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GEOCHEMISTRY

First Data on the Raman Microspectrometry of Ore-Forming Fluids of Gold and Uranium Mineralizations in Aldan (Republic of Sakha, Yakutia)

A. N. Krasnov[a], **T. Lhomme**[b], **T. L. Krylova**[a], **and E. O. Groznova**[a]

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The central Aldan gold–uranium ore district (Sakha Republic, Yakutia) is characterized by a unique juxtaposition of gold and uranium mineralizations genetically related to the Mesozoic alkaline magmatism [1, 2]. However, data on the formation conditions of these two mineralization types in the Aldan Shield are very rare. The available data are mainly related to the thermal regime. We investigated fluid inclusions in minerals of the Samolazovskoe gold deposit located in the southern area of the central Aldan region and obtained new data on the evolution of fluid composition in the course of endogenous gold and uranium mineralizations.

The Samolazovskoe deposit is confined to the skarnized contact of syenite sills with Lower Cambrian dolomites. The main commercial ore (Au *n*–600 g/t) is represented by weathering products related to the intense disintegration and supergene reworking of primary rocks and ores. Primary endogenous mineralization is observed as rare relicts in orebodies and their periphery [3].

Endogenous mineralization of the deposit can be divided into the following stages: (1) formation of skarns with an Au content in bulk samples up to 0.2 g/t (based on neutron activation data); (2) development of quartz–fluorite veins (Au 0.02–0.05 g/t); (3) formation of beresite-type metasomatites with gold stringers and high Au contents (up to 5 g/t); and (4) stringer–disseminated uranium mineralization [4].

The data obtained show that the primary gold mineralization of the Samolazovskoe deposit is associated with the beresite-type metasomatites crosscut by quartz–ankerite veinlets with sericite and fluorite. The content of ore minerals in the veinlets is as much as 20 vol %. The major ore minerals are as follows: pyrite, fahlores (tennantite and tetrahedrite), sphalerite, marcasite, chalcopyrite, and galena. Bornite, covellite, pyrrhotite, sulvanite, and molybdenite are less abundant. Gold shows a close geochemical correlation with Sb, Zn, V, As, Bi, Mo, and Ag.

The subordinate stringer–disseminated uranium mineralization is represented by uraninite, pitchblende, and coffinite associated with marcasite, quartz, fluorite, and calcite. Based on the bulk XFA data, the U content varies from 3 to 120 g/t (average 15–20 g/t). Mineralogical investigations indicate that the uranium compounds mentioned above are the youngest formations in the deposit. However, this conclusion is not supported by the presence of uraninite, which can form at sufficiently high temperatures (250–280°C).

We studied individual fluid inclusions by microthermometric methods using a Linkam-THMSG 600 thermocryogenic stage equipped with an Olimpus lens (magnification 80) at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry. The bulk composition of fluid inclusions was analyzed by gas chromatography at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow [5]. Compositions of solutions and gaseous phases in individual fluid inclusions from the Central Aldan region were investigated for the first time by the Raman microspectrometric method using a DILOR XY device in the G2R laboratory of Poincaré University.

We analyzed the following varieties of fluid inclusion: (i) primary and secondary fluid inclusions in quartz from quartz–sulfide veinlets with the gold ore association; (ii) primary fluid inclusions in quartz from U-rich veinlets. The genetic classification of inclusions was based on Roedder's criteria [6].

Quartz from the gold ore association. The quartz includes primary inclusions of the following three types: solid phase inclusions (gas + solution + liquid carbon dioxide), two-phase inclusions (gas + solution),

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[a] *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia; e-mail: kras2003@rambler.ru*

[b] *CREGU, UMR G2R 7566-Universite Henri Poincare, BR239, 54506, Vandoeuvre-les-Nancy, France*

Table 1. Results of microthermometry of fluid inclusions in quartz samples from the Samolazovskoe deposit

Sample no.	Inclusion type	n	Composition of inclusions	T_h, °C	T_{em}, °C	$T_{m\,i}$, °C	C_{NaCl}, wt %, NaCl equiv.	T_m, °C	T_m CO_2, °C	T_h CO_2, °C
Quartz of the gold ore association										
ANS-1	P	10	g + s + CO_2l	347–320	–16.7 to –18.1	–8.0 to –4.7	11.7–7.5	7.2–5.9	–57.6 to –57.0	21.4–19.3 L
C-7	P	5	g + s	330–322	–14.1 to –17.6	–7.5 to –0.2	11.1–0.4	9.9–4.5	–58.6 to –57.1	–
C-7	P	2	g	–	–	–	–	–	–57.3 to –57.2	–13.9 to –14.0 L
446	P	6	g + s	327–306	–16.4 to –19.6	–0.6 to –0.2	1.1–0.4	–	–	–
729/108	P	2	g + s	321–317	–21.7 to –22.3	–7.5 to –7.0	11.1–10.5	14.0–11.0	–	–
C-13	P	16	g + s	300–228	–11.2 to –28.1	–8.5 to –3.0	12.3–4.9	17.1–9.8	–60.9 to –58.9	–
C-14	P	5	g + s	308–311	–16.7 to –24.8	–6.5 to –4.9	9.9–7.7	7.8–6.5	–58.0 to –59.8	–
C-14	P	26	g + s	311–300	–24.0 to –25.0	–	9.0	7.8	–	–
C-14	P	3	g + s + CO_2l	310 G	–23.0 to –24.0	–6.5 to –6.4	8.0	6.5	–59.0 to –58.9	11.8 G
Sam 51	P	6	g + s	260–255	–30.0 to –33.0	–7.5 to –7.0	7.0	4.6	–	–
729/108	S	2	g + s	178–163	–21.1 to –21.9	–3.8 to –3.6	6.2–5.9	–	–	–
Quartz of the uranium ore association										
445	P	5	g + s	206–149	–24 to –24.5	–5.5 to –5.4	8.6–8.4	–	–	–
S-01-20	P	4	g + s	203–199	–18.3 to –23.2	–4.6 to –3.8	7.3–6.2	16.3–8.4	–	–
S-01-30	P	8	g + s	195–170	–20 to –24.3	–2.7 to –2.5	4.5–4.2	–	–	–
492	P	6	g + s	189–179	–16.4 to –20	–4.9 to –2.8	7.7–4.7	12.0–3.0	–	–

Note: Inclusion types: (P) primary, (S) secondary; inclusion composition: (g) gaseous, (s) solution, (CO_2l); liquid carbon dioxide; temperature parameters: (T_{ih}) inclusion homogenization, (T_{em}) eutectic melting, ($T_{m\,i}$) ice melting, ($T_{m\,s}$) salt hydrate melting, (T_m CO_2) carbon dioxide melting, (T_h CO_2) carbon dioxide homogenization into (L) liquid and (G) gas; (C) salt concentration in solution, wt % NaCl equiv.

and one-phase inclusions. Two-phase fluid inclusions are the predominant type. The three- and one-phase varieties are rare. One-phase fluid inclusions occur together with the two-phase variety in growth zones; i.e., they were entrapped simultaneously. This fact indicates the existence of a heterogeneous fluid. The secondary inclusions are composed of gas and solution.

The homogenization temperature (T_h) of primary fluid inclusions ranges from 255 to 347°C (Table 1). The eutectic temperature of solutions in primary two- and three-phase fluid inclusions varies from –33 to –21.4°C. This temperature range is typical of NaCl solutions. However, the dissolution of salt hydrates at 0–32°C indicates the presence of bicarbonate or sulfate ions in the solutions [7]. Higher values of the eutectic melting temperature, T_{em} (from –19.6 to –14.1°C), are typical of both KCl and bicarbonate (or sulfate) solutions. Therefore, the implication of such values is ambiguous. The salt concentration varies from 11.7 to 0.4 wt % NaCl equiv. Carbon dioxide in the three-phase fluid inclusion is characterized by a melting temperature ranging from –60.9 to –57.2°C and homogenization into gas at 11 or 12°C.

In the two-phase fluid inclusion, the liquid CO_2 usually appears as a thin rim in the course of microthermometric cooling of the sample. The existence of this submicroscopic liquid phase is indicated by its freezing temperature ranging from –100 to –120°C and melting temperature ranging from –60.8 to –58°C. We did not record its homogenization into gas. Hence, the gaseous phase of a fluid inclusion always contains a variable amount of liquid CO_2. We believe that the mineral-forming fluids had a constant composition during the formation of veinlets. Only the proportions of components in the fluids changed in this process.

The one-phase fluid inclusion contains liquid CO_2 (T_m –57.2°C, T_h –14.0°C, density 1.004 g/cm^3). The determination of pressure by the Kalyuzhnyi method [8] for quartz with relicts of heterogeneous fluid yielded 250 bar at 311°C. Homogenization of carbon dioxide into the gaseous phase also testifies to a low fluid density, i.e., a low-pressure setting of gold mineralization. Hence, the parameter T_h reflects real temperatures of mineral formation.

The T_h value of secondary inclusions ranges from 178 to 163°C. They contain NaCl solutions (T_{em} varies

Table 2. Results of the Raman microspectrometry of fluid inclusions in quartz samples from the Samolazovskoe deposit

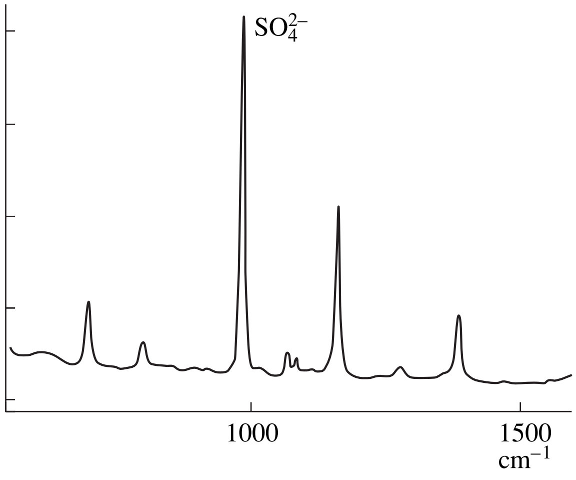
Quartz	CO_2	CH_4	N_2	H_2	H_2S	HCO_3^{-}*	SO_4^{2-}
	mol %						
Quartz of the gold ore association	>97	<0.1	2.5	–	<0.1	0.13	Present
	>98	?	2.0	–	0.2	<0.05	″
	>98	<0.1	1.5	–	<0.1	0.10	″
Quartz of the uranium ore association	>97	–	2.5	<0.5		0.13	″

Note: (*) The mole content in 1000 g H_2O is calculated for 0.5 M NaCl solution.

from –21.9 to –21.1°C; salt concentration, from 6.2 to 5.9 wt % NaCl equiv).

Based on gas chromatography data, the fluid is mainly composed of water (up to 94 mol %). The gaseous phase also contains carbon dioxide (up to 5.1 mol %), nitrogen (up to 0.9 mol %), and methane (up to 0.05 mol %). The decrease in the T_m CO_2 value at temperatures below 300°C (Table 1) suggests an increase in the concentration of the gas admixture (methane, according to chromatography data).

Application of Raman microspectrometry made it possible to refine significantly the fluid inclusion composition in quartz from gold ore veinlets (Table 2). Solutions in primary fluid inclusions contain bicarbonate ions (from 0.05 to 0.13 mol %, based on calculation for the 0.5 M NaCl solution) and an appreciable amount of SO_4^{2-}. This fact confirms our conclusions based on the microthermometric data (figure). In the gaseous phase of fluid inclusions, in which cryometric analysis did not record carbon dioxide, we detected the following components (mol %): CO_2 97–95, CH_4 <0.1, nitrogen 1.5–2.5, and H_2S 0.2–0.1.



The SO_4^{2-} peak observed in the Raman spectrum of the primary fluid inclusion in quartz from the gold ore association.

Based on the Raman microspectrometric data, the solution in the secondary fluid inclusion also contains bicarbonate and sulfate ions, while the gaseous phase contains CO_2 (up to 97 mol % or more) and nitrogen (up to 2.5 mol %). Methane and hydrogen sulfide were not detected. It is interesting that the secondary fluid inclusion contains molecular hydrogen (up to 0.5 mol %), which is an alien component in the presence of carbon dioxide.

Molecular H_2 and O_2 have been detected recently in the mineral-hosted fluid inclusions at many uranium deposits [9–11]. The appearance of these phases is related to the radiolysis of water under the impact of radioactive emanation. Radiolysis products can form inside the inclusion if the solution contains some uranium, or they can be entrapped in the course of the percolation of mineral-forming solutions in the uranium mineralization zone and the subsequent growth of quartz crystals. Based on statistical data, the prevalence of H_2 is an indicator of low-grade uranium ores, while the predominance of O_2 in the fluid inclusion suggests the development of high-grade ores. Hence, the presence of secondary fluid inclusions with molecular hydrogen in the quartz of gold ore veinlets characterizes the uranium ore process.

Primary fluid inclusions in the uranium ore quartz are represented by the two-phase (gas + solution) variety with the homogenization temperature ranging from 206 to 149°C (Table 1). This temperature interval also includes the T_h value of secondary fluid inclusions from the gold ore quartz. The solutions are characterized by T_{em} varying from –24.5 to –16.4°C. The melting temperature of salt hydrates varies from 16.3 to 3.0°C, respectively. Data on secondary fluid inclusions with molecular hydrogen in quartz of gold ore veinlets suggest that the solutions have a sodium chloride–bicarbonate–sulfate composition. The salt concentration varies from 8.4 to 4.2 wt % NaCl equiv.

Thus, the primary gold mineralization took place at a temperature range of 350–250°C in a water-rich medium from sodium chloride–bicarbonate–sulfate solutions with CO_2, N_2, CH_4, and H_2S. The coexistence of both SO_4^{2-} and H_2S in the solution and gaseous phase, respectively, of the fluid inclusion indicates instability of the redox potential of fluids. The parameter *Eh* can serve as the main factor responsible for the deposition of primary gold. According to our data, the methane concentration in fluids correlates with the Au content in ores.

Uranium mineralization evolved at a lower temperature interval (200–180°C) from sodium chloride–sulfate–bicarbonate solutions that were similar to the auriferous solutions. The secondary nature of the fluid inclusion with molecular hydrogen indicates unambiguously that the deposition of uranium minerals postdated gold mineralization. Such interrelations between Mesozoic uranium and gold mineralizations are typical of not only the Samolazovskoe deposit, but also of all types of deposits in the central Aldan region.

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