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## Fractionation of W in the topsoil of a meadow soil above the oxidation zone of the W deposit: results of sequential extraction and LA-ICP-MS analysis of soil from the Grantcharitsa deposit, Bulgaria

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## Фракционирание на W в горния слой на ливадна почва над окислителната зона на W находище: резултати от последователна екстракция и LA-ICP-MS анализ на почва от находище Грънчарица, България

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**Abstract.** A four-step sequential extraction procedure (SEP) was used to assess the distribution of W fractionation in the topsoil (0–20 cm) of the soil above the oxidation zone of the W deposit. Data on the extraction of W and other elements were obtained using LA-ICP-MS and SEM-EDX analyses of the dried, sieved and finely grinded original soil and residual samples after each step of the procedure. When processing LA-ICP-MS data, the SiO<sub>2</sub> content of the original soil was used as an internal standard for all samples in the sequential extraction procedure. It was found that of the approximately 90 ppm of total W content in the soil, about 25% is associated with organic matter, 40% with amorphous hydrous Fe oxides (ferrihydrite), 25% with crystalline hydrous Fe oxides (goethite), and about 10% with residual material (scheelite, silicates).

**Keywords:** tungsten fractionation, sequential extraction, meadow soil, oxidation zone.

### Introduction

Nowadays, tungsten (W) is not only a critical raw material with a wide range of applications, but also an object of intense scrutiny for its impact on the environment, one of the most important elements of which is soil (Bolan et al., 2023). The sources of W in soils, its content, distribution, bioavailability, toxicity, mobility and migration are key research topics, especially for areas with current or past mining and metallurgical activities. A common feature of the soils in these areas is a tendency for the concentration of W to increase in the surface soil layer (topsoil) caused by surface and airborne transport

of W-containing dust particles from mines or smelters (Zheng et al., 2020; Du et al., 2022). Getting into the soil, W-containing particles (W-minerals, W-metal) interact with aqueous solutions of the soil, resulting in the fractionation of W into various forms – from soluble species to solid carriers of W (aqueous oxides of Fe and Al, organic matter and others). Information on the distribution and speciation of W in soil is necessary to assess the mobility, bioavailability, and possible transport of W. For identification and semi-quantitative assessment of these forms of W, various sequential extraction procedure (SEP) schemes are used by different authors (Li et al., 2019; Hobson et al., 2020; Du et al.,

2022). The two most used SEP schemes for various elements are those of Tessier et al. (1979) and Wenzel et al. (2001), with the second scheme as assessed by Li et al. (2019) being more suitable for W.

Our recent study of soils in the area of the Grantcharitsa scheelite-pyrite deposit (Tarassov et al., 2021) revealed a pronounced trend of increasing W content in the topsoil of the alluvial soil covering the oxidation zone of the deposit. Since there is currently no mining or geological exploration on the deposit that could cause airborne transport of W-bearing particles, it is assumed that the behavior of W here is mainly determined by natural processes. In present work, we study the distribution of W fractionation in a selected topsoil sample from the Grantcharitsa deposit using a combined 4-step sequential extraction procedure based on the Wenzel et al. (2001) and Mossop et al. (2003) SEP schemes and specifically targeted for soils above oxidation zones.

## Experimental

**Sequential extraction procedure.** We previously established (Tarassov et al., 2021) that the W content in alluvial soils is strongly correlated with the content of C and Fe, but is not associated with the presence of sporadic grains of scheelite, W-bearing crystalline goethite, hematite and rutile visualized and identified in SEM-EDX. It was assumed that distribution of W in the soil is controlled by the organic matter and the Fe oxide/hydroxide compounds (ferrihydrite) formed in the soils. This means that the two most used SEP schemes of Wenzel et al. (SEP-W) and Tessier et al. (SEP-T) are generally unsuitable for the studied soils. The SEP-W scheme does not have an extraction step for organic matter, but includes two steps of sequential extraction of two reducible fractions (1) amor-

phous hydrous Fe and Al oxide (ferrihydrite) and (2) crystalline hydrous Fe and Al oxide (goethite), which are not present in the SEP-T scheme. The two steps of the SEP-W for amorphous and crystalline Fe/Al hydrous oxides extraction are included in our SEP scheme (Table 1, steps 2 and 3).

The SEP-T scheme includes two first steps aimed at extracting the water-soluble/exchangeable fraction (step 1) and the carbonate fraction (step 2). In our SEP scheme (Table 1, step 1) these two fractions are combined into step 1 as is proposed in the BCR (Community Bureau of Reference) SEP scheme of Mossop et al. (2003). The final step in the SEP of Mossop et al. (2003) targeting an oxidizable fraction with nominal target phases – organic matter and sulfides is also used in our SEP scheme (Table 1, step 4).

**Analytical approach: analysis of solid residuals.** Unlike traditional approaches, in which the amount of extracted target elements is determined by analyzing aqueous solutions of extractants, this work uses the opposite approach, namely, the analysis of solid residual material after each step of SEP. From the data presented in Tessier et al. (1979) follows that silica behaves inertly at all stages of SEP, and measured losses are calculated at 0.8–1.3% of 100% of the initial silica content. This allows us to use the concentration of SiO<sub>2</sub> in the original soil sample as an internal standard when analyzing residual materials after each SEP step. The amount of extracted W is calculated as the difference between the content of the element in the solid residues of the previous and current steps of the SEP at a constant silica content.

**Sample preparation.** Preliminary preparation of the studied soil included drying (40 °C), sieving (<1 mm), homogenization and quartering, separation of about 20 g, milling and micro mill-

Table 1. Sequential extraction procedure used in the present work

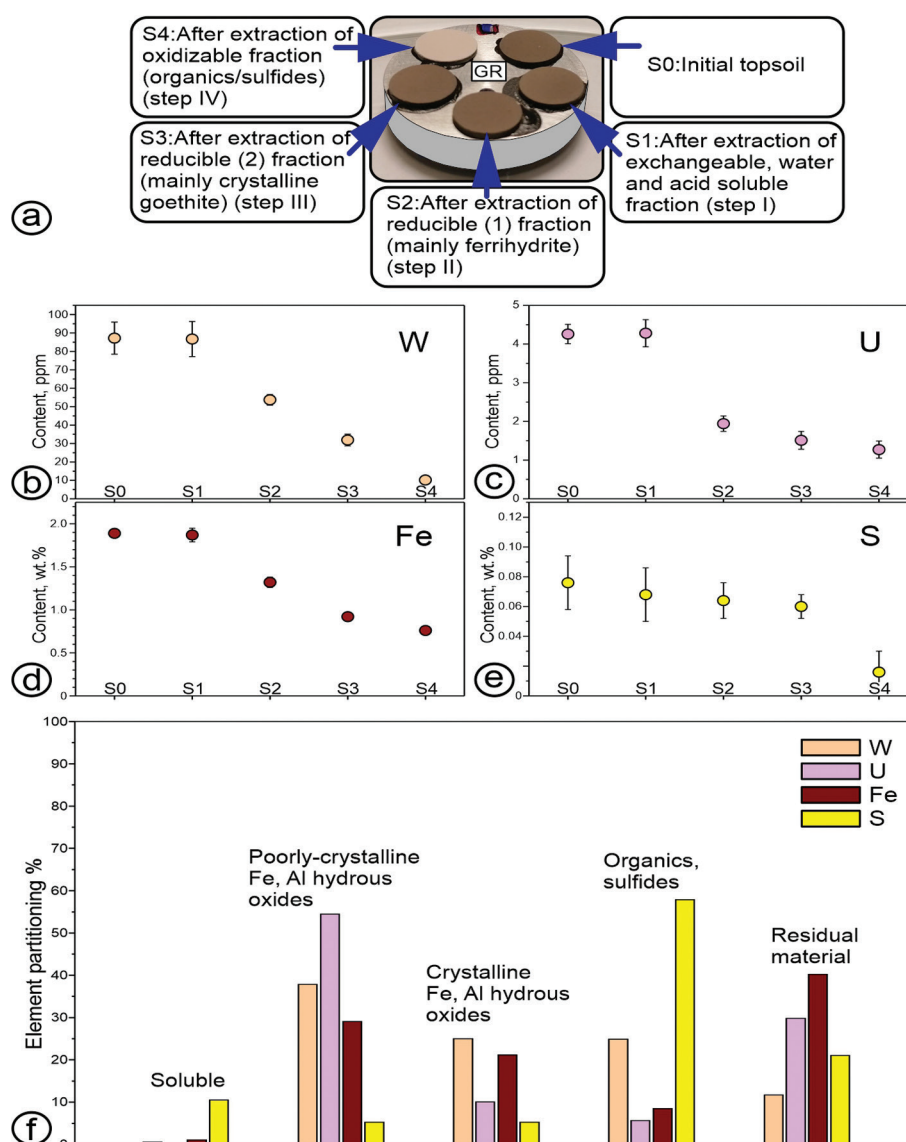
Step	Fraction	Nominal target phases	Procedure	Soil-solution ratio	Reference
1.	Exchangeable, water and acid soluble	soluble species, carbonates, cation exchange sites	0.11 M acetic acid; 10 h shaking, 20 °C; centrifuged	1:40	Mossop et al., 2003
2.	Reducible (1)	poorly crystalline and amorphous hydrous oxides of Fe and Al	0.2 M NH <sub>4</sub> -oxalate buffer in the dark (pH = 3.25); 4 h shaking; 20 °C	1:25	Wenzel et al., 2001
3.	Reducible (2)	well-crystallized hydrous oxides of Fe and Al	0.2 M NH <sub>4</sub> -oxalate buffer + 0.1 M ascorbic acid (pH = 3.25) in the light; 0.5 h in water basin at 96 ± 3 °C	1:25	Wenzel et al., 2001
4.	Oxidizable	organic matter and sulfides	1) 30% H <sub>2</sub> O <sub>2</sub> ; 1h shaking 20 °C; 85 °C evaporated – 2 times 2) 1M NH <sub>4</sub> -acetate + HNO <sub>3</sub> (pH = 2); 16 h shaking, 25 °C	2×10 ml 50 ml	Mossop et al., 2003

ing ( $<5 \mu\text{m}$ ). For the present study, 3 g of the latter material was taken, which after the homogenization was divided into 1 g for analysis as the original soil sample and 2 g for the SEP. After each SEP step, 0.2 g of the homogenized residual material was taken for analysis. A total of 5 samples were prepared for analysis using LA-ICP-MS and SEM-EDX: (1) S0 original, (2) S1 residual 1 (after step 1), (3) S2 residual 2; (4) S3 residual 3, and (5) S4 residual 4. All samples were pelleted using a hydraulic press (35 bar). To prepare the pellets, 0.1 g of each sample was additionally thoroughly grinded in an agate mortar for 20 min with 3 drops of alcohol. No additives were added to the materials. The pellets obtained are shown in Figure 1a.

*LA-ICP-MS and SEM-EDX analyses.* Conditions and standards for LA-ICP-MS and SEM-EDX analyses of the pellets are the same as described in Tarassov et al. (2021). For LA-ICP-MS analysis we used maximal laser diameter of  $100 \mu\text{m}$ . A total of 4 spots, distributed uniformly as apices and center of an equilateral triangle, were used for LA-ICP-MS analysis of each sample. The final composition of each sample is an average of 4 analyses.

## Results and discussion

The obtained results are illustrated in Fig. 1. Macroscopically, the most dramatic changes in the soil occur after the 4<sup>th</sup> step after the removal of organic



**Fig. 1.** (a) Pelleted samples (S0-S4) of the SEP on an Al disc (diameter 25.5 mm) before analysis with LA-ICP-MS and SEM-EDX; (b-e) change in the content of W (b), U (c), Fe (d) and S (e) after all steps of the applied SEP; (f) partitioning (%) of W, U, Fe and S in the studied soil.

matter (sample S4) – the material changes color from brown to light beige (Fig. 1a). The total relative weight loss after step 4 is about  $13.5 \pm 1\%$  (calculated from weight (g) difference of S3 and S4), which approximately corresponds to 13 wt % organics in the original dry soil (taking into account the loss of matter during SEP). Combination of this result with the data of SEM-EDX and LA-ICP-MS analyses gives the following chemical composition of the original dry soil (in wt %): Na<sub>2</sub>O – 2.74; MgO – 0.67, Al<sub>2</sub>O<sub>3</sub> – 14.62, SiO<sub>2</sub> – 59.63, P<sub>2</sub>O<sub>5</sub> – 0.19, SO<sub>3</sub> – 0.19, K<sub>2</sub>O – 3.02, CaO – 1.76, TiO<sub>2</sub> – 0.35, MnO – 0.09, Fe<sub>2</sub>O<sub>3</sub> – 2.7, organics ~13, and W –  $87.2 \pm 8.7$  ppm and U (for comparison) –  $4.26 \pm 0.25$  ppm.

Changes in the content of W, U (LA-ICP-MS), Fe and S (EDX) during the all steps of the applied by us SEP, depicted in Figure 1b–e show negligible significance of soluble species of W, U and Fe in the soil. Moreover, the EDX analyses of S0 and S1 do not differ within the statistical uncertainty. This well correlates with the low mineralization of the ground water there (EC < 100 μS/cm). Figure 1f shows partitioning of W, U, Fe and S between the 4 specified groups (Table 1) + 1 (residual 4), derived from the data in Figure 1b–e. From these data follows that of the nearly 90 ppm total W content in the soil studied, about 25% is associated with organic matter, 40% with amorphous hydrous iron oxides (ferrihydrite), 25% with crystalline hydrous iron oxides (goethite), and about 10% with residual material (scheelite, silicates). In absolute values, ~33 ppm of W is associated with 0.81 wt % of Fe<sub>2</sub>O<sub>3</sub> of amorphous phase (ferrihydrite), ~22 ppm with 13 wt % of organics, and ~22 ppm with 0.57 wt % of Fe<sub>2</sub>O<sub>3</sub> of crystalline phase (goethite). The results obtained are in good agreement with the conclusions of our previous work (Tarassov et al., 2021) on the crucial role of organic matter and amorphous iron oxides in the distribution of W in the studied soils. Crystalline W-containing goethite found is typical for the oxidation zone of the deposit (Tarassov, Tarassova, 2018) and is present in the soil in the form of a mechanically transported substance. The distribution of U shows its predominant association with amorphous hydrous iron oxide (>55%). About 60% of sulfur is associated with sulfides and organic material.

## Conclusion

Although it is known (Tessier et al., 1979) that SEPs are rather semi-quantitative estimates of the distribution of elements between different fractions in soils and sediments, the SEPs we use, specifically targeting soils above the oxidation zones, for the case of the Grantcharitsa W deposit give very plausible results. The implementation of the proposed

SEP through the analysis of solid residues after each stage of SEP, rather than solutions, has a serious advantage – materials after SEP can be stored in non-special conditions for an unlimited time.

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## References

- Bolan, S., H. Wijesekara, A. Ireshika, T. Zhang, M. Pu, G. Petruzzelli, F. Pedron, D. Hou, L. Wang, S. Zhou, H. Zhao, K. H. M. Siddique, H. Wang, J. Rinklebe, M. B. Kirkham, N. Bolan. 2023. Tungsten contamination, behavior and remediation in complex environmental settings. – *Environment International*, 181, 108276; <https://doi.org/10.1016/j.envint.2023.108276>.
- Du, H., Y. Li, D. Wan, C. Sun, J. Sun. 2022. Tungsten distribution and vertical migration in soils near a typical abandoned tungsten smelter. – *J. Hazardous Materials*, 429, 128292; <https://doi.org/10.1016/j.jhazmat.2022.128292>.
- Hobson, C., H. V. Kulkarni, K. H. Johannesson, A. Bednar, R. Tappero, T. J. Mohajerin, P. R. Sheppard, M. L. Witten, G. M. Hettiarachchi, S. Datta. 2020. Origin of tungsten and geochemical controls on its occurrence and mobilization in shallow sediments from Fallon, Nevada, USA. – *Chemosphere*, 260, 127577; <https://doi.org/10.1016/j.chemosphere.2020.127577>.
- Li, R., W. Wang, S. Wang, C. Lin, X. Wang, L. Menga, X. Yuanc. 2019. Comparison of two sequential extraction procedures for tungsten fractionation in the tungsten mining soils. – *RSC Adv.*, 9, 35456–35462; <https://doi.org/10.1039/C9RA07158J>.
- Mossop, K. F., Ch. M. Davidson. 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. – *Analytica Chimica Acta*, 478, 111–118; [https://doi.org/10.1016/S0003-2670\(02\)01485-X](https://doi.org/10.1016/S0003-2670(02)01485-X).
- Tarassov, M. P., E. D. Tarassova, 2018. Structural and chemical evolution of mineral forms of tungsten in the oxidation zone of the Grantcharitza deposit (Western Rhodopes, Bulgaria). – *Bulgarian Chemical Communications*, 50 (Special Issue J), 270–280.
- Tarassov, M., E. Tarassova, M. Stavrev, A. Benderev, E. Tacheva. 2021. Modes of occurrence of tungsten in alluvial soils and river sediments in the area of the Grantcharitsa tungsten deposit, Western Rhodopes, Bulgaria. – *Rev. Bulg. Geol. Soc.*, 82, 3 (Geosciences 2021), 31–33; <https://doi.org/10.52215/rev.bgs.2021.82.3.31>.
- Tessier, A., P. G. C. Campbell, M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. – *Analytical Chemistry*, 51, 7, 844–851; <https://doi.org/10.1021/ac50043a017>.
- Wenzel, W. W., N. Kirchbaumer, Th. Prohaska, G. Stingeder, E. Lombic, D. C. Adriano. 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. – *Analytica Chimica Acta*, 436, 309–323; [https://doi.org/10.1016/S0003-2670\(01\)00924-2](https://doi.org/10.1016/S0003-2670(01)00924-2).
- Zheng, X. J., M. Chen, J. F. Wang, F. G. Li, Y. Liu, Y. C. Liu. 2020. Ecological risk assessment of heavy metals in the vicinity of tungsten mining areas, Southern Jiangxi province. – *Soil and Sediment Contamination: An International J.*, 29, 6, 665–679; <https://doi.org/10.1080/15320383.2020.1763912>.