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Examiner's report
of the thesis

"MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS AND THE PROBLEMS OF THE GENESIS OF THE KUTYN GOLD DEPOSIT, KHABAROVSK KRAI"

for the degree of candidate of geological and mineralogical sciences of St. Petersburg State University
Scientific specialty 1.6.4.
Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration

It is a pleasure to write this recommendation letter for acceptance of the degree of candidate of geological and mineralogical sciences submitted by Adel Maratovna Azarian.

At first, I would like to clarify that I never met Ms. Azarian in person and will thus be able to only judge her written performance.

Ms. Azarian's thesis consists of eight main chapters and a paragraph with conclusions at the end of the written thesis.

Three individual publications do exist with Ms. Azarian being first author. It seems to me that 2 articles are in Russian and the third article is an English translation and published in Doklady Earth Sciences - Geology of ore deposits. Her Russian scientific supervisor at State University St. Petersburg, Associate Professor, Candidate of Geological and Mineralogical Sciences, E.V. Badanina, is - beyond

others - co-author of all articles. Ms. Azarian presented her research also at various international and Russian conferences.

In the following, I will individually summarize and comment on each of the eight main chapters, i.e. chapters 1 to 8 in the written thesis.

In Chapter 1 (General information about gold deposits), the candidate provides a comprehensive overview of the general classification of gold deposits as well as the gold deposits of the studied region.

Although Figure 1.1. (Tectonic position of various types of gold deposits, taken from the literature) is a nice overview about the tectonic settings, the geologic correlation of the Khabarovsk Krai gold deposits as information added to Figure 1.1. would be beneficial.

Chapter 2 (Geological structure of the Kutyn deposit area) with its subchapter 2.1. (Brief geological characteristics and history of the region's development), 2.2. (Geological structure of the Ulban terrane), and 2.3. (Geological position of the Kutyn deposit) seems to be a detailed literature review.

However, in subchapter 2.1. the tectonic framework and distribution of igneous rocks would have been a nice add-on, in subchapter 2.2. the information about the geological structure of the Ulban terrane would have tremendously benefitted from a geological cross-section and in subchapter 2.3. a figure as well as information related to the geodynamic setting is missing. Further, the need of Figure 2.3, especially as the figure is not discussed in the main text, is questionable.

Chapter 3 (Petrographic characteristics of granodiorites and metasomatites) with at first information regarding the petrographic features of granodiorites of the Birandjinsky massif (subchapter 3.1.) and as a second information the petrographic features of metasomatites (subchapter 3.2.) is a well-thought division of the petrographic chapter.

Although subchapter 3.1. is very brief and only marginally detailed, it is still sufficiently detailed enough. Subchapter 3.2. provides excellent observations of metasomatic overprints and new mineralization and/or changes based on metasomatic processes.

Chapter 4 is dedicated to the geochemical characteristics of granodiorites and metasomatites and, as is was in chapter 3, chapter 4 is subdivided in the results of the geochemistry of the investigated granitoids (subchapter 4.1.) and metasomatites (subchapter 4.2.).

Based on the geochemical data of the granitoids the candidate was able to unravel the geodynamic conditions. Further, the geochemical data of the metasomatites allowed to gain information about the element transfer and change of composition during ore-bearing metasomatic processes that finally formed the beresite-like rocks.

Although the analyses were performed at the analytical laboratories of VSEGEI, and, thus, not done by the candidate herself, details about the used analytical devices, analytical parameters and e.g., detection limits, are still crucial information that are needed to be able to judge the quality of the data.
The candidate should have added this information in her written thesis and at least needs to be knowledgeable regarding the analytical parameters and conditions at the day of her defense.

Chapter 5 (Mineralogy of metasomatites of the Kutyn deposit) consists of in total 4 subchapters. Subchapter 5.1. (Mineral composition of rocks and metasomatites) provides information about all mineral phases that are present in the studied magmatic and metasomatic rocks. Subchapter 5.2. (Characteristics of ore minerals) presents the results of a superb and carefully conducted study on the various ore mineral associations (namely: (i) pyrite-arsenopyrite mineral association, (ii) gold-tetrahedrite-arsenopyrite mineral association, (iii) gold-pyrite mineral association, (iv) telluride mineral association, and (v) goethite-arsenate mineral association). Subchapter 5.3. (Gold presence forms in the ores of the Kutyn deposit) seems to be more a literature review about possible occurrences of gold and Figure 5.14 is taken directly from the literature. The candidate used TEM to detect "invisible" gold in pyrite and arsenopyrite. Chapter 5 is concluded by subchapter 5.4. (Comparison of the mineral composition of the ores of the Kutyn and Albazino deposits) with a brief comparison of the Kutyn deposit (well-studied by the candidate) and the Albazino deposit.

The results presented in subchapter 5.1. are based on XRD analyses and the provided information about the analytical parameters are sufficient enough, although solely descriptive.

The results of the distribution of ore minerals (subchapter 5.2.) as well as the identification of the various ore-forming stages are carefully derived and figure 5.12. is a nice and illustrative summary of all different the associations of the ore minerals of the Kutyn deposit.

The information about the details of the TEM analyses are sufficient enough (subchapter 5.3.). Even the name of the analyst (technician) is provided. Unfortunately, no native gold was found. The candidate should provide further information about the selection criteria of the pyrite and arsenopyrite samples analyzed by TEM in her final defense.

In subchapter 5.4. The candidate did not sufficiently provide information where her knowledge of the Albazino deposit is coming from. No references are provided. The reader is thus puzzled about the quality but also the need of this comparison.

Chapter 6 (Physico-chemical parameters of the formation of the Kutyn deposit) provides in 4 subchapters information about formation conditions, i.e. temperature, pressure, and homogenization temperatures based on studies of individual fluid inclusion as well as based on complex thermal analysis by thermogravimetric analysis and differential scanning.

The candidate wrote in subchapter 6.1. "The temperature calculated from the chlorite of granodiorites varies from 229°C to 278°C, averaging 257°C (14 points of analysis) (Table 6.1). The temperature of chlorite formation in metasomatized sandstones varies from 213°C to 236°C (4 points of analysis) (Table 6.1)." Table 6.1. only lists in total 4 points of analysis, namely 2 chlorite analyses of metasomatized granodiorites and 2 chlorite analyses of metasomatized sandstones. Why are not all 18 analyses listed? What are the errors of the analyses, i.e. what will be the additional errors added to those of the standard deviation of the average temperature values?

Besides those more critical questions, I would like to point out that the candidate performed calculations in the S-Te-activity space and were able to nail down the conditions of the paragenesis of minerals of the gold-tetrahedrite-arsenopyrite association with hessite of the Kutyn deposit. Well done!

The calculated pressure conditions (average ~1.6 kbar, see subchapter 6.2.) seem to be likely as they represent shallow to upper crustal depth. However, more information about the uncertainties of the pressure calculations would have been beneficial.

Subchapters 6.3. and 6.4. carefully derive homogenization temperatures based on fluid inclusion studies (thermo- and cryometric studies of fluid inclusions in quartz as well as Raman spectroscopic studies of the gas phase of the inclusions in quartz) as well as bulk thermal analysis (TG, DSC) of quartz of the gold-pyrite association of the vein stage. Those studies are perfectly preformed and reveal consistent temperatures regardless if the temperatures are derived based on the microthermal studies of individual fluid inclusions or on the complex thermal analysis of quartz. The results really allow to nail down the stages of mineral formation. Well done!

Chapter 7 (Isotope-geochronological and isotope-geochemical studies of granodiorites of the Birandjinsky massif and metasomatites) with its 2 main subchapters (7.1. Isotope-geochronological studies of granodiorites of the Biranjinsky massif and metasomatites; 7.2. Isotope-geochemical studies) allows not only age determination of the granodiorites (U-Pb ages of zircon: 90.7±1.7 Ma; Rb-Sr ages of bulk rock and minerals (K-feldspar, K-Na feldspar and biotite): 93 ± 1 Ma) but also derivation of the age of the gold-bearing quartz-sericite-carbonate metasomatic rocks of the Kutyn deposit (Rb-Sr ages of sericite and albitized K-feldspar: 79.3 ± 0.5 Ma). Further, the isotope-geochemical studies (O, C, S, Pb) allow statements regarding (1) the origin of the metasomatic fluids based on $\delta^{18}O$ and $\delta^{13}C$ values (quote (page 223): "mixture of fluids of various origins - isotope-heavy magmatogenic and/or metamorphogenic and isotope-light meteoric, which confirms the complex nature of ore-forming solutions, including fluids separated from the magmatic chamber or formed during dehydration during contact or regional metamorphism, as well as deep meteoric waters"), (2) the likelihood of a single homogeneous source of ore material based on the narrow range of $\delta^{34}S$ values of pyrite and arsenopyrite, and (3) the possibility of rocks of the Okhotsk Early Archean complex located southwest of the Kutyn deposit as probable single homogeneous source of ore material of the Kutyn deposit based on isotopic composition of Pb in pyrite and arsenopyrite of the gold-tetrahedrite-arsenopyrite association.

All isotope measurements were performed by analysts (technicians) of various Russian state-of-the-art laboratories (VSEGEI - St. Petersburg; IPGG RAS - St. Petersburg; GI SB RAS - Ulan-Ude, IGM SB RAS - Novosibirsk) and the candidate succeeded in providing sufficient information about the analytical details. However, more information about the selection criteria and procedure of the samples should be provided in the oral defense.

Chapter 8 (On the genesis of the Kutyn deposit) with its 4 subchapters (8.1. Age ratios of ore-bearing metasomatites and granodiorites of the Birandjinsky massif; 8.2. Geochemistry of the metasomatic process; 8.3. Physico-chemical conditions of ore deposition; 8.4. Sources of ore matter and ore-forming solutions) solely summarizes all findings of the previous chapters.

A schematic illustration of the geodynamic setting and the various stages of ore formation would be a nice addition. The candidate should provide such a graphical summary in her oral defense.

The final chapter of the thesis is the conclusion chapter that briefly lists again the findings already summarized in more detail in chapter 8. Unfortunately, some kind of an outlook to future needed work is missing.

As consequential thought, a question for the candidate might be to provide a reflection about important and still missing information as well as to define urgently needed future work at the Q&A-part of her defense.

Unfortunately, some flaws in the written part of the thesis linked to sloppiness and careless performance of the English version of the thesis exist. Citations like "(Gold-bearing..., 2010)" (see page 144), "(Geodynamics ..., 2006)" (see pages 147, 150, 218, 232), or "(Wolfram..., 1996)" (see page 166; please note: this reference is even missing in the list of references!) are examples of the sloppiness and are highly unprofessional.

Further, a very important information is missing: Although the candidate described the geological regions, more detailed information regarding sample locations and a map with the sample locations are missing!

However, still it is beyond doubt that the submitted thesis of Ms. Azarian is a 'solid piece of work' and the high level of the PhD is out of question.

The thoughts of mine above regarding flaw, questions and topics for discussion should not be counted or judged as severe criticism of Ms. Azarian's work and her findings.

Ms. Azarian should be granted the award of candidate of geological and mineralogical sciences at St. Petersburg State University - scientific specialty 1.6.4.: Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration.

No violations of paragraphs 9 and 11 of the Order No.11181/1 as of November 19, 2021 "On the Procedure for Awarding Academic Degrees at St. Petersburg State University" have been detected.

With kind regards,

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