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-- To whom it may concern --St. Petersburg State University Prof. Dr. Astrid Holzheid Experimental and Theoretical Petrology

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Examiner's report of the thesis

"Ecological and geochemical characteristics of the soils and sediments of the territory adjacent to the zinc ore enrichment plant of the Chaabet-El-Hamra mine (Algeria)"

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 Rima Omara.

At first, I would like to clarify that I do not know Ms. Omara in person and will thus be able to only judge her written performance.

Ms. Omara's thesis consists of six main chapters. The first chapter provides an overview about the geological setting of study area, including the ore deposit of Chaabet-El-Hamra. This is followed by sampling and laboratory methods (chapter 2). Chapter 3 provides more information about the sampled sediments and samples from the dumps (technogenic sediments) regarding mineralogy and soil characteristics, including organic matter content, granulometric composition and pH values as well as the spatial distribution. Chapters 4 and 5 provide in-depth details on the chemical distribution of the three mainly studied and most important elements Zn, Pb, and Cd as well as on the mobile forms of those elements within the entire sampled area. Chapter 6 is dedicated to thermodynamic modeling with the aim to predict changes in the mineral composition of soils and technogenic sediments of the minerals while interacting with surface and precipitation waters and to assess the potential contamination risk of ground water. These chapters are bracketed by a detailed introduction chapter and a conclusion chapter.

Four individual publications do exist with Ms. Omara being first author in three out of the four publications. Two of the publications are in Russian, and two are in English with three out of the four publications (one English and both Russian articles) published in international peer-reviewed and indexed journals. Her Russian scientific supervisor at State University St. Petersburg, Professor Dr. M. V. Charykova, is - beyond others - co-author of those three articles. Ms. Omara is single author on the fourth article.

The <u>introduction chapter</u> of her written thesis is a well-structured short introduction which highlights the relevance of the study and summarizes e.g., envisaged aims, individual tasks, used methods, key results, presentations at conferences and publications, respectively, and concludes with acknowledgements. Ms. Omara refers to her 4 scientific articles as well as her contributions as author to the articles.

In the following, I will individually summarize and comment on each of the six main chapters.

<u>Chapter 1</u> (General characteristics of the study area) provides (i) a brief information about the location of the deposit and geological setting, (ii) detailed information about the characteristics of the deposit including a stratigraphic section and first impressions about the mineralization, and (iii) the extraction methods of the ore, including the environmental impact due to mineral reactions that lead to formation of acid mine drainage (AMD).

The majority of the information is listed facts and observations without really scientific in-depth knowledge. However, the last part of the chapter is of great significance as it provides own thoughts regarding the formation of AMD based on the most common minerals and further geochemical processes as well as the formation of near-neutral waters during the mining process. The candidate mentions some possibilities to protect the environment. It would be of interest, if some of the mentioned ways are used at the Kherzet Yousef mining complex already. The candidate should comment on that.

In <u>chapter 2</u> (Evaluation methodologies) Ms. Omara introduces her sampling strategy and the used analytical methodologies. The provided information is sufficient enough.

<u>Chapter 3</u> (General characteristics of soils and technogenic sediments) provides information about the soil characteristics, including color characterization and granulometric composition, lithological and mineralogical characterization, CHN (carbon, hydrogen and nitrogen elemental content) and pH analysis nicely correlated to the entire sampling area.

It would be nice if the candidate could comment on the mineralogical characterization and put the characterization in relation to the geological bedrocks during the Q&A-part of her defense.

In <u>Chapter 4</u> (General assessment of soil and sediment contamination by heavy metals) Ms. Omara provides at first an overview about the various definitions of heavy metals in the literature and in Algeria with the most toxic heavy metals being Pb, Zn, Hg, As and the less toxic heavy metals Cr, Ni, Se, Mn and Co. This is followed by information about the content of those elements as well as other major, minor and trace elements in soils and dump samples and an assessment by the main pollutants, including the spatial distribution. Ms. Omara correlates the abundances of the various studied elements to the observed mineral paragenesis. Mr. Omara also summarizes the Hg spatial distribution and provides an assessment of Pb, Zn, and Cd concentrations in plants.

As some of the elements are soluble in water, a correlation with the subsurface water network would have been a nice add-on, although being in an arid area.

<u>Chapter 5</u> (Mobile forms of Zn, Pb and Cd in soils and technogenic sediments) starts with general information about possible mobile forms based on literature, is followed by a protocol for sequential extraction and the results of those solution runs, including determination of the mobile forms of Zn, Pb, and Cd. Ms. Omara's results reveal Cd as the most easily releasable element into the environment at the mining site as Pb and Zn are less soluble in arid climates.

Although Cr is defined as less toxic element, it is known that Cr with its various valence states could be also mobile. The candidate should comment on that.

In <u>Chapter 6</u> (Physico-chemical modeling of the interaction of soils and sediments with natural waters) the flaws of solution experiments are straightened out by using thermodynamic computer modeling. Ms. Omara used SELECTOR, one of the most recognized low temperature codes that is used for low temperature geochemical and environmental modeling. Ms. Omara used 5 samples, carefully chosen to represent the various sampling sites and pollution degrees, for the calculations that added knowledge regarding pH changes, equilibrium mineral compositions as well as equilibrium solutions compositions. The results are in accordance to the observed mineral alteration and elevated pollution levels of the studied area.

Why are only Eh-pH diagrams for Cr-H₂O and As-H₂O systems included in the written part of the thesis? What was the rationale behind this? The candidate should comment on that.

The <u>final chapter as conclusion chapter</u> summarizes the findings as it consecutively lists all findings. Most important is the second part of the conclusion chapter as Ms. Omara comments on the environmental impact of the production activity at the Kherzet Yousef mining complex and possible solutions to restore an intact environment at the site.

The candidate mentions phyto-extraction as a possible method and refers to her preliminary results on it (see Chapter 4). It might be nice to learn more about other possible methods during the Q&A-part of her defense.

All chapters are reasoned in themselves and also logic flow exists for all consecutive chapters.

Ms. Omara conducted a well-thought out study on the impact of mining activity at the Kherzet Yousef mining complex. However, more thoughts regarding remediation possibilities and techniques would have perfected the study even more.

It is beyond doubt that the submitted thesis of Ms. Omara meets the requirements of a successfully conducted PhD project.

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

Ms. Omara 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.

With kind regards,

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