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Report on the dissertation thesis entitled
Effects of phosphate on the mobility of arsenic in contaminated areas
Presented by Petra Stubbe to obtain the grade of
Doctor of Charles University In Applied Geology

The dissertation of Petra Stubbe concerns the geochemical behavior of arsenic and phosphorus and their competition in the mineral structure of host phases such as iron (oxy-)hydroxides, phosphates, and clay minerals. These two elements are widely distributed in the environment, both naturally occurring and because of anthropogenic activity. A variety of cases and environments, including soils, sediments, and waters, have been studied to understand how efficient the competition between As and P and its impact on arsenic mobility into the environment is. Based on *in-situ* studies, i.e., natural samples and within local environments, the competition between As and P was also studied after *ex-situ* work, using synthetic materials to better highlight and understand the mechanisms of substitution and sequestration in some specific conditions (phosphate-rich solutions). This work is based on direct observations of the crystal chemistry evolutions of the As and P-bearing phases: XRD, Raman spectroscopy, ATR-FTIR, SEM and EPMA. The dissolved fractions were analyzed by ICP-OES and studied by geochemical modeling.

General comments about the dissertation

The manuscript is in the overall well-written and easy to read, with only a few typos or incorrect figure references. The report, which is of 181 pages long and includes appendices, is divided into five chapters. Three of these chapters correspond to published or under review scientific articles in high-ranking journals, with Petra Stubbe as the first author. One of these articles was published in 2022 in *Environmental Pollution* and concerns the influence of P on the mobility of As in stream sediments in WWTP context. The third chapter corresponds to an article published in 2023 in *Applied Geochemistry* about As and Sb solid speciation and geochemical behavior in soils in contact with various phosphate solutions. The fourth chapter of the report was submitted to *Journal of Hazardous Material* and is currently under review. This article presents the results on the role of P on the stability and crystal chemistry evolution of poorly to nano-crystalline As-bearing phases. The manuscript begins with an overview of the main geochemical characteristics and mineralogy of As and P phases, and it concludes with a synthesis on the importance of the role of P towards As mobility, given its abundance in natural and anthropogenic-impacted environments.

The first chapter offers a comprehensive overview of the principal geochemical properties of As and P in soils and fluvial systems, as evidenced by scientific literature. The distribution and affinities of these elements with solid phases are also discussed. The chapter already highlights the

similar sequestration mechanisms and therefore competition within the solid phases between As and P. However, given the results discussed in the Chapter 3, a section concerning Sb is likely missing or at least a discussion on the similarity between As and Sb.

The second chapter examines the impact of water treatment facilities on the disposal of phosphate-rich effluents and the influence of P on As-rich stream sediments from a gold mining district. This study demonstrates that the P concentrations in dissolved fractions are not fully controlled, despite P being sequestered in stream bed sediments at the expense of As. The enhanced sequestration of P within the sediments resulted in the release of As into the water, as indicated by the higher As concentrations observed in the water samples collected from up to downstream locations. Further investigation would have been interesting to determine the relationship between flow rates and dissolved concentration, as well as the importance of the grain size and solid transport flows.

The third chapter is based on the assumed similarities in the geochemical behavior of As and Sb regarding their competition with P at low concentrations, which can occur in mining waste and agricultural soils. The investigation also examined the weathering products of primary minerals (sulfides and sulfosalts) and the redistribution of As and Sb within the secondary solid phases (mainly various As-Sb-bearing Fe +/- Ca phases and clay minerals). The study revealed distinct distributions of As and Sb within solid phases, with As predominantly associated with Fe (oxy)hydroxides when Sb was more frequently detected in clay minerals. This is a crucial consideration when evaluating the dynamics of As and Sb in the environment. The study also found that there was minimal transport between mining sites and nearby soils with the concentrations of As and Sb in soils significantly lower. This section concludes that two mechanisms control the behavior of As and Sb when in contact with P. Even at low concentrations, P can increase As mobility, but Sb mobility is controlled by pH rather than the presence of P.

The fourth chapter is devoted to experimental work on synthetic amorphous or nano-crystalline As-components – X-Ray amorphous ferric arsenate and yukonite respectively, as well as natural samples (soils and mine waste). The primary objective is to examine the impact of aqueous P effect on the stability of the As-bearing phases from various sources, given the extensive use of P in agricultural contexts or in remediation strategies. Long-term batch experiments were conducted over a period of up to one year. The results demonstrated that high phosphate treatments induced the precipitation of newly formed phases as brushite or amorphous Fe(III) phosphate, while low phosphate treatments led to the precipitation of Fe(III) (oxyhydr-)oxides. The study found that high phosphate concentration treatments may promote the As mobility and should be carefully considered.

The dissertation concluded globally that competition between As and P for the same crystallographic site in the solid fraction may promote mobility of As. It is therefore recommended that the use of phosphate as a fertilizer, for domestic purposes or for remediation strategies, should be carried out with caution.

More specific scientific remarks and questions

I particularly appreciate the synthetic form of the manuscript, the fact it avoids redundancy particularly in the material and methods section, which has been fully integrated within each article. However, I believe the SI appendices should have been included within the manuscript, after each published article.

As a mineralogist and regarding the work presented in the dissertation, I am also a little bit frustrated regarding the identification of the various carrier phases. Further characterization could have been performed to identify any remaining phases, and to address the limitations of Raman analyses due to fluorescence for instance. The assessment of solid speciation is of primary importance to evaluate the mobility of As and Sb in continental sub-surface environments. Furthermore, the use of the term "soils" to describe a heterogeneous group of materials is confusing. Do all agricultural soils have the same composition and properties? What about the

variation in the organic matter amount or clay fraction, which are among the most important parameters and have a significant effect on the mobility of As and P?

In Chapter 2, does the agricultural and urban area of 2.5 km² represent the entire watershed? It would be beneficial to have a geochemical background concerning As and P to facilitate a comparison of the added or discharged substances. It would also be helpful to have a water chemical composition before the WWTP was installed. A sampling point after the confluence would have been useful to assess the dilution effect. Was this done? No explanation was provided for the four-field campaign. Were the different meteorological conditions driven by the goal of testing the influence of the flow rate? In addition, what is the source of As in this fluvial system? Would it have been possible to assess the As load? What is the abundance of each As-bearing phase in the stream sediments? Can the bulk As concentrations be explained by the presence of less As-bearing phases? Could the exact nature of the P coatings observed around the sediment particles in Fig. 2.3 be clarified? Are there any insights into the kinetics of the reactions leading to the formation of these rims? Have such features been observed in upstream sediments?

Regarding the chapter 3, what are the average background concentrations of As, Sb and P in the Czech Republic? It would be beneficial to ascertain the quantity of arsenic released or extracted during the mining period, as well as the current concentration of arsenic in the waste. The results indicated that Raman spectroscopy analyses were sometimes not possible. However, what about spectra on amorphous or poorly crystalline phases? It is unclear why all the Fe (hydr-)oxides EPMA data are presented together, rather than distinguishing between goethite, which is more or less crystalline depending on the studied site, hematite, HFO and other forms. It is stated that Mn (hydr-)oxides contain less As and Sb. Could the observed differences be attributed to variations in crystallinity between the iron and manganese mineral(oid)s? The study revealed a discrepancy in the bearing phases between As and Sb, with Sb demonstrating a stronger affinity for clay minerals. The clay mineralogy indicated the prevalence of chlorite and illite. What could be the mechanism by which Sb is incorporated into the sheet silicate structure?

Chapter 4 presents the challenge of experiments conducted under static conditions, which represent a closed system that is difficult to relate to natural conditions. The evolution of the leaching solutions and the potential for secondary precipitate formation (e.g., as brushite or amorphous Fe(III) phosphate) may differ, making it difficult to apply the results to "in-situ" agricultural contexts. It would be beneficial to have a visual representation of the MW samples prior to the leaching experiments, illustrating the distribution of P around the arsenopyrite grains or within the phyllosilicates. It is unclear if the phyllosilicates already contained phosphorus prior to the leaching experiments.

In conclusion, the scientific approach developed is based on multidisciplinary tools. The quality and the quantity of the work carried out within the framework of this thesis are to be emphasized and new insights are brought into the understanding of complex systems of poorly to nanocrystalline phases, the mechanisms involved in the As and P competition at the scale of supergene environments. Therefore, I fully recommend that this thesis be defended and accepted for the award of the degree of Doctor of the Charles University in Applied Geology.

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