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GEOCHEMISTRY

Relationship between the Fineness of Crystallizing Gold and the Proportion of Alkali Metals in Fluids during Their Interaction with Wall Rocks: Evidence from Deposits of the Amur Region

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The fineness of gold from endogenic gold deposits varies from 500 to 999. The causes of this wide variation have been discussed by many researchers and were comprehensively considered by Petrovskaya [1]. Differences in depth and temperature regime of deposit formation, composition of gold-bearing mineral assemblages, age of mineralization, and other factors were regarded as crucial in this respect. However, the fineness of gold from hypabyssal and abyssal deposits is rather similar, although the statistical peaks of their frequency of occurrence are significantly different [2]. It was established that the temperature interval of native gold deposition at abyssal and hypabyssal deposits is also similar [3]. Therefore, the critical influence of temperature on the fineness of gold is doubtful. However, this parameter certainly raises the fineness during the subsequent thermal impact [4].

The causes listed above cannot explain the appreciable lateral and vertical variations in the fineness of gold in some deposits and even in particular orebodies. We believe that the chemical composition of host rocks might be one more cause responsible for the variation in the fineness of gold.

Such a relationship has not been examined in the available publications. To fill this gap, we studied three gold deposits in the Upper Selemdzha ore district (Amur region), where the ore veins are hosted in the genetically and chemically contrasting Paleozoic rocks of the Mongol–Okhotsk Foldbelt (Fig. 1). The deposits formed at a medium depth and pertain to the same gold–sulfide–quartz formation. The sulfide content does not exceed 3%. Arsenopyrite, pyrite, galena, sphalerite, and gold (fineness 640–950) are major minerals. The relationship between proportions of alkali metals in fracture-pore fluids resulted from wall rock–fluid interaction, on the one hand, and fineness of gold in ore, on the other.

The most altered wall rocks were sampled with a spacing of 0.1, 0.5, and 2.0 m from veins. The least altered rocks were sampled with a spacing of 25–40 m or more. The degree of hydrothermal alteration was established by microscopic examination of thin sections. The balance of gain and loss of elements (in wt % adjusted to 100%) in the wall rock–fracture-pore fluid

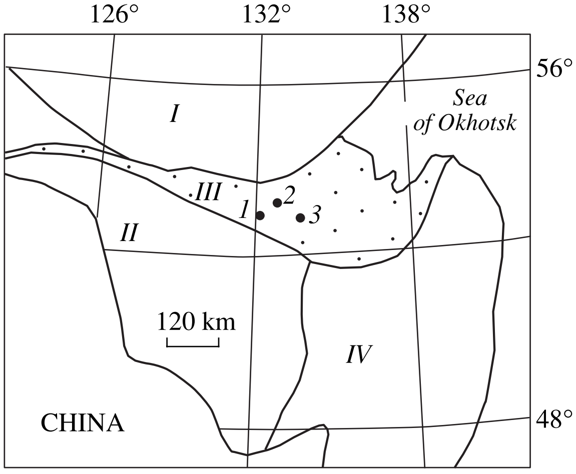

Fig. 1. Index map of the studied gold deposits in the Amur region. Based on *Tectonic Map*, (2005) edited by L.P. Korsakov et al. (*I*) Siberian Platform, (*II*) Amur microcontinent (superterrane), (*III*) Mongol–Okhotsk Foldbelt, (*IV*) Sikhote Alin Foldbelt. Deposits: (*1*) Upper Myna, (*2*) Tokur, (*3*) Kharga.

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system was determined from chemical compositions of altered and unaltered rocks. In connection with the joint transfer and deposition of Au and Ag by hydrothermal solutions, the behavior of only K and Na is considered in this communication, because experimental results [3, 6, 7] show that precisely these alkali metals control the solubility and mobility of these metals in hydrothermal solutions. We used the sodic index of fluid (Tables 1, 2), which characterizes the differential mobility of alkali metals in a hydrothermal process, based on the balance of alkali metals in altered wall rocks according to the formula

$$I_{\mathrm{Na}}^{\mathrm{Fl}} = (\pm\mathrm{Na_2O})^{\mathrm{Fl}} - (\pm\mathrm{K_2O})^{\mathrm{Fl}},$$

$(\pm\mathrm{Na_2O})^{\mathrm{Fl}}$ and $(\pm\mathrm{K_2O})^{\mathrm{Fl}}$ reflect variations of Na^+ and K^+ concentrations in the fracture-pore fluid. Because these concentrations in the initial fluid transported to the lower level of ore deposition are unknown, the sodic index only reflects the trend of increase (+) or decrease (–) in the relative amount of Na^+ as a result of interaction with wall rocks. The sodic index is an approximate quantitative measure of the variation in the alkalinity of fluid in particular segments of the hydrothermal system.

The *Upper Myna deposit* is situated near the contact of the Late Paleozoic Lukachek granitoid pluton with the terrigenous rocks. The gold–sulfide–quartz veins are steeply dipping.

The host amphibole–biotite granite is characterized by normal alkalinity with the prevalence of K_2O over Na_2O (Table 1, sample N-36). Native gold in veins is characterized by a low fineness (640–700). In the narrow near-vein zone (0.05–0.3 m), granite is transformed into light beresite and impregnated with sulfides. At a greater distance from veins, granite is altered much less with retention of the primary structure. The beresite (phyllic) alteration was accompanied by a loss of approximately equal portions of Na_2O and K_2O (sample N-35) and other components. Therefore, the proportion of Na and K inherent to the initial fluid remained almost unchanged in the process of its interaction with host granites ($I_{\mathrm{Na}}^{\mathrm{Fl}} = +0.14$).

The *Kharga deposit* is located in the metavolcanic–metaterrigenous rocks of presumably Early or Middle Paleozoic age. Some veins are hosted in the K- and Na-rich albite–quartz–mica schists, others are located in Na-rich metabasic rocks (Table 1, sample N-232). The steep veins extend in the near-latitudinal direction and crosscut the host rocks along the dip. The Main and Scheelite veins consist of scheelite–arsenopyrite–quartz ores with a fineness of gold equal to 890–950. The most intense wall-rock alteration of metabasic host rocks is noted only within 0–1 m on both sides of the Scheelite Vein. The wall rock is replaced with epidote, chlorite, muscovite, and sulfides. The loss of Na_2O and gain of K_2O is notable at 0–20 cm from the contact of the vein (Table 1, sample N-222). In the next zone (0.5 ± 0.3 m), Na_2O and partly K_2O are removed. At a distance of more than 1 m, the gain and loss of alkali metals become insignificant. Therefore, the $I_{\mathrm{Na}}^{\mathrm{Fl}}$ value is highest (+3.1 and +3.2) 0–1 m from the vein and abruptly decreases at a distance of 2 m or more from the vein (Table 1, samples N-222, N-224, and N-232). The formation of similar metasomatic rocks within the ore-controlling normal fault zone (sample N-617) was also accompanied by a marked concentration of Na in the fracture-pore fluid.

The Tishin Vein hosted in quartz–mica schist is close in mineral composition to the Main and Scheelite veins but distinguished by a low scheelite content. The fineness of gold in this and other veins hosted in the same rocks is much lower (800–850) [4]. At 0–1 m from the contact of the Tishin Vein, the host rocks are silicified with an intense loss of Na_2O and a less intense loss of K_2O (Table 1, samples N-209 and N-213). Therefore, the host rock affected the Na concentration in fluid to a lesser degree ($I_{\mathrm{Na}}^{\mathrm{Fl}}$ varies from +0.67 to +0.85) than near the Scheelite Vein. The data on veins at the Kharga deposit, which is undoubtedly formed from a single deep source of solutions but hosted in rocks with different Na contents, testify to the influence of host rocks on the composition of fluids and the fineness of gold.

The *Tokur deposit,* the largest in the ore district, is hosted in the Upper Paleozoic terrigenous rocks at the southern limb of anticline. The geological setting of this deposit is described in [5]. In the unaltered sandstone, $Na_2O > K_2O$, whereas inverse proportions are noted in mudstone (Tables 1 and 2). The host sandstones, siltstones, and mudstones are most altered (sericitized, sulfidized, and silicified) at a distance of 1–3 m from veins. At the lower levels of the deposit, the main veins and disseminated ore zones are localized in sandstones and siltstones. The metasomatic alteration is accompanied here by preferential loss of Na_2O (Table 1, sample N-717). A similar alteration was established in the narrow sandstone zone that hosts the Khabarovsk Vein at the intermediate level of 700 m (Table 1, sample N-751).

The influence of rocks on the Na and K proportions in fracture-pore fluids at different levels of the deposit is exemplified in Vein 184 (Table 2). This vein crosses sandstone at a level of 700 m and mudstone at levels of 590 and 777 m (Fig. 2). In the intermediate (0.5 m) and outer (2.0 m) zones from the vein, the altered mudstones and sandstones at levels of 590 and 700 m were depleted in Na_2O. At the upper level (777 m), mudstones were enriched in Na_2O. The inner zone (<0.1 m from vein) is characterized by an insignificant removal of Na_2O at level of 590 m and its concentration in sandstones and mudstones at the middle and upper levels. The average gain–loss balance of Na_2O in wall-rock alteration zones 0–1 and 0–2 m wide are shown in

Table 1. Redistribution of alkali metals between host rocks and fluid at gold deposits of the Upper Selemdzha ore district, the Amur region

Deposit, host rock, and orebody	Sample no.	Rock, distance from vein (m)	Content, wt %			Gain (+) and loss (–)				I^{Fl}_{Na}	Fineness of gold, ‰
			SiO_2	Na_2O	K_2O	in rock		in fluid			
						Na_2O	K_2O	Na_2O	K_2O		
Upper Myna deposit in granites, Vein 1	N-36	Unaltered granite	69.2	1.70	4.0					+0.14	640–700***
	N-35	Metasomatic rock (0.1)	72.55	1.02	3.46	–0.68	–0.54	+0.68	+0.54		
Kharga deposit in metavolcanic–metaterrigenous rocks, Scheelite Vein	Average (3)*	Unaltered metabasic rock	49.05	3.51	0.42						890–950 [4]
	N-222	Metasomatic rock (0.2)	55.94	1.58	1.69	–1.93	+1.27	+1.93	–1.27	+3.2	
	N-223	Metasomatic rock (0.5)	74.71	0.28	0.28	–3.23	–0.14	+3.28	+0.14	+3.09	
	N-224	Slightly altered metabasic rock (2.0)	49.0	3.12	0.5	–0.39	+0.08	+0.39	–0.08	+0.47	
	N-232	Slightly altered metabasic rock (40)	49.3	3.38	0.41	–0.13	–0.01	+0.13	+0.01	+0.12	
Mineralized zone	N-617	Metasomatic rock	49.35	0.89	1.62	–2.49	+1.21	+2.49	–1.21	+3.7	
Tishin Vein	Average (3)	Unaltered quartz–mica schist	71.0	3.20	2.66						800–850 [4]
	N-209	Metasomatic rock (0.1)	78.02	1.76	2.07	–1.44	–0.59	+1.44	+0.59	+0.85	
	N-213	Metasomatic rock (0.6)	82.59	0.87	1.0	–2.33	–1.66	+2.33	+1.66	+0.67	
Tokur deposit in terrigenous rocks, Khabarovsk Vein, level of 700 m	Average (6)	Unaltered sandstone	66.9	3.81	3.22					(–0.14)**	736–757
	N-751	Altered sandstone (0.1)	69.29	5.16	3.19	–0.65	–0.03	+0.65	+0.03	+0.68	
	N-752	The same (0.5)	67.74	5.03	2.45	+1.22	–0.74	–1.22	+0.74	–1.96	
Zone of disseminated mineralization, level of 590 m	N-157	Unaltered silty mudstone	61.24	1.98	4.38						No data
	N-717	Metasomatic rock	83.49	0.19	4.07	–1.79	–0.31	+1.79	+0.31	+1.48	

Note: (*) Numerals in parentheses designate samples used for calculating the average composition.
(**) Average of 6 analyses of altered sandstones taken at a distance of 4 m from hanging and footwalls of vein.
(***) Results of the AAS analysis of author's samples (V.T. Dobraya and I.D. Zaikin, analysts; AmurKNII, Blagoveshchensk).

Table 2. Redistribution of alkali metals between host rocks of gold–quartz vein and fracture-pore fluid at the Tokur deposit, Vein 184

Level of deposit and distance of sample from vein	Sample	Rock	Content in rock, wt %			Gain (+) and loss (–)				Sodic index I_{Na}^{Fl}			Fineness of gold, ‰	
			SiO$_2$	Na$_2$O	K$_2$O	in rock		in fluid		at sampling point	in wall-rock zone, 0–1 m	in wall-rock zone, 0–2 m	after author's data**	after [14]
						Na$_2$O	K$_2$O	Na$_2$O^{Fl}	K$_2$O^{Fl}					
Level 777 m	Average composition (2)	Unaltered mudstone	62.15	2.37	4.14								$\frac{691–733}{711}$(6)	718
25 m	N-178	Slightly altered sandstone	66.01	2.92	3.58									
0.1 m	N-261	Mudstone*	63.98	2.90	4.45	+0.53	+0.31	–0.53	–0.31	–0.22	–0.34	–0.44		
0.5 m	N-262	Sandstone*	68.29	3.22	3.43	+0.3	–0.15	–0.3	+0.15	–0.45				
2.0 m	N-264	Mudstone*	62.75	2.61	3.92	+0.24	–0.22	–0.24	+0.22	–0.68				
Level 700 m	N-178	Slightly altered sandstone	66.01	2.92	3.58								$\frac{734–854}{789}$(7)	$\frac{700–803}{757}$
0.1 m	N-175	Sandstone*	66.36	4.11	2.89	+1.19	–0.69	–1.19	+0.69	–1.88	–0.53	–0.08		
0.5 m	N-176	The same	63.97	2.75	4.22	–0.17	+0.64	+0.17	–0.64	+0.81				
2.0 m	N-177	″	64.68	2.80	4.29	–0.12	+0.71	+0.12	–0.71	+0.83				
Level 590 m	N-157	Unaltered mudstone	61.24	1.98	4.38								$\frac{747–845}{811}$(5)	No data
0.1 m	N-151	Mudstone*	62.78	1.89	4.50	–0.09	+0.12	+0.09	–0.12	+0.21	+0.46	+0.40		
0.5 m	N-152	The same	62.17	1.80	4.92	–0.18	+0.54	+0.18	–0.54	+0.72				
2.0 m	N-153	″	61.89	1.51	4.17	–0.47	–0.21	+0.47	+0.21	+0.26				

Note: Numerals in parentheses designate samples.
(*) Altered rocks.
(**) Variation range is shown in the nominator; average value, in the denominator.

Fig. 2 (lines *1* and *2*, respectively). The hydrothermal alteration of rocks in these zones was accompanied by the loss of Na_2O at the lower level and its gain in rocks at the intermediate and upper levels.

The calculated average I_{Na}^{Fl} values of fracture-pore fluids for wall-rock alteration zones at 0–1 and 0–2 m (Table 2) are close to each other at the same level, while the Na content decreases and the K content increases upsection (Fig. 2, trends *3* and *4*). Various levels of the deposit show consistent trends of I_{Na}^{Fl} and average fineness of gold (trend *5*), which decreases upsection on average by 80–100‰.

Thus, the data on three deposits demonstrate a close correlation between the proportions of alkali metals in host rocks and the fineness of native gold, consistent with experimental results. It was established [3] that, at $T = 200–250°C$ and $P = 20$ bar, the intensity of Au solubility in the NaCl solution is 1.53 times higher than that in the KCl solution, whereas the inverse relationship is revealed for silver. The Ag solubility in KCl solution is 9.8 times higher (on average) than the Au solubility. At a higher temperature (600–700°C, NNO buffer), this tendency is retained but the contrast increases: Au solubility is equal to 0.4×10^{-5} mol/kg in 2M KCl solution [6] increases to 0.6×10^{-3} mol/kg in 2M NaCl solution [7].

Therefore, it is reasonable to suggest that Na^+ serves as a counter ion, which stabilizes negatively charged gold chloride complexes $[AuCl_2]^-$ and $[AuCl_4]^-$ dominating in acid chloride solutions at medium and higher temperatures [8]. The removal of K^+ from rocks into solution and, conversely, the input of Na^+ from rocks into solution favor the concentration and stabilization of gold complexes relative to silver under equilibrium conditions. The fineness of crystallizing gold is eventually a function of the relationship of concentrations of complex Au and Ag ions dissolved in fluids, as follows from thermodynamic calculations [9]. The relationship, in turn, depends on the relationship of concentrations of alkali metals.

In terms of the model of self-development of screened ore-forming hydrothermal systems [10], the supply (suction) of the transformed fracture-pore fluids into the newly formed cavities and their mixing with deep fluids and heterogenization due to the pressure release promoted an intense deposition of minerals and crystallization of gold. The type and size of the newly formed cavities governed the formation of veins (or 3D stockworks) and stringer-disseminated ore lodes with gold. The fineness of gold therein was predetermined by the proportions of alkali metals in fracture-pore fluid during the preore metasomatic alteration of host rocks.

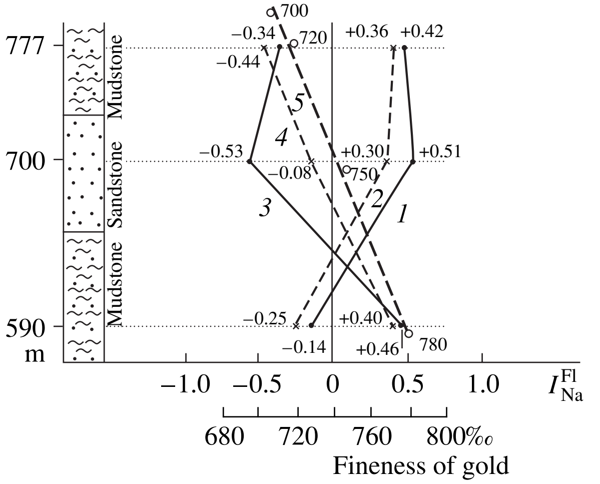

Fig. 2. Trends of sodic index of fluid (I_{Na}^{Fl}) for Vein 184 and fineness of gold at different levels of the Tokur deposit. (*1, 2*) Averaged loss (–) of Na_2O from hydrothermally altered rocks or gain (+) at (*1*) 0–1 m and (*2*) 0–2 m from the vein contact; (*3, 4*) vertical trends of I_{Na}^{Fl} of fluid due to its interaction with host rocks at (*3*) 0–1 m and (*4*) 0–2 m from the vein contact; (*5*) vertical trend of fineness of gold (based on average values from the available data).

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