determined by the equation  $C_{red} = C_{gross} - C_{ox}$ , where  $C_{gross}$  is the gross NM concentration in a sample. The correlation ( $C_{ox}/C_{red}$ ) of an individual NM with geometric dimensions is given by the equation (1), where  $n$  is the number of minerals, varying from  $i = 1, 2, \dots, n$ ;  $i$  is the mineral order number;  $r_i$  is the mineral  $i$ -radius,  $r$  is the average mineral radius,  $\mu\text{m}$ ;  $r = \sum r_i/n$ ;  $S_{sp}$  is the sphere square;  $V_{sp}$  is the sphere volume.*

$$N_{NM} = \frac{C_{ox}}{C_{red}} \cong \left( \frac{S_{sp}}{V_{sp}} \right) = \frac{3}{\bar{r}} = 3n \sum_{i=1}^n \frac{1}{r_i}$$

*For surface waters, soils and plants, the  $C_{ox}/C_{red}$  values representing the NM formation process and their scattering in natural landscapes are determined. It is shown that the number of oxidized forms of NM depends on the chemical nature of a certain NM, its gross concentration, the average radius of its minerals, and physicochemical properties of the open stationary system (temperature, pressure, pH, and Eh).*

**KEYWORDS:** *Geochemistry, thermodynamics, noble metals.*

The gold deposits of the hydrothermal type, which have been formed due to metal crystallization from hot water solutions formed in their turn as the result of magma solidification, are of great industrial importance [1]. The ore mineralization of noble metals (NM) in the Amur River Basin is mainly exemplified by the primary and alluvial gold deposits in the territory of the Amur Region. The NM ores are included in the biogeochemical cycle of matter. The mineral associations of alluvial NM interacting with the environment on the phase boundary have the highest degree of involvement into the cycle process. NM possess low reactivity in oxidation reactions; they close the electrochemical range of metal activity with the values of standard electrode oxidative potentials  $E^\circ = + (0.45-1.85)$  V for water solutions at standard thermodynamic conditions (the pressure of  $10^5$  Pa and the temperature of  $25^\circ\text{C}$ ). The  $\Delta G^\circ$  value (isobaric-isothermal potential) determines the reaction direction

$\Delta G = -E^{\circ}zF$ , where  $z$  is the number of electrons participating in the reaction,  $F$  is the Faraday number of 96500 C/mol. Since all the values in the right part of the oxidation equation for NM are positive, then  $\Delta G$  takes negative values. The latter characterizes the behavior of oxidation reactions as thermodynamically possible and spontaneous. For the cases different from the thermodynamically standard ones, the oxidation reaction potential is usually written in the following way:  $E = E^{\circ} + (0.059/z)\lg(C_{ox}/C_{red})$ , where  $C_{ox}/C_{red}$  are the ratios for the oxidized form ( $C_{ox}$ ) to the reduced form ( $C_{red}$ ),  $z$  is the number of electrons participating in the reaction [2]. However, the equilibrium constants of such reactions are small and hence characterized by low values of oxidation process rate.

The purpose of this paper was to determine the equilibrium concentration ratio for NM of both oxidized and reduced forms, which is required for the thermodynamic calculation of the parameters of dissolution and mineral formation for NM.

The gross NM content was determined by the authors in the Laboratory of Chemical Analysis of the Geology and Environmental Management Institute, the Far East Department of Russian Academy of Science, from a 10 g sample, after multi-level cinefaction up to 600°C, at the rate of 100°C/h. The mass fractions of Au, Ag, Rh, Pd, and Pt were determined by the atomic absorption method; the mass fractions of Os and Ir were determined by the kinetic method; the mass fractions of Ru were determined by the catalytic method. The oxidized NM forms ( $C_{ox}$ ) were determined according to the technique, based on mineral raw solubilizing in acids, which are not oxidants (hydrochloric acid). We took into account the insolubility of the reduced NM forms and further standard analysis of an acidic extract by the extraction methods of the atomic absorption analysis. The analysis was carried out according to accuracy category III, the maximum error of the NM determination was  $\pm 30\%$  [3].

The concentrations of the reduced NM forms ( $C_{red}$ ) were calculated according to the equation  $C_{red} = C_{gross} - C_{ox}$ .

In non-reversible processes, the entropy dispersion ( $S$ ) is minimal and its rate of production in time takes the minimum positive value for the given conditions according to the I. Prigogine's theorem  $\Delta S/\Delta\tau \rightarrow 0$ , where  $\Delta S$  is the system entropy change during the period of time ( $\Delta\tau$ ) [4]. For a thermodynamic system, the ratio of the oxidized and reduced NM forms is given by  $1 = T\Delta S/\Delta H$ , where  $T$  is the absolute temperature, °K,  $\Delta H$  is the system enthalpy change. Then the physical meaning of the desired expression is determined by the ratio of the sums of noble metals atoms which possess the excessive energy (specific for oxidized forms) and the insufficient activation energy (specific for reduced forms) of the mineral dissolution process. The atoms located inside the mineral have the values of  $H = 0$  kJmol<sup>-1</sup> and  $S = 8.29$  Jmol<sup>-1</sup>uK<sup>-1</sup>, but for the atoms located on the crystal surface these values are  $H = 13.394$  kJmol<sup>-1</sup> and  $S = 29.47$  Jmol<sup>-1</sup>uK<sup>-1</sup>, respectively [2].

If the NM mineral size is decreased to nanoscale level, its form tends to a sphere, therefore the ratio of the number of the atoms located on the surface to the number of the atoms located inside will be in proportion to the ratio of the surface area to the volume. This value has a physical meaning characterizing the dispersion degree and the dimensionality [ $m^{-1}$ ] in the Si-system. Taking into account the following values:  $S_{sh} = 4\pi r^2$ ,  $V_{sh} = 4\pi r^3/3$ , where  $S_{sh}$  is the area of a sphere,  $V_{sh}$

is the volume of a sphere,  $\pi$  is the ratio of the circumference to the diameter,  $r$  is the radius of a sphere, we get the following ratio:  $S_{sh}/V_{sh} = 3/r$ .

For an open stationary system, the ratio value for the concentrations of the oxidized form to the reduced one for a certain NM noted here as  $N_{NM}$  is equal to tripled inverse average arithmetic radius of minerals, where  $n$  is the number of minerals, varying from  $i = 1, 2, \dots, n$ ;  $i$  is the mineral order number;  $r_i$  is the mineral  $i$ -radius,  $r$  is the average mineral radius,  $\mu\text{m}$ , where  $r = \sum r_i/n$ . Then the desired ratios can be represented as the equation:

$$N_{NM} = \frac{C_{ox}}{C_{red}} \cong \left( \frac{S_{sp}}{V_{sp}} \right) = \frac{3}{\bar{r}} = 3n \sum_{i=1}^n \frac{1}{r_i} \quad (1)$$

The NM atoms located on the surface possess an excess of potential energy and increased reactivity as compared to the atoms located inside the volume of the crystal lattice, and the oxidized forms of certain NM elements located in the open stationary system outside the minerals possess even more increased energy reserves as compared with the atoms located on the crystal surface. Therefore, according to the Thomsen-Berthelot's principle of energy efficiency, the process of reviving NM atoms on the mineral surface will occur spontaneously and with an energy release ( $\Delta H < 0$ ). The reviving process for NM is in equilibrium with their oxidation process, also occurring on the surface, but requiring more energy consumption for it.

The impact of an industrial sector on the environment of the Amur River Basin exhibits in the gold extraction in the amount of 13-18 tons per year and the NM nanomineral dispersion in the environment, which leads to a shift of the natural equilibrium between the oxidized and reduced forms toward the formation of reduced forms according to the Le Chatelier-Braun's principle of conservatism. The reducing character of the geochemical situation in the surface waters of the region also contributes to these processes according to a negative value of redox potential in them  $Eh = -0.250$  B [5].

The analysis of the thermodynamic NM constants showed the preferred energy efficiency of the native mineral state in natural geochemical systems as compared to all the other, according to which they are arranged in the following sequence: Pt > Rh > Ru > Os > Ir > Pd > Au > Ag. The most common and relatively stable are the ions which have the valence given in brackets: Ru (IV, V), Rh (III), Pd (II), Ag (I), Os (IV, VI), Ir (III), Pt (II), Au (I, III). Their stability is determined by the ionization potential [6].

The exposure of platinum mineralization in the hardrock gold deposits and auriferous alluvials was registered within the Verhneamursk province area. Various platinoid minerals, their size being from 1 to 3,000  $\mu\text{m}$ , were registered [7]. The native gold of exogenous formation differs from the gold of endogenous ore occurrence by its larger size. Thus, the average size of gold grains for the Pokrovsky ore deposit with the occurrence of two mineralization types (the primary and alluvial gold deposits) is 6.7  $\mu\text{m}$  and 115  $\mu\text{m}$ , respectively [8]. If we apply formula (1), we obtain the values ( $N_{Au_i} = 0.9$  for the primary type and ( $N_{Au_p} = 0.05$  for the alluvial type. Apparently, this evaluation is the result of the established equilibrium between the oxidized and reduced NM forms and the mineral sizes calculated by the equation (1) for the natural system of the Amur River Basin. We suppose that this equilibrium ratio must be also true for non-metallic ore objects, in which the biogeochemical

cycle of matter occurs in the form of scattered fine-dispersed NM forms. The ratios of oxidized and reduced forms were calculated for the surface waters, soils and plants of the Amur River Basin (Table 1).

L. Kovalevsky was the first to pay his attention to the existence of qualitative relation between native gold and its concentrations in plants growing above, while studying Pt and Pd crystals in the magmatic and biological material in Transbaikal region. He did not register significant distinctions between the minerals having different genetic origin [9]. This confirms the priority principles of thermodynamic interpretation of the mineral formation processes, which depend on the physicochemical parameters of the medium, which is the background one for the forming minerals of NM group. The maximum Pt and Pd concentrations in the ash of plants have the values similar to those in the platinum-bearing rocks and ores:  $1\text{-}30\cdot 10^{-4}\%$  for Pt, and  $1\text{-}15\cdot 10^{-4}\%$  for Pd. The size of NM minerals of Au and Pt microbiolites and of other metals of the platinum group are:  $2\text{-}20\ \mu\text{m}$  in old parts of the plants and roots; they are smaller in branches and other above-ground parts  $<0,2\text{-}2\ \mu\text{m}$ ; they are not registered in leaves [9], [10]. The ratio of the oxidized and reduced NM forms is  $N_{NM} = 0.27$  for the microbiolites of the platinum group with the sizes of  $2\text{-}20\ \mu\text{m}$ , and it is  $N_{NM} = 2.73$  for the small crystals. According to the data presented in Table 1, the experimental  $N_{nm}$  values for plants vary from 0.01 to 1.26. The nearest  $N_{Au}$  values indicate the same dimension of microbiolites of gold, platinum, and palladium [9], [10].

Table 1

**The concentration ratio  $N = C_{ox} / C_{red}$  for the oxidized forms to reduced forms of noble metals in the natural objects of the Amur River Basin**

Sample	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au	Average
Water, $n = 32$	0.011	0.001	0.045	0.025	0.25	0.005	0.01	0.357	0.088
Soil, $n = 78$	0.10	0.20	0.05	0.28	0.37	0.02	0.10	0.03	0.18
Plants, $n = 125$	0.01	0.28	1.26	0.56	0.54	0.01	0.06	0.35	0.38

Note:  $n$  is the number of trials.

For surface waters, the average values of  $N_{NM} = C_{ox} / C_{red}$  are higher than the expected ones, despite the reducing character of the geochemical situation in the surface waters of the Amur River Basin, since NM mainly migrate with suspended matter in the form of dispersed intermetallic nanoscale particles. Natural gold is visually registered in the bottom sediments of the Amur River in fractions of  $0.063\text{-}0.1\ \text{mm}$  and  $0.1\text{-}0.25\ \text{mm}$ . The dissolved portion of gold accounts for about  $4.5\%$  of its gross amount [5].

The average  $N_{NM}$  values for soils exceed the expected ones. They are determined by the stabilization of the oxidized NM forms by fulvic complexes of soils according to the data given in [11]. For the *water-soil-plants* system, the increased  $N_{NM}$  value is registered with the increase of the chain link status determined by the stabilization of the oxidized NM forms by the organic ligand complexes of the chelate type

which have the maximum stability. In the biogeochemical objects, increased values of oxidized NM forms statistically exceed the expected  $N_{NM}$  ratios for the mineral forms of noble metal mineralization in the Amur River Basin. The portion of oxidized NM forms increases with the decrease of mineral size.

The physicochemical parameters of the background medium are favorable for the processes of reduction and mineral formation, and the reduction reaction rate exceeds the oxidation reaction rate for surface waters, soil, and plants  $C_{ox}/C_{red} < 1$ .

Thus, the number of oxidized NM forms depends on the chemical nature of a certain NM, its gross concentration  $C_{ox} = (C_{gross} - C_{red})$ , the average radius of its minerals ( $r$ ) and the physicochemical properties of the open stationary system. This can be presented by the formula:  $N_{NM} = C_{ox}/C_{red} \approx 3/r = 3n \sum 1/r_i$ .

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