

Geochemical features of the distribution of major and trace elements in sediments and soils of the Zarafshon River Valley

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Research Article

Keywords: Sediments, soil Zarafshon Yagnob, Fondarya Neutron Activation Analysis Pegmatite, Granitoid

Posted Date: April 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-392380/v1>

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Abstract

Purpose

The aim of this research was to estimate impact of the geochemical features to distribution of major and trace elements in soil and sediments, assess of anthropogenic and natural factors in terrestrial ecosystems of Zarafshon. As well as to answer the common criticism of the water, soil and sediment pollution in Zarafshon. In this way this research will be reasonable substantial information about distribution of major and trace elements in mountains and piedmont regions.

Materials and methods

In view of a planned detailed investigation, and to get more data concerning the geochemistry of sediments and soils along the Zarafshon Valley of Western Tajikistan, as well as to assess of the local environmental situation, the mass fraction of eight major, rock-forming elements together with other 38 trace elements were determined by Instrumental Neutron Activation Analysis. To accomplish this task 116 samples of sediment and an equal number of soils were collected around the Tajik sector of the Zarafshon catchment basin and its main tributaries.

Results and discussion

Both major and trace elements proved a significant similarity between soil and sediments including potentially contaminating elements As, Sb and Hg, whose mass fractions showed in some places to be significantly higher. An analysis of the distribution of major elements oxides as well as of incompatible trace elements Sc, Zr, REE, Th, and U suggested that the analysed soil and sediments have rather a felsic origin. A more careful examination revealed a reduced degree of recycling and for some location, a certain degree of weathering. All these peculiarities could be ascribed to a vast investigated area spread onto a significant diversity of geological formations.

Conclusion

The process of soil weathering of the studied area takes place relatively quick, but mainly it's has a natural character rather. The high content of accumulation of major and trace element in the sediment also related to rock source but only in rare cases is it of an anthropogenic nature. Based on these results, it can be predicted that the seriously environmental threat was not observed in the Zarafshon river valley. The activities of industrial facilities cover only a small part of this region and their impacts on the ecological state of the Zarafshon river valley is very small.

1 Introduction

The Zarafshon River rises in a homonym glacier, at an altitude of 2775 m at the junction of Turkestan and Zarafshon ranges (Prokhorov, 1969–1978). The initial part of the river, about 300 km long, lies in a narrow and deep valley. On the southern left bank, flowing between Turkestan and Zarafshon ranges, it receives Fondarya, Arthuch (Kshtut) and Mogiyon, as well as many small tributaries (Prokhorov, 1969–1978, Panjakent, 1989, Urgut, 1989). After the city of Panjakent, the river follows a flat region and crosses, the Tajikistan-Uzbekistan border (Urgut, 1989) passes the city of Samarkand and Bukhara and finally, it is lost in the desert in the vicinity of the city of Karakul without reaching the Amu Darya river whose formerly it was a major tributary (Sadikov et al. 1979).

The Zarafshon catchment basin, with an area of 17700 km² covers diverse geological formations which are spread from the alpine zone 3200–3500 m above sea level to less than 150 m westward the city of Karakul, where the Zarafshon river disappears in the vicinity of Kyzylkum desert. In the Zarafshon mountain gorges, below 1500 m there are small areas of semi-savannahs as well as mountain-forests. Here, the sierozem is prevalent (Geoportal, 2020), while in the western sector of Zarafshon valley, loess deposits reaching a thickness of 100 m are common. In mountain gorges terraces of alluvial deposits and outflow cones of lateral tributaries serve as the basis for soil components. However, in some areas, due to the geographical features and diversity of rock formation, a thin layer of soil cover was formed. For this reason, these places could be considered highly arid zones while sandstone generated by weathering of surrounding rocks represents the major components of soil.

The "Zarafshon" which in Farsi means "spreader of gold" reflects the existence of ore fields along the river valley. These together with other outcrops of nonferrous ores makes the eastern valley as well as its tributaries a mineral rich province which requires detailed investigation. Moreover, until present there are no systematic studies concerning the geochemistry of the Tajik section of Zarafshon Valley. This investigation could provide more data evidencing the origin of clastic material which compose the recent sediments as well as the interrelation between them and adjacent soil. For this reason, the distribution of major and rock-forming elements as well as of incompatible lithophile elements such as Sc, Ti, V, Cr, Zr, lanthanides Th or more soluble U together with siderophile Co and Ni showed to be very useful in inferring the nature of source rocks (Bhatia and Crook, 1986, Taylor and McLennan, 1991, McLennan et al., 1993, Armstrong-Altrin, 2009).

To accomplish this project, in the period of spring-autumn 2018 the Institute of Water Problems, Hydropower and Ecology of the Academy of Science of Tajikistan organized a field expedition to collect the most representative samples of sediments and soils from the Tajik sector of Zarafshon catching basin. The samples were collected along the Zarafshon River, its main tributaries, as well as lakes and mine adits located on their upper reaches (Fig. 1). This permitted collection of 116 samples of sediments as well as an equal number of soil samples which further were analysed at the Neutron Activation Analysis Section of the Frank Laboratory of Neutron Physics (FLNP) of the Joint Institute for Nuclear Research (JINR), Dubna, Russian Federation. To determine the mass fractions of all above mentioned elements in sediments and soil samples, we have used the Instrumental Neutron Activation Analysis (INAA), in both thermal and epithermal neutron variants (Zeisler et al., 2011, Frontasyeva, 2011). The

INAA permits determining the mass fractions of about 40 elements with a sensitivity of about 1 mg/kg without any preliminary chemical processing of samples such as acid digestion. The results of this project will be further presented and discussed.

2 The Geochemical Features Of The Investigated Regions

When studying the distribution of major and trace elements in soils and sediments it is important to take into account the influence of parent rocks, mineralization and geochemical parameters of the studied objects. Since the Zarafshon River and its sub-basins originate from the high mountains glaciers and wash away the soils and minerals of rocks on their way. Therefore, it is very important to take this factor into account both in studying the geochemical features of the distribution of major and trace elements by waterways and during the ecological assessing of the investigated region. By addition, depending on the biogeochemical and physical processes, the distribution and accumulation of major and trace elements occurs in different ways. Due to its location between two important mountain ranges - Turkestan and Zarafshon, the Zarafshon catchments basin covers a great diversity of geological formation whose clastic material represents the main component of its sediments and of bordering soils.

According to (Vinogradov, 1961, Mamadvafoev et al. 2015), the ore field of the Zarafshon valleys are divided into three subzones - the North-Zarafshon zone, the Pasrud-Yagnob zone and the Mogiyon-Karakul zone. In total, these zones have 10 ore wings (such as: 1 - Artuch-Vashan, 2 - Urech-Pasrud, 3 - Djidjikrut-Novimateksk, 4 - Yagnob, 5 - Shing-Mogiyon, 6 - Archamaidan, 7 - Dukdon, 8 - Konchoch, 9 - Repishkut, 10 - Uchkadinsk) and 15 deposits and ore occurrences: (1 - Taror, 2 - Djilau, 3 - Chashmaniyat, 4 - Valangi-Daroz, 5 - Sharshaga, 6 - Turkparida, 7 - Kavnok, 8 - Chatma, 9 - Buzinova, 10 - Chorrog, 11 - Skalnoe, 12 - Chore, 13 - Djidjikrut, 14 - Pindar, 15 - Uchkado). The main tributaries which have the most impact on the mineral composition of the Zarafshon River were conditionally divided into four sub-zones as Djidjikrut, Yagnob, Fondarya and Mogiyon. The confluence of these rivers was chosen as the boundaries of the sub-basins (Fig. 1).

The Djidjikrut River flowing in the Ayni district with an area of 112 km² and 17 km long is a left tributary of the Yagnob River and falls into it in 9.4th km from the estuary of the river. According to the reference book "Surface Water Resources of the USSR" (1971), the Djidjikrut flows among rocks such as carbonates, clays, marls, limestones, dolomites and salts, which are strongly affect to the elemental composition of waters and sediments of the river. And the chemical composition of bank soil is also strongly associated with these rocks. In addition, at the estuary of the river within the eponymous ore field is located the Djidjikrut deposit, relating to Zarafshan-Gissar mercury-antimony belt with folded carbonate and terrigenous formations of the Middle and Upper Paleozoic. The main ore minerals in this deposits are antimonite (Sb₂S₃ with an admixture of As, Bi, Pb, Fe, Cu, Au, and Ag), and cinnabar (α-HgS), and metacinnabarite (β-HgS), pyrite (FeS₂ with an admixture of Co, Ni, As, Cu, Au Se), marcasite (FeS₂ with an admixture of As, Sb, Co, Ta, Bi, Cu), realgar (AsS), orpiment (As₂S₃), sphalerite (ZnS), hematite (Fe₂S₃). The main components of the ores are antimony and mercury (in a ratio of 100: 1), but the presence of thallium, selenium, tellurium and arsenic has been established.

At present, at the confluence of the Djidjikrut and Yagnob on the northern slope of the Gissar range is operating the Anzob mining and processing plant (Geoportal, 2020) specializing on the underground mining of ores with the final release of Hg-Sb concentrate. Sb and Hg rich ore fractions are separated by a lead nitrate flotation which may be significantly contaminates sediment and soil in the downstream of the river.

The Yagnob River flows westward through the narrow mountain gorge along the southern edge of the Zarafshon mountains being the first tributary of the Fondarya River. The total length of the Yagnob River is 114 km, and its basin area is 1660 km². The mineral composition in the upper reaches of the Yagnob River is poorly studied. It should be noted that the Fon-Yagnob coal deposit is located downstream occupying almost the entire left-bank site between Djidjikrut and Pasrud tributaries. In this territory in the Kuhi Malik tract on the Fon-Yagnob coal deposit, located in the valley of the Yagnob river due to exothermic oxidation of sulfides-containing compounds of the near surface coal layers (mainly pyrite and marcasite) a self-ignition process take place. The coal deposit occupies almost the entire left-bank part of the Yagnob river valley between its tributaries Djidjikrut and Pasrud.

Recently, is not excluded a certain role of a human in the emergence of new foci of ignition due to the development of coal seams. According by research work devoted to the mineralogy of one of paralavas, which is the highest-temperature formation of a coal fire in the Kuhi-Malik tract it was revealed that they are products of complete melting sedimentary rocks enclosing coal seams (Sharygin, et al., 2009). The paralava contains such rocks like fayalite (Fe₂SiO₄), sekaninaite (Fe²⁺, Mg)₂Al₃[AlSi₅O₁₈] with an admixture of Ti, Mn, Ca, Na, K), hercynite (FeAl₂O₄), Ti-magnetite, as well as minerals belonging to the silicas - tridymite (SiO₂) and sour glass. Also the globules of sulfides (mainly pyrrhotite), Fe-Ti-oxides, and greenalite (Fe²⁺, Fe³⁺)₂₋₃Si₂O₅(OH)₄ were identified. In addition, in the locally present hematites (Fe₂O₃) and low-calcium pyroxenes (clinoferrosilite - Fe²⁺SiO₃) contains the high concentrations of Al₂O₃ and MnO (4.5–5.8 and 0.6–0.8 wt%, respectively) and low concentrations of CaO, TiO₂, and Na₂O (< 0.25 wt%). In coal fire formation paralava, besides the product of complete melting of rocks and coal seams were identified a native Se. (Novikov., 1986, Belakovsky., et al., 1988, Sharygin et.al., 2009, Mirakovet al., 2017, Nasdala L., et al., 1993). Also, the underground coal fire may contribute to diagenesis of some REE minerals such as godovikovite, efremovit, maskanite and so on.

The Fondarya River with a significant catchment basin of 3230 km² is formed by the confluence of the Yagnob and Iskandardarya which crosses the Zarafshon ridge and flows into the Zarafshon River. In addition, the Fondarya is fed by the waters of the Sarvoda River which originates from the Alovdin lakes, as well as the lower and upper Kumarg tributaries, Chore and Pete.

It should be noted that in the upper flows of the Iskandardarya River operates the mining and processing plant "Tolko-Gold", which extracts and processes Au, Ag, Hg, Sb ore as well as fluorite. Also the operation is carried out at the gold deposit in the Kumargi Bolo gorge. The Chore gorge (Chore river gorge) are classified as gold-quartz deposits and it is a gold ore deposit at the Turkestan-Chore ore zones of Central

Tajikistan (Madzhidov B., 2017). This deposit was discovered in 1960, and during 1974–1984 a detailed exploration was carried out within drilling of wells and adits at seven horizons a depth of 500–600 meters. In the Chore gorge are widespread carbonate-terrigenous deposits and rocks of granitoid magmatism are quite rare. In addition to pyrite and arsenopyrite which constitute more than 95% of all ore minerals, also occur antimonites, chalcopyrite, sphalerite, pyrrhotite, and others [Novozhilov Yu.I. et al.1999].

The Pete tributary flows between the Pete-Takfon ore field representing Takfon, Pete, Simich and other deposits. In the geological structure of the ore field Paleozoic formations are widely developed, which are represented by Silurian (shales, limestones, dolomites with interlayers of quartzites), Devonian (siliceous and micaceous shales with interlayers of cherts and limestones) and Carboniferous (limestones with horizons of clay shales, sandstones) and Cong deposits. To the south of the ore field area the complex of Paleozoic formations is overlapped by sub-platform sediments of the Mesozoic. The Igneous formations are represented by the Pete intrusions of granodiorites, dikes of granodiorite-porphry and lamprophyres. There are also tin and silver, lead and zinc-containing ores (Fayziev et al. 2017).

At its turn, the Mogiyon River with a length of 68 km and a basin area of 1100 km² is one of the largest Zarafshon tributaries. From the source to the village of Mogin in a narrow valley, the river flows in a northern direction, cutting through the Zarafshon ridge with a deep transverse gorge. Further, having received its largest tributary - the Shing River, it continues to flow in a narrow rapids channel with a width of up to 10 m. Nine kilometers above the city of Panjakent, leaving the gorge and passing through the village of Sujina falls into the Zarafshon River. Between the Shing and Mogiyon interfluvium is located the Taror ore field, belonging to the Western Zarafshon-Gissar metallogenic zone (Blokhina, 1984). However, along with gold-sulphide mineralization, silver-tin-base metal mineralization, localized in its upper and middle horizons is also developed. The silver deposit in the Taror ore field belongs to the Mirkhant deposit and its mineralization is predominantly represented by a silver-tin-polymetallic association spatially combined with sulphide showing the closest correlation between Ag and Sb (Fayziev et al. 2017). It is worth noting that in the Taror gold ore deposit operates the Joint Venture "Zarafshon" whose main product consists of Ag-Au alloy (Solihov, 2018).

In the valley of the Zarafshon River and around its tributaries is quite developed the mining and metallurgical industry, based on the extraction and processing of non-ferrous metals. The main metallurgical industries could be listed as including the Anzob mining and processing plant (AMPP) and Taror gold ore plant (TGOP). Recently, work has been carried out at the Upper Kumarg and Kanchoch fields. AGOK specializes in the production of antimony-mercury concentrates, TGOP in the production of gold.

In this regard, the investigated regions are the object of controversy between scientists and environmental experts from governmental and non-governmental organizations. The activities of industrial enterprises are often criticized which is the main goal of this research. Since, disregarding the geochemical features of a particular region, it is not entirely correct to assess their ecological state. So that authors decided to

analyse the unexposed and exposed to anthropogenic impacts sediments and soil samples and compare the obtained data between it.

3 Materials And Methods

3.1 Samples

An equal number of 116 sediment and soil samples were collected in the investigated area, using an AMS 12 Multi Stage Sediment Sampler equipped with tubular glass sampler (AFMS Inc. American Falls, ID). Unconsolidated columns of sediment, 20 to 30 cm long, were handpicked from the riverbeds during a high-water period. From each sampling point, three sub-samples covering an area of about 10m² were collected and carefully mixed to form a composite sample. Any possible recent contamination was avoided by removing the top layers of soil and sediment columns and by washing the glass sampler with acid before any sampling.

To highlight a possible local human influence, sampling zones were divided into two parts: -i. A number of unexposed 91 sediments and 92 soil samples were collected directly on the banks of the lakes, rivers and mountain tributaries with no human activities. -ii. Opposite these, 25 sediments and 24 soil samples were collected around the road tunnels, near the industrial zones, coal mining, mines and adits, some of still under exploration (Fig. 1 ((b)), Table S1 and Table S2).

Samples consisting of silty greyish sand without organic detritus were placed into the plastic container with cooled refrigerant and kept at a 4⁰C. In the laboratory, all samples were again cleaned from alien materials and dried at 70⁰C at constant weight and ground. Finally, the dried material was sieved using a 0.425 mm (42 mesh) sieve, homogenized and sent to the Frank Laboratory of Neutron Physics (FLNP) of Joint Institute for Nuclear Research (JINR) for further Instrumental Neutron Activation Analysis (INAA).

Here, 10 g of each sample were homogenized again for 15 min in a planetary ball mill (PULVERISETTE 6, Fritsch Laboratory Instruments GmbH, Germany) at 400 rpm. To increase the precision and accuracy of measurements, six aliquots of about 0.3 g were selected from each sample and independently analysed.

3.2 INAA measurements

For INAA, before irradiation at the IBR-2 reactor of the JINR FLNP in Dubna, each aliquot was packed in polyethylene bags for the determination of short-living isotopes (three aliquots) and in aluminium foil (three aliquots) for long-living ones. It is worth mentioning that the mass fractions of short-living isotopes were determined by thermal neutron activation while in the case of long-living isotopes we have used epithermal neutrons. More details concerning irradiation time and neutron flux densities in each irradiation channel can be found in (Abdusamadzoda et al. 2020).

The gamma spectra of each sample were measured with an HPGe detector with a resolution of 1.9 keV for the ⁶⁰Co 1332 keV line, analysed using the Canberra software Genie 2000 and processed by using a

proprietary (Pavlov et al. 2016). By means of this software, the mass fractions of each element together with the associated Combined Standard Uncertainty (CSU) (Farrance and Frenke, 2012) were calculated. It is worth mentioning that the CSU was estimated by taking into account the statistical error, influence of measurement geometry, detector efficiency, the content as well the error of each element for all Certified Standard Material (CSM) utilized for calibration. To avoid any environmental contamination, all resulting radioactive materials were deposited in a permanent low activity repository.

3.3 Quality control

The quality control was assured in the case of sediments and soils by a simultaneous analysis of Standard Reference Materials (SRM) provided by the National Institute for Standard and Technologies (NIST), i.e. 1633c Coal fly ash, 667 Estuarine sediment, 2710 Montana Soil and 1547 Peach leaves for short half-life time isotopes. In the case of long life-time isotopes in sediments, the best results were obtained by using - SRM – 2709 Trace elements in soil, SRM-1632c Trace elements in coal, SRM-690CC Calcareous soil and SRM – 2709a San Joaquin soil, SRM-1632c Trace elements in coal and SRM- AGV2 Andesite in the case of soil samples.

Further, by using all the above-mentioned SRM it was realized a Group of Standard Sample (GSS) which were irradiated together with the investigated samples permitting in this way to calculate the mass fractions of about 40 elements. This was done by proprietary software which, besides determining the mass fractions of chosen elements, checked to which extent the mass concentration of CRM corresponds to certified ones (Pavlov et al. 2016, Zinicovscaia et al. 2018). Following this procedure, the accuracy quantified by means of standard deviation corresponding to each group of three aliquots was lower than 10%. In the case of SRM, the CSU varied between 3 and 26%, higher in the case of REE. In our opinion, the observed discrepancy was due not to the experimental conditions of measurements, but to the fact that only in a few cases, the SRM provides certified values instead of recommended ones whose interval of uncertainty was significantly higher. Regardless of these remarks, the CSU was never greater than 20%.

4 Results And Discussion

The complete data concerning the content of 38 elements in 116 soil and sediment samples can be found in Mendeley repository (Abdusamadzoda, et al., 2020), while in Table 1 reproduced only the average values of mass fractions of these elements together with corresponding values of the Upper Continental Crust (UCC), (Rudnick and Gao, 2003), North American Shale Composite (NASC) (Gromet et al. 1984), Post Archaean Australian Shale (PAAS), (Taylor and McLennan, 1991), Average Earth Crust (AEC) (Vinogradov, 1961), Suspended Matter of the World's Rivers (SMWR), (Savenko, 2007), as well as Average World Suspended Sediment (AWSS) (Viers et al., 2009).

Table 1

The mass fraction of investigated elements in sediments and soil with the main literature references: UCC (Rudnick and Gao, 2004), NASC (Gromet et al., 1984), PAAS (Taylor and McLennan, 1991), Average Earth Crust (AEC) (Vinogradov, 1961), SMWR (Savenko, 2007), AWSS (Viers et al., 2009). CU stays for Combined Uncertainty resulted by combining standard deviation with instrumental errors. The mass fraction of oxides expressed in %, while for the other elements it is expressed in mg/kg

Element	Sedi- ment	CU	Soils	CU	UCC	NASC	PAAS	AEC	SMWR	AWSS
SiO ₂	62.75	12.65	59.39	9.7	66.62	64.48	62.8	63.11	54.76	54.34
TiO ₂	0.62	0.22	0.83	1.06	0.64	0.72	1	0.75	0.65	0.73
Al ₂ O ₃	9.9	3.52	12.92	4.07	15.4	16.9	2.2	15.21	16.31	16.48
FeO	3.79	2.5	5.78	2.01	5.04	5.7	18.9	5.98	6.47	7.47
MnO ₂	0.07	0.07	0.09	0.03	0.1	0.06	0.11	0.16	0.15	0.22
MgO	6.32	3.42	5.8	2.72	2.48	2.85	—	3.10	2.39	2.09
CaO	10.59	10.71	9.46	9.06	3.59	3.56	1.3	4.14	3.64	3.62
K ₂ O	2.4	0.99	2.83	0.79	2.8	3.99	3.7	3.01	2.59	2.04
Na ₂ O	1.4	0.79	0.9	0.41	3.27	1.15	1.2	3.37	1.11	0.96
Sc	9.6	4	11	5	14	15	16	10	14	18
V	101	56	254	1500	97	—	—	90	12	129
Cr	71	40	90	57	92	124	110	83	853	130
Co	11.5	6.4	14.5	7.1	17.3	—	—	18	19	22.5
Ni	46	32	65	31	47	58	55	58	50	74
Zn	102	57	119	54	67	—	—	83	130	208
As	63	254	84	600	4.8	28.4	—	1.7	14	36.3
Br	2.6	4.3	1.9	1.6	1.6	0.9	—	2.1	9	21.5
Rb	92	41	103	39	84	126	160	150	77.0	79
Sr	143	63	177	100	320	142	200	340	150.0	187
Zr	220	133	210	101	193	200	210	170	150.0	160
Sb	59	560	38	270	0.4	—	—	0.5	1.4	2.2
Cs	4.5	570	7.5	3.6	4.9	5.2	15	3.7	5.2	6.3
Ba	724	450	784	500	624	636	650	650	500	522

Element	Sedi- ment	CU	Soils	CU	UCC	NASC	PAAS	AEC	SMWR	AWSS
La	28	14	32	12	31	31	38.2	29	32	37
Ce	53	26	61	25	63	67	79.6	70	68	73.6
Nd	27	15	32	17	27	27	33.9	37	29	32.2
Sm	5	2.5	6.3	3.4	4.7	5.6	5.6	8	5.8	6.1
Eu	0.9	0.6	1.1	0.8	1	1.2	1.1	1.3	1.4	1.3
Gd	3.9	3.3	2.9	2.4	4	—	4.7	8	5.6	5.3
Tb	0.7	0.3	1	0.4	0.7	0.9	0.8	4.3	0.8	0.8
Tm	0.3	0.3	0.5	0.5	0.3	—	0.4	0.3	0.4	0.4
Yb	1.9	1.2	2.2	1.5	2	3.1	2.8	0.3	2.5	2.1
Hf	5.5	3	5.8	2.6	5.3	6.3	—	1	4.4	4
Ta	0.8	0.4	1	0.5	0.9	1.12	14.6	2.5	0.9	1.3
W	2.5	5.7	2.8	2.7	1.9	2.1	—	1.3	1.4	2
Hg	2.5	14.7	1.1	4.5	0.1	—	—	0.08	0.1	—
Th	8.9	4.3	10.9	3.5	10.5	12.3	3.2	13	10	12.1
U	3	1.5	3.9	1.7	2.7	2.7	—	2.5	2.4	3.3

In this regard, in (Fig. 2) was illustrated by means of box and whiskers diagrams the mass fractions of investigated elements in soils and sediments normalized to the UCC (Rudnick and Gao, 2004) and SMWR (Savenko, 2007) respectively. The UCC (Rudnick and Gao, 2004) was chosen as one of the best descriptors of the most accessible portion of the continental crust. A choice of SMWR (Savenko, 2007) to normalize sediments are drawing on the theory of lithogenesis (Strakhov, 1960). According to the theory of lithogenesis the mobilization of suspended and dissolved materials in drainage basins are the initial stage of the formation of sedimentary rocks. The major portion of chemical elements are transported by the river suspensions, including alkaline and calc-alkaline metals, which are highly mobile in the supergene zone. Indeed, other descriptors such as NASC (Gromet et al. 1984), AWSS (Viers et al. 2009) or Post Achaean Australian Shale (PAAS) (Taylor and McLennan, 1991) showed to be almost identical.

When the compositional interpreting data of the elemental content of river sediment and soil their geochemical features should be taken into account, which is determined in a great measure by the geochemistry of local geological formations. Therefore, due to sediment mobility various mineral fractions are mixed and deposited depending on water speed, grain sizes and specific gravity.

According to (Fig. 2) from the point of view of mass fraction the investigated soils and sediments shows both major and trace elements and excepting chalcophile Zn, As, Sb and Hg, are closer to UCC (Rudnick and Gao, 2003) and SMWR (Savenko, 2007). Moreover, at more careful analysis of mass fraction data, reproduced in (Table 1S and 2S), the content of As, Sb and Hg showed higher mass fractions only in few sediment and soils samples collected in the vicinity of mines and adits located on Djidjikrut, Kanchoch, Chore and Mogiyon tributaries (Fig. 1).

In spite of these small inconsistencies, the elemental content of sediment and soils showed to be relatively closer as Spearman's correlation coefficient of 0.83 suggests (Fig. 3). As sediment and soil samples were collected from the same locations, this fact suggests also that sediments represent in a greater measure the basic component of soil.

4.1 Major elements

The average values of the mass fractions of major, rock-forming elements excepting MgO and CaO showed to be relatively closer to UCC (Rudnick and Gao, (2004), to the other sedimentary system and even to AEC (Vinogradov, 1961). It should be also remarked that silica represents the main major constituent of all investigated samples, its mass fraction varying around $62.8 \pm 11.9\%$ percent in the case of sediments and $59.4 \pm 8.8\%$ in the case of soils. Represented on total alkali-silica discriminating diagrams $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}$ and $\text{SiO}_2 - \text{Na}_2\text{O} + \text{K}_2\text{O}$ the composition of investigated materials suggests a rather felsic to the intermediate origin with small contribution of mafic material, as the case of Pete intrusion mentioned before this one of granodiorites, dikes of granodiorite porphyries and lamprophyres. Its average mass fraction is closer to the UCC (Rudnick and Gao, 2004) but with only a few exceptions in the sediments collected in the vicinity of Anzob tunnel, Sarvoda 1 and Sarvoda 2 as well as soils from Chore1 and 3, Djidjikrut 1, Obi Sara 1, Saritag 2, as well as Sarvoda 1 to Sarvoda 7. In all these points, the lower content of silica was due to an increased content of calcium oxide whose mass fractions varied between 26 and 47%.

With respect to UCC the aluminium oxide Al_2O_3 showed in sediment an average mass fraction $9.91 \pm 3.2\%$, lower than the soils one of $12.92 \pm 3.7\%$, both of them lower than the UCC (Rudnick and Gao, 2004) and NASC (Gromet et al. 1994) ones of 15.4 and 16.96% respectively and probably due to low content of plagioclase. In its turn, the sodium oxide Na_2O has an average mass fraction in sediments and especially in soils smaller than the corresponding UCC (Rudnick and Gao, 2004), suggesting a low content of albite, and by consequence predominance of a sedimentary substrate (Fig. 4 ((a ,b))). This finding is confirmed by the discriminating ternary diagram reproduced in (Fig. 4 ((b))), the points corresponding to sediment and soils are grouped around UCC (Rudnick and Gao, 2004) and NASC (Gromet et al., 1984). Here, some points are shifted towards lower SiO_2 content, which could be due to an increased content of CaO, whose mass fraction in some places reached 28 % (Table 1S and 2S).

The third discriminating diagram, the ternary K-A-CN one, evidenced a clear influence of weathering on both sediment and soils (Fig. 4 ((c))). Here the increased fraction of CaO can be remarked on the lower left

corner of the diagram. In this regard, it is an interest to remark that, according to the tables of Spearman's correlation coefficients (Table 2), CaO correlates positively only with MgO in sediment as well as in soils. The most plausible, this could be explained by the presence of dolomite where CaO mass fraction significantly overpass the UCC (Rudnick and Gao, 2004) one. On the other hand, the significant variability of the rest of the major elements could be explained by the fact that both sediment and soils were collected along about 600 km of Zarafshon Valley and its tributaries, at altitudes varying between 883 and 3629 m. Therefore, the sampling points cover a significant diversity of geological formations with different geochemistry (see the previous Geochemistry section). The mass fractions of the oxides of other major elements, i.e. TiO_2 , FeO, and MnO were closer to the UCC (Rudnick and Gao, 2004) ones in conformity with the previous remarks concerning a rather felsic origin of both sediment and soils (Table 1).

Table 2

The matrix of Spearman's correlation coefficients of major elements (as oxides) in soil and sediments. All correlations significant at $p < 0.05$ are represented in red or blue colour

Sediments								
	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO ₂	MgO	CaO	K ₂ O
TiO ₂	-0.251							
Al ₂ O ₃	-0.302	0.840						
FeO	-0.340	0.758	0.819					
MnO ₂	-0.018	0.621	0.639	0.510				
MgO	-0.804	0.381	0.357	0.382	0.013			
CaO	-0.752	-0.195	-0.184	-0.153	-0.191	0.577		
K ₂ O	-0.155	0.612	0.627	0.728	0.392	0.268	-0.260	
Na ₂ O	0.204	0.419	0.410	0.276	0.313	-0.066	-0.435	0.262
Soils								
	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO ₂	MgO	CaO	K ₂ O
TiO ₂	-0.081							
Al ₂ O ₃	-0.119	0.645						
FeO	-0.291	0.445	0.348					
MnO ₂	-0.009	0.442	0.456	0.300				
MgO	-0.671	0.062	-0.035	0.153	0.022			
CaO	-0.668	-0.436	-0.527	-0.123	-0.356	0.463		
K ₂ O	-0.213	0.543	0.626	0.459	0.255	0.108	-0.276	
Na ₂ O	-0.081	0.536	0.403	0.422	0.378	-0.011	-0.268	0.431

4.2 Trace Elements

More data concerning the origin of investigated sedimentary materials can be inferred by analysing the distribution of trace elements and especially those considered incompatible and insoluble. The same kind of analysis could reveal a possible anthropogenic influence in particular concerning mines and quarries of mineral resources such as non-ferrous minerals or building material.

In the first case, using by geochemical indexes for low mobility and incompatible trace elements such as Sc, Zr, La, Ce, Nd, Sm, Eu, Gd, Tm, Yb as well as Th and U (Bhatia and Crook, 1986, Taylor and McLennan, 1991, Wang et al., 2012) the geochemical features of sediment and soils were characterized. Also, in the case of possible anthropogenic contamination V, Cr, Ni, Zn, As, Sb and Hg showed to be the most appropriate.

Notably, the felsic rocks are richer in Th and light REE, whereas mafic rocks contain more Sc, Cr, Co, Ni and an increased fraction of heavy REE. In this regard, the Sc whose average mass fraction is less than 20 mg/kg in felsic rocks but increases to 20–40 mg/kg in mafic ones, (Norman and Haskin 1968) has proven to be one of the most appropriate discriminating elements. In the case of our investigated sediment and soils the Sc mass fractions were 9.56 ± 4 and 11.4 ± 4.6 mg/kg respectively and confirming the previous inference concerning the felsic origin of sedimentary material in Zarafshon Valley. On this reason, there are different discriminating diagrams able to evidence the sedimentary provenance or the source of rock compositions (Armstrong et al., 2013).

Accordingly, discriminating ternary Sc-La-Th diagram (Fig. 5 ((a))) and Th/Co vs La/Sc bi-plot (Cullers, 2002) (Fig. 5 ((b))) suggests that analysed samples are closer to acidic than to basic rocks, supporting the hypothesis of felsic nature of the source some with possible traces of the basic rocks as well. At the same time, most experimental data of sediment and soil on both diagrams are distributed around UCC (Rudnick and Gao, 2004) and NASC (Gromet et al. 1984).

Using the La/Th vs Hf diagram (Floyd and Leveridge, 1987) provides another discriminating useful evidence for the source material, because Hf has an increasing tendency to be enriched during the erosion of ancient (meta) sedimentary rocks. This peculiarity allows more detailed analysis of the sediment and soil source material along great investigated areas. With few exceptions the investigated sediment and soil presented to have a felsic origin confirming the previous inference based on distribution of major and trace elements for the same samples. Only the sediments and soils collected around Fondarya tributary, Kumargi poyon, Yangob and Chore estuary showed a mixed felsic/basic sourced characterized by a higher a La/Th ratio simultaneously with a reduced Hf mass fraction (Fig. 6 ((a))), Table 1S and 2S). On contrary, the increased mass fraction of Hf together with reduced values of La/Th ratio suggest the presence of old sediment sources in the Mastchohi kuhi, Shahrison and some regions of Panjekent (Fig. 6 ((a))), Table 1S and 2S).

Application aspects of the geochemical indexes can be extended using a Th/Sc versus Zr/Sc bivariate plot which characterized the hydraulic sorting and sedimentary recycling (McLennan, 1993). Whereas Th is incompatible in igneous systems and Sc is compatible in igneous systems (Lee et al. 2009). Therefore, the Th/Sc ratio is a good proxy for igneous chemical differentiation processes. Unlike Zr, which is strongly enriched due to the extreme resilience of zircon mineral to abrasion, Sc generally preserves a signature of provenance. This makes Zr/Sc ratio a useful index for Zr enrichment (McLennan et al., 1993) (Fig. 6 ((b))). At a more detailed analysis the Th/Sc versus Zr/Sc curve presents two trends, i.e. the first one, for a Th/Sc ration less than unity corresponds to a natural igneous differentiation which does

not involve to Zr enrichment, and a second one, above this limit which characterizes Zr enrichment occurring during sedimentary sorting and recycling (McLennan et al. 1993, Nagarajan et al 2015).

In the case of Zarafshon sediment and soils illustrates the Zr enrichment seems to be less significant suggesting a weak sorting process, in good correlation with the fresh nature of sedimentary material (Fig. 6 ((b))).

REE represents a group of 17 elements, including 15 lanthanides, Sc and Y as well. In this regard, lanthanides play a special role in investigating the provenance of rocks, because all of them have closer chemical properties, but ionic radii monotonously decrease from La to Lu. Traditionally, lanthanides are classified in light lanthanide or light REE (LREE) – La to Sm and heavy REE (HREE) – from Eu to Lu. Moreover, REE are not easily fractionated during sedimentation so they keep the "fingerprints" of mother rocks making them helpful in establishing their origin. Moreover, the Eu which can exist in two valence states (Eu^{2+} and Eu^{3+}) in its bivalent state, due to a smaller ionic radius can substitute by Sr^{2+} ions in plagioclase feldspars. As this process takes place only in reduced conditions which can be found only in the superior mantle or lower crust and this leads to a distinct negative anomaly in rocks coming from the upper crust. Another lanthanide REE distinctive characteristic, useful in evidencing the rock origin is related to the asymmetry of LREE and HREE in felsic rocks being enriched in LREE with respect to mafic ones, depleted in this category of REE.

In its turn, the La/Th ratio could be useful in inferring the provenance of sedimentary material, by considering that for the UCC (Rudnick and Gao, 2004) and NASC (Gromet et al. 1984) this ratio is around 2.8 while in the case of average MORB (Gale et al. 2013) it is estimated between 7.2 and 15.6. In the case of Zarafshon the La/Th ratio for sediments and soils were closer to 3.23 ± 1 and 3.03 ± 0.9 respectively, for a Spearman's correlation coefficient of 0.621 at $p < 0.01$ and both of them closer to the UCC ratio of 2.96 (Rudnick and Gao, 2004) and of 2.53 for NASC (Gromet et al. 1984) (Fig. 7 ((a))).

Further analysis of the distribution function of the mass fraction of eight REE, i.e. La, Ce, Nd, Sm, Eu, Gd, Tb, Tm and Yb, showed to be closer to the UCC (Rudnick and Gao, 2004) one. The same peculiarity we have noticed in the case of La/Yb ratio, as well as concerning the Eu negative anomaly (Fig. 7 ((b))), Table 3).

Table 3
The La/Yb and Eu* values for sediment, soils, and, for comparison, for UCC (Rudnick and Gao, 2004) and NASC (Gromet et al. 1986)

	La/Sm	Gd/Yb	Eu*
Sediment	4.91 ± 1.8	1.92 ± 1.3	0.69 ± 0.27
Soils	5.81 ± 2.4	1.49 ± 1.1	0.8 ± 0.32
UCC	6.6	1.9	0.72
NASC	5.56	—	—

The Th/U ratio represents another proxy useful in characterizing the investigated systems. In the case of Zarafshon sediment and soils, the Th/U ratio was equal to 3.01 ± 0.9 and 3.12 ± 1.1 respectively, comparable within one St.Dev, but smaller than 3.89 in the case of UCC (Rudnick and Gao, 2004) or 4.62 for NASC (Gromet et al. 1984). A possible explanation of this small discrepancy could be rather related to an increased U content whose average mass fraction varied between 3.04 ± 1.38 mg/kg in sediment and 3.8 ± 1.5 mg/kg in soils.

These results confirm once more the previous conclusion, which point toward a felsic origin of sedimentary material, sustaining the hypotheses that sediments are the main material of the Zarafshon soils. On the other hand, it should be mentioned that, although the average values of all above mentioned ratios are closed to the UCC ones, the REE mass fractions showed a considerable spreading which could sustain the hypothesis of the prevalence of the felsic material, the other constituents from basaltic to rich silica rhyolite (Fig. 4 ((b))).

5 Anthropogenic Influence

The assessment of ecological condition of investigated more details described on the second part of this research (Abdusamadzoda et al, 2020) which was previously published. As expected, the impact of anthropogenic sources was quite specific in the case of As, Sb, Hg and at a lesser extent for Zn and V. In this regards it is worth mentioning that we have restrained our study only to elements considered as contaminants according to the most severe official regulations of the Tajikistan, Russian Federation (Anonymous, 1992) and Romania (Anonymous, 2020).

The most serious contamination we have noticed in the vicinity of Anzob ore-mining combine (Djidjikrut 1,2 and 7 sampling points) and Kanchoch mine adit (Supplementary Material). Here, the mass fractions of Zn, Hg and especially Sb were ten to a hundred times greater than the Russian Federation (Anonymous, 1992) and Romania (Anonymous, 2020) norms (Fig. 2, Table 1S and 2S). At the same time, we have noticed increased amounts of V, Cr and Ni, all of them related to mining and processing plants. This is the case of V whose mass fractions varied between 154 and 14500 mg/kg around Anzob mining and processing plant, Kumargi Bolo gold-mining combine, Chore 2 to Chore 4 adits or Shahrison tunnel.

In the last case, the shredded solid were scattered near the Shahrison tributary contaminating both soil and sediment along Shahrison tunnel.

The influence of local geochemical features leads to increased mass fraction values of As, Sb, Hg, REE as well as Ta and natural radioactive elements Th and U. But these fluctuations had a local character, mass fraction rarely exceeding the UCC ones (Rudnick and Gao, 2004) values.

6 Conclusion

The Instrumental Neutron Activation Analysis due to its ability to simultaneously determine the content of up to 40 elements, including rock-forming ones was used to investigate the distribution of 38 major and trace elements in the Tajik sector of Zarafshon catchment basin. To accomplish this task 116 samples of sediment and an equal number of soils were collected at altitudes between 883 and 3629 m along the Zarafshon River and its main tributaries. All data were generally compared and analysed in correlation with similar ones for the Upper Continental Crust and North American Shale Composite. As a general conclusion, the mass fraction distribution of all 38 elements excepting As, Sb and Hg showed a remarkable similarity in sediment and soils suggesting the local influence of sedimentary materials. At the same time, the numerical values concerning mass fractions of both major and trace elements presented a significant variability characterized by coefficients of variation between 15 and 200% which could be attributed to the diversity of geological formation covering the Zarafshon Valley.

A detailed analysis of the major element oxides pointed towards a felsic origin of the collected material with a small contribution of mafic suggested in the alkali-silica discriminating diagrams $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}$. At the same time, the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO} + \text{Na}_2\text{O}$ ternary diagram pointed towards the presence of a certain degree of weathering processes. Only in some places we have noticed a significant presence of magnesium and calcium oxides related to local deposits of limestone and dolomite.

The significant information was obtained by analysing the distribution of low mobility and incompatible Sc, Zr, La, Ce, Nd, Sm, Eu, Gd, Tm, Yb as well as Th and U. The Sc presented an average mass fraction of 10 to 11 mg/kg which characterise for the felsic origin. This conclusion sustained also by the reciprocal distribution of Sc, Co, La and Th, La, Th and Hf, or Sc, La and Th which confirmed in different modes. The relative freshness of the sedimentary material was confirmed by the Th/Sc vs. Zr/Sc bi-plot which suggested the absence of a significant sorting and recycling of both sediment and soils.

Also, the felsic origin was confirmed by analyzing the distribution of eight REEs and an average value of La to Sm ratio (for LREE) and Gd to Yb (for HREE) are closer to UCC and NASC ones. The same peculiarity was observed in the case of negative Eu anomaly and showed to be closer to UCC for both sediments and soils.

For a possible anthropogenic contamination, the content of Zn, V, As, Sb and Hg showed to be the most appropriate. But in spite of pristine nature in the Zarafshon Valley in very few places with mining and non-ferrous ore factories were found which could be significantly polluting an environment with As, Sb

and Hg. Even in unexposed (normal and uncontaminated) sediment and soils samples the content of As, Sb and Hg showed to be higher at levels exceeding tens to hundred times compared by reference materials, which evidence about geochemical features of investigated regions.

Given the surface of the investigated area, more than 15 000 km² as well as the diversity of geological formation still insufficiently explored and investigated, the presented results should be seen as an original data for further detailed exploration.

Declarations

Acknowledgments The research was performed within the framework of the Cooperation Agreement between the Institute of Water Problems, Hydropower and Ecology of Academy of Sciences of Tajikistan and Sector of Neutron Activation Analysis and Applied Research of Frank Laboratory of Neutron Physics of JINR. OGD wishes to acknowledge his contribution was done within the Cooperation Protocol no. 4322-4-1017/2019 between the University of Bucharest and the Joint Institute of Nuclear Research, Dubna, Russian Federation. The authors are grateful to the staff of the SNAAPI of Frank Laboratory of Neutron Physics of JINR for carrying out the neutron activation analysis of samples.

CRedit authorship contribution statement Daler Abdusamadzoda: conceptualization, methodology, validation, formal analysis, investigation, data curation, roles/writing—original draft, writing—review and editing, visualization; Djamshed A. Abdushukurov: conceptualization, methodology, validation, data curation, visualization; Octavian G. Dului: conceptualization, data curation, methodology, validation, investigation, resources, data curation, writing—review and editing, visualization; Inga Zinicovskaia: conceptualization, formal analysis, validation, roles/writing original draft, writing—review and editing, visualization; Pavel S. Nekhoroshkov: conceptualization, validation, resources, data curation, writing—review and editing.

Founding No funds, grants, or other support was received for conducting this research and the authors did not receive support from any organization for the submitted research.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Code availability Not applicable

Consent to participate Field study was carried out on agreement of local authorities and all orally consented to performing this study. The study did not involve endangered or protected zone.

References

Abdusamadzoda D, Abdushukurov DjA, Octavian DG., Zinicovskaia I (2020) Assessment of the Toxic Metals Pollution of Soil and Sediment in Zarafshon Valley, Northwest Tajikistan (Part II). *Toxics*, 8(4),

113. <https://doi:10.3390/toxics8040113>.

Abdusamadzoda D, Abdushukurov DjA, Zinicovscaia I, Octavian DG, Vergel KN (2020) Assessment of the ecological and geochemical conditions in surface sediments of the Varzob River, Tajikistan, *Microchem. J.*, 158, 105173. <https://doi.org/10.1016/j.microc.2020.105173>.

American Federation of Mineralogical Societies. Mohs Scale of Mineral Hardness. https://www.amfed.org/t_mohs.htm.

Anonymous (1992) Methodological Guidelines for the Determination of Heavy Metals in Agricultural Soils and Crop Products; Russian Federation Ministry for Agriculture: Moscow, Russian Federation (in Russian)

Anonymous (2006) GN 2.1.7.2041-06: Hygienic normative concerning the maximum permitted concentrations of chemical compounds in soil. Federal Center of Hygienic and Epidemiologic Survey of Russian Federation (Rospotrebnadzor), Moscow, pp. 16. (in Russian)

Anonymous (2020) Regulations of 3 November 1997 (updated) on the Assessment of Environmental Pollution. Legislative Portal. Ministry of Public Works, Development and Administration, Romania. <https://legislatie.just.ro/Public/DetaliuDocumentAfis/151788>, (in Romanian)

Anonymous (2007) Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems. Sanitary rules and norms SanPiN 2.1.4.004-07. State Sanitary and Epidemiological Service of the Republic of Tajikistan., Ministry of Health of the Republic of Tajikistan, Dushanbe, pp. 47. (in Russian) <https://istemol.tj/wp-content/uploads/2020/03/SanPin-2.1.4.004-07-Gigienicheskie-trebovanija-k-kachestvu-vody-1.pdf>.

Armstrong-Altrin JS (2009) Provenance of sands from Cazonas, Acapulco, and Bahia Kino beaches, Mexico. *Rev. Mex. Cienc. Geol.* 26, 764–782. <https://www.scielo.org.mx/pdf/rmcg/v26n3/v26n3a16.pdf>.

Armstrong AJS, Nagarajan R, Madhavaraju J, Nagarajan R, Madhavaraju J, Rosalez HL, Lee YI, Balaram V, Cruz MA, Avila GR, (2013) Geochemistry of the Jurassic and Upper Cretaceous shales from the Molango Region, Hidalgo, eastern Mexico: Implications for source-area weathering, provenance, and tectonic setting. *Comp. Ren. Geosci.* 345, 185–202. <https://dx.doi.org/10.1016/j.crte.2013.03.004>.

Belakovski D (1990) Die Mineralien der brennenden Kohlefloetze von Ravat in Tadshikistan. *Lapis*, 15, 21–26, (in German)

Bharat LS, Keshaw PR, Shobhana R, Jaron I (2016) Geochemistry of Rare Earth Elements in Sediment of Central India. *J. Environ. Protect.* 7, 705-714. <https://dx.doi.org/10.4236/jep.2016.75063>.

Bhatia MR, Crook KAW (1986) Trace element characteristics of graywackes and tectonic setting discrimination of sedimentary basins. *Contrib. Mineral. Petrol.* 92, 181–193.

Blokhina NA (1984) Mineralogy, geochemistry and formation conditions of gold sulfide deposits in the formation of magnesian skarns (Central Tajikistan), Danish Press, Dushanbe, 277 pp. (in Russian)

Cullers RL (2002) Implications of elemental concentrations for provenance, redox conditions, and metamorphic studies of shales and limestones near Pueblo, CO, USA. *Chem. Geol.* 191, 305–327.

Geoportal (2020) Mineral resources of the Republic of Tajikistan, Central Asia Geoportal, https://www.geoportal-tj.org/index.php/geology/deposits_ Accessed 17 March 2021

Gromet LP, Haskin LY, Korotev RL, Dymek RF (1984) The “North American shale composite”: Its compilation, major and trace element characteristics, *Geochim. Cosmochim. Acta*, 48, 2469-2482.

Chub VE (2007) The climate changes and its influence on the hydrometeorological processes, agrockymatical and hydroresources of the Republic of Uzbekistan, Voris Nashriyot Press, Dushanbe, Tajikistan, 133pp. (in Russian)

Everitt BS, Skrondal A (2010) *The Cambridge Dictionary of Statistics*. Fourth Edition. Cambridge University Press, 480pp. <https://196.43.179.3:8080/xmlui/handle/123456789/1213> Accessed 17 March 2021

Farrance I, Frenkel R (2012) Uncertainty of Measurement: A Review of the Rules for Calculating Uncertainty Components through Functional Relationships. *Clin. Biochem Rev.* 33, 49-75.

Fayziev FA, Fayziev AR, Kayumarsi M (2017) On the silver mineralization of Central Tajikistan. *News Ural State Min. Univ.* 4, 18-22. (in Russian)

Floyd PA, Leveridge BE (1987) Tectonic environment of the Devonian Gramscatho basin, south Cornwall: frame-work mode and geochemical evidence from turbiditic sandstones. *J. Geol. Soc.*, 144(4) 531. <https://doi.org/10.1144/gsjgs.144.4.0531>.

Frontasyeva M V (2011) Neutron activation analysis in the life sciences. *Phys. Part. Nucl.* 42, 332–378. <https://doi:10.1134/S1063779611020043>.

Allison G, Dalton CA, Langmuir CH, Su Y (2013) The mean composition of ocean ridge basalts. *Geoch., Geoph., Geosys.*, 14(3). 489-518. <https://doi.org/10.1029/2012GC004334>.

Lee YI (2009) Geochemistry of shales of the Upper Cretaceous Hayang Group, SE Korea: Implications for provenance and source weathering at an active continental margin. *Sedim. Geol.* 215. <https://doi.org/10.1016/j.sedgeo.2008.12.004>.

Madjidov BS (2017) Organizational and economic substantiation of the development of the gold mining industry in the region during the formation of the precious metals market: the example of the Republic of Tajikistan. Publ. doctoral dissertation, SORSUGP, Moscow, 198pp. (in Russian).

<https://www.dslib.net/economika-xoziajstva/organizacionno-jekonomicheskoe-obosnovanie-razvitija-zolotodobyvajuwej-otrasli.html>. Accessed 30 February 2021

Mamadvafoev MM, Bakhtdavlatov RD, Mirzoev B, Bakhronov N (2015) Farob ore field (Central Tajikistan): geology and assessment of perspectives of industrial gold mineralisation. *Proc. Acad. Sci. Rep. Tajik.* 58, 845-852, (in Russian). <https://cyberleninka.ru/article/n/farobskoe-rudnoe-pole-tsentralnyy-tadzhikistan-geologiya-i-otsenka-perspektiv-promyshlennoy-zolotonosnosti>. Accessed 30 February 2021

Mirakov MA, Fayziev AR, Pautov LA (2017) Native selenium in the products of underground fire of Fan-Yagnob coal deposit (Central Tajikistan). *Proc. Acad. Sci. Rep. Tajik.* 60, 456-460 (in Russian). <https://cyberleninka.ru/article/n/samorodnyy-selen-v-produktah-podzemnogo-pozhara-fan-yagnobskogo-ugolnogo-mestorozhdeniya-tsentralnyy-tadzhikistan>. Accessed 30 February 2021

McLennan SM, Hemming S, McDaniel DK, Hanson GN (1993) Geochemical approaches to sedimentation, provenance and tectonics, In: *Processes Controlling the Composition of Clastic Sediments* (Johnsson, M.J. and Basu, A., eds.), *Geol. Soc. Amer., Special Papers*, 285. <https://dx.doi.org/10.1130/SPE284-p21>

Nagarajan R, Armstrong-Altrin JS, Kessler FL, Hidalgo-Moral EL, Dodge-Wan D, Nur IT (2015) Provenance and tectonic setting of Miocene siliciclastic sediments, Sibuti Formation, northwestern Borneo. *Arab. J. Geosci.* 8, 8549–8565. <https://doi.org/10.1007/s12517-015-1833-4>.

Norman JC, Haskin LA (1968) The geochemistry of Sc: a comparison to the rare earths and Fe. *Geochim. Cosmochim. Acta* 32, 93–108.

Novojhilov Yul, Gavrillov AM (1999) Gold-sulphide deposits in carbon-terrigenous layers. *Publ.house of CRIGP, Moscow*, 174 pp. (in Russian)

Taylor SR, McLennan SM (1991) *The Continental Crust: its Composition and Evolution: an examination of the geochemical record preserved in sedimentary rocks*, Blackwell Scientific Publications, Oxford, 312–pp.

Panjakent (1989) Map of Panjakert. <https://mapj42.narod.ru/map1/index016.html>. Accessed 30 February 2021

Pavlov SS, Dmitriev AY, Frontasyeva MV (2016) Automation system for neutron activation analysis at the reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia, *J. Radioanal. Nucl. Chem.* 309, 27–38. <https://doi.org/10.1007/s10967-016-4864-8>

Prokhorov AM (1968-1978) Varzob, *Great Soviet Encyclopedia*, 3rd ed., vol. 30, (in Russian).

Rudnick RL, Gao S (2004) Composition of the continental crust, in: *Treatise on Geochemistry*: (H.D. Holland, Turekian, K.K. eds.), 3, Elsevier-Pergamon, Oxford-London, 2004, 64pp.

- Strakhov NM (1995) Principles of Lithogenesis. in: (S.I Tomkeieff, J.E. Hemingway eds.), Springer, 1, Boston, MA, 1995. <https://doi.org/10.1007/978-1-4684-8923-1>.
- Sadikov AS, Mamarasulov SM, Poslavskiy VV (1979) Irrigation in Uzbekistan: Current State and Prospects of Irrigation Development in the Amudarya River Basin, Tashkent, Uzbekistan, pp. 57–63 (in Russian)
- Sahu B, Rajhans K, Ramteke S, Patel K, Wysocka I, Jaron I (2016) Geochemistry of Rare Earth Elements in Sediment of Central India. *J. Envir. Protec*, 7. <https://doi:10.4236/jep.2016.75063>
- Savenko VS (2007) Chemical composition of sediment load carried by rivers. *Geochem. Int.* 45, 816–824.
- Sharygin VV, Sokol EV, Belakovskii DI (2009) Fayalite-sekaninaite paralava from the Ravat coal fire (Central Tajikistan). *Geol. Geophys.* 50, 703-721 (in Russian)
- Solikhov MM, Aksenov AV, Vasiliev AA, Karimov MA, Rahmanov OB (2018) Search for optimal processing technology for Taror deposit refractory gold ores (Republic of Tajikistan). *Proc. Irkutsk State Tech. Univ.*, 22. <https://dx.doi.org/10.21285/1814-3520-2018-2-182-192> (in Russian).
- Urgut, (1989) Map of Urgut, <https://mapj42.narod.ru/map1/index015.html>. Accessed 30 February 2021
- Vendrov SL, Kalinin GP (1960) Surface-water resources of the USSR: their utilization and study. *Soviet Geogr.*, 1, 35-49. <https://doi.org/10.1080/00385417.1960.10769853>
- Viers J, Dupre B, Gaillardet G (2009) Chemical composition of suspended sediments in World Rivers: new insights from a new database, *Sci. Total Environ.* 407. <https://doi:10.1016/j.scitotenv.2008.09.053>.
- Vinogradov PD (1961) Information collection of All-Union Scientific Research Geological Institute, USSR, 1961, Volume 46, 192- 207. (in Russian)
- Wang W, Chen F, Hu R, Chu Y, Yang YZ (2012) Provenance and tectonic setting of Neoproterozoic sedimentary sequences in the South China Block: evidence from detrital zircon ages and Hf-eNd isotopes. *Int. J. Earth Sci.* 101, 1723-1744. <https://dx.doi.org/10.1007/s00531-011-0746-z>
- Zeisler R, Vajda N, Kennedy G, Lamaze G, Molnar GL (2011) Activation analysis, in: A. Vértes, S. Nagy, Z. Klencsár, et al. (Eds.), *Handbook of Nuclear Chemistry*, Springer, pp. 1555–1620. <https://doi.org/10.1007/978-1-4419-0720-2>.
- Zinicovscaia, I., Dului, O.G., Culicov, O.A., Frontasyeva, M.V., Rodica, S., 2018. Major and trace elements distribution in Moldavian soils, *Rom. Rep. Phys.* 70, 701.

Figures

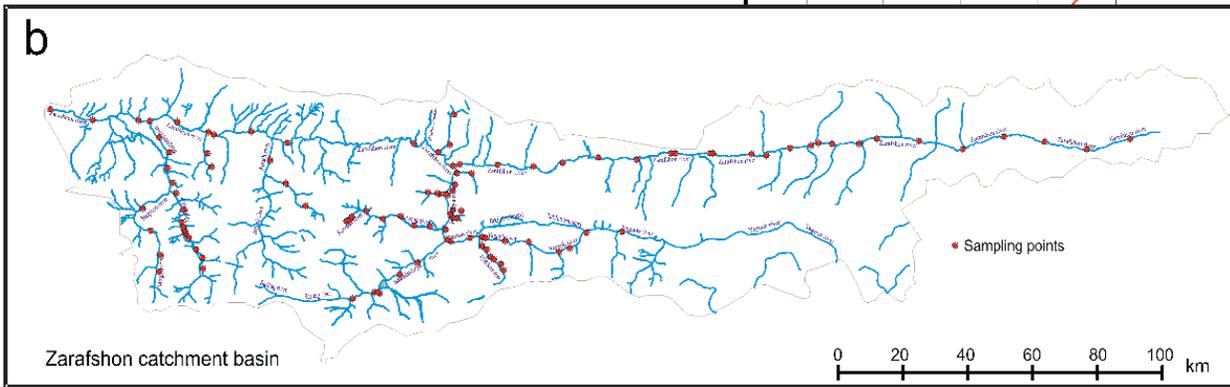
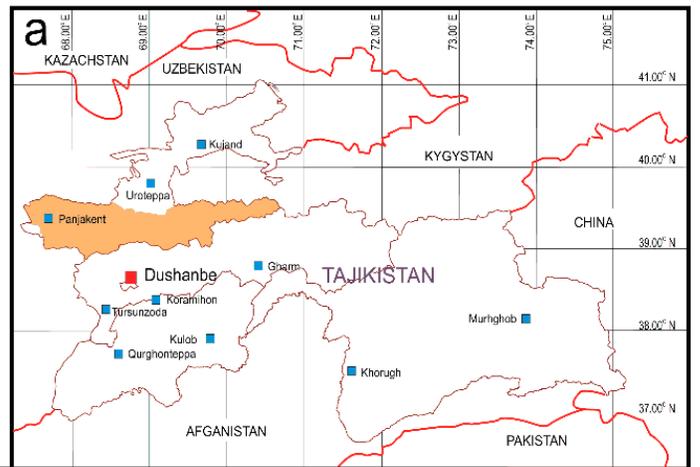


Figure 1

The map of Zarafshon Valley (b) showing its position within the Tajikistan territory (a)

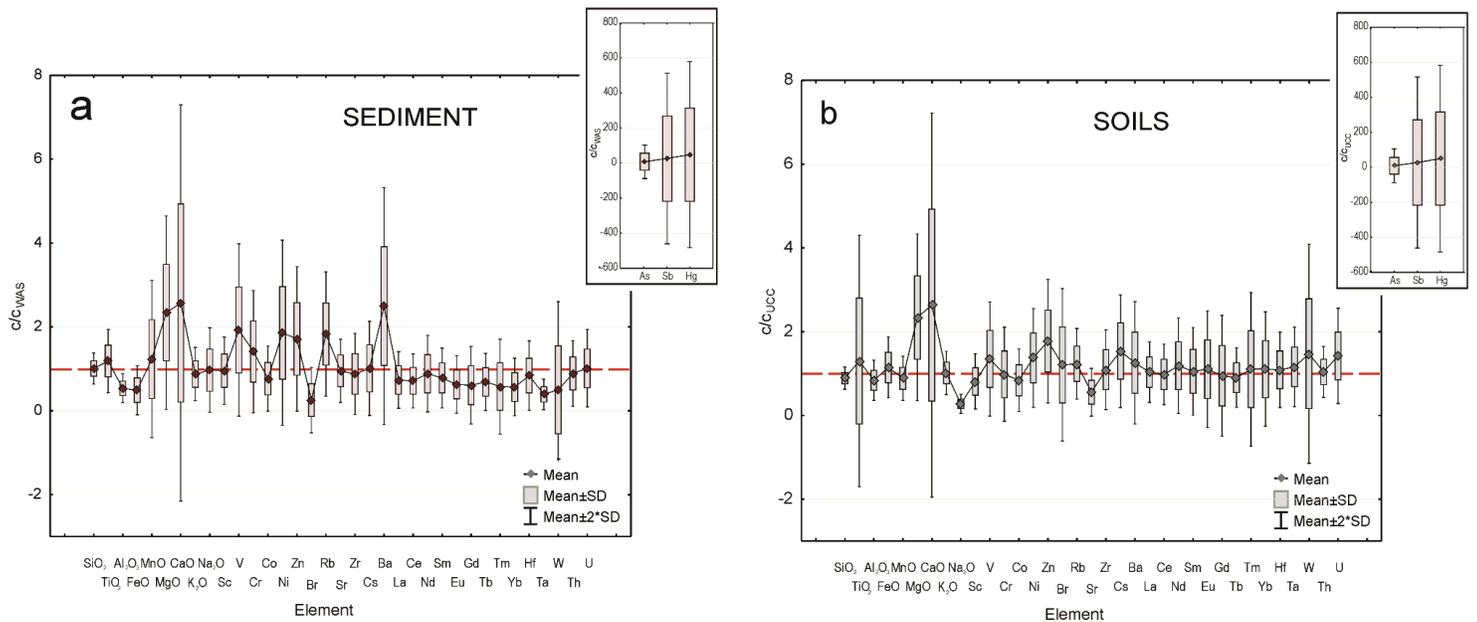


Figure 2

Box-plots illustrating the distribution of investigated elements in Zarafshon sediments (a) and soils (b). All mass fractions of soils normalized to UCC (Rudnick and Gao, 2004) and sediments to SMWR (Savenko, 2007). The values corresponding to As and Hg are divided by 10 and by 100 in the case of Sb. Due to the fact that increased content of As, Sb and Hg were recorded only in very few places, the corresponding standard deviations are disproportional higher.

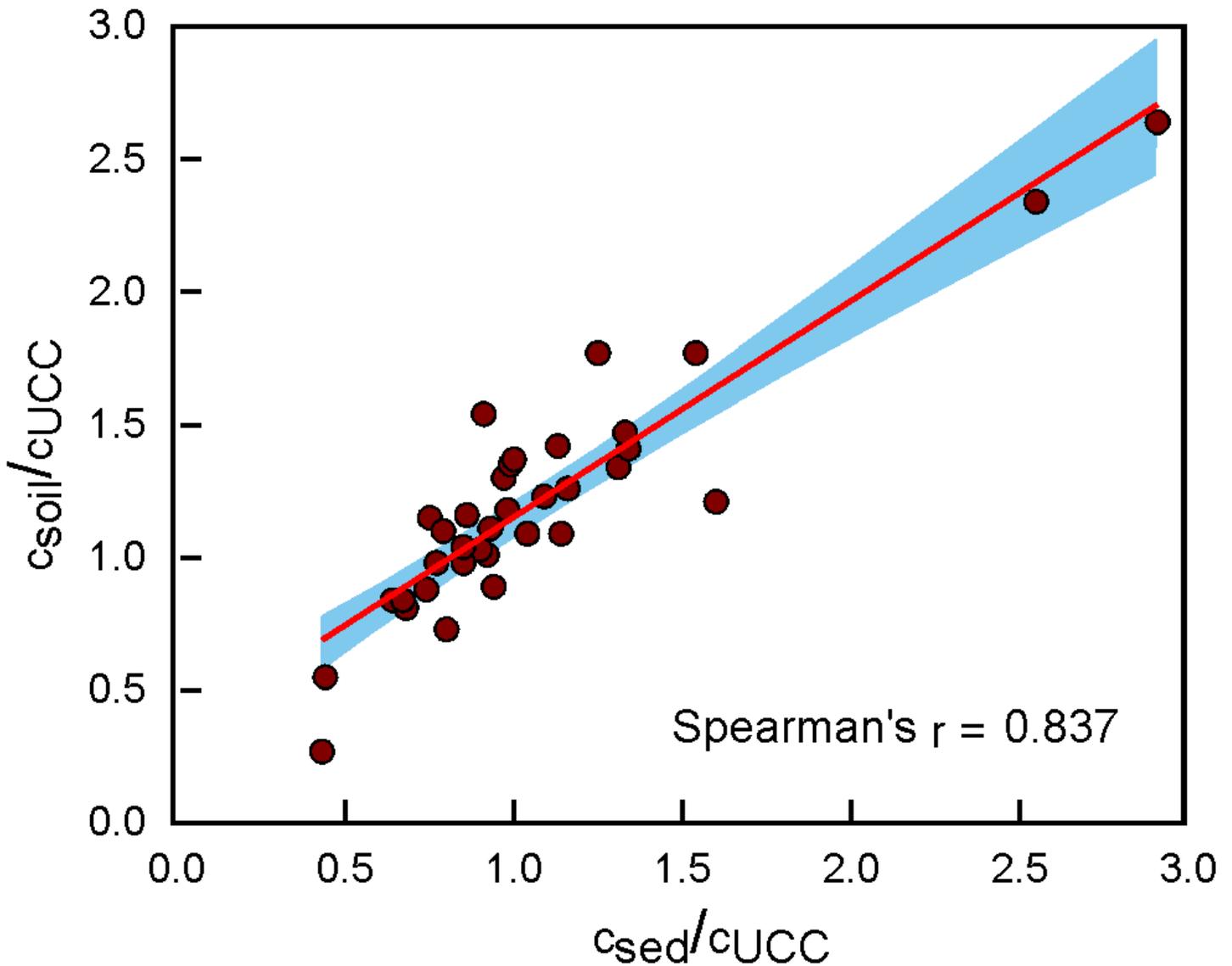


Figure 3

Bi-plot illustrating the reciprocal distribution of investigated elements in sediment and soil excepting the Zn, As, Sb and Hg, i.e. elements whose mass fractions in some places overpasses the UCC ones by on to two order of magnitude. A Spearman's correlation coefficient of 0.837 at $p < 0.01$

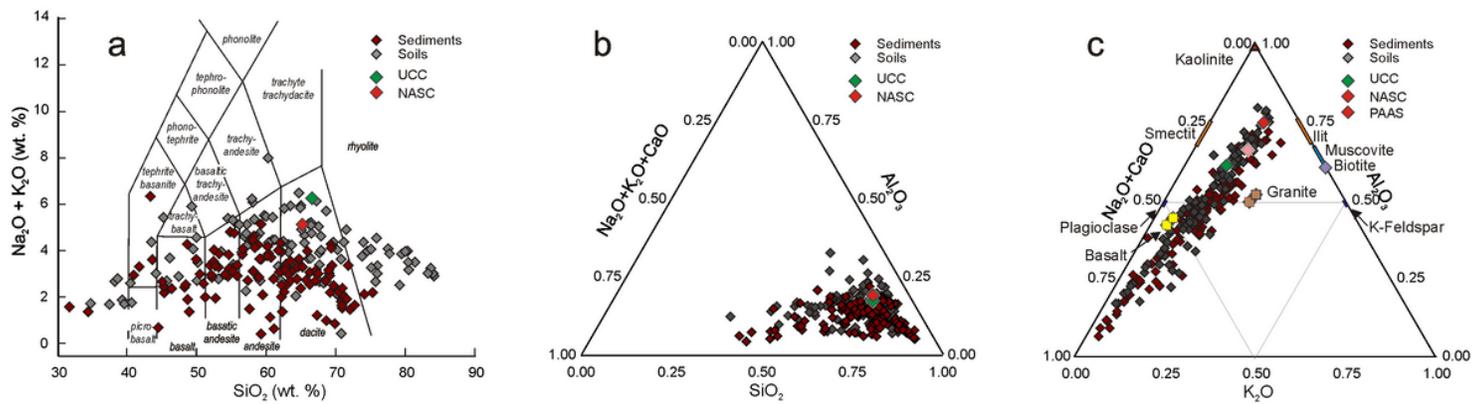


Figure 4

Discriminating total alkali metal oxides vs. SiO_2 biplot (a), ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO}$ (b) and K-A-CN illustrating the preponderance of felsic material in Zarafshon sediment and soils as well as the significant presence of weathered material.

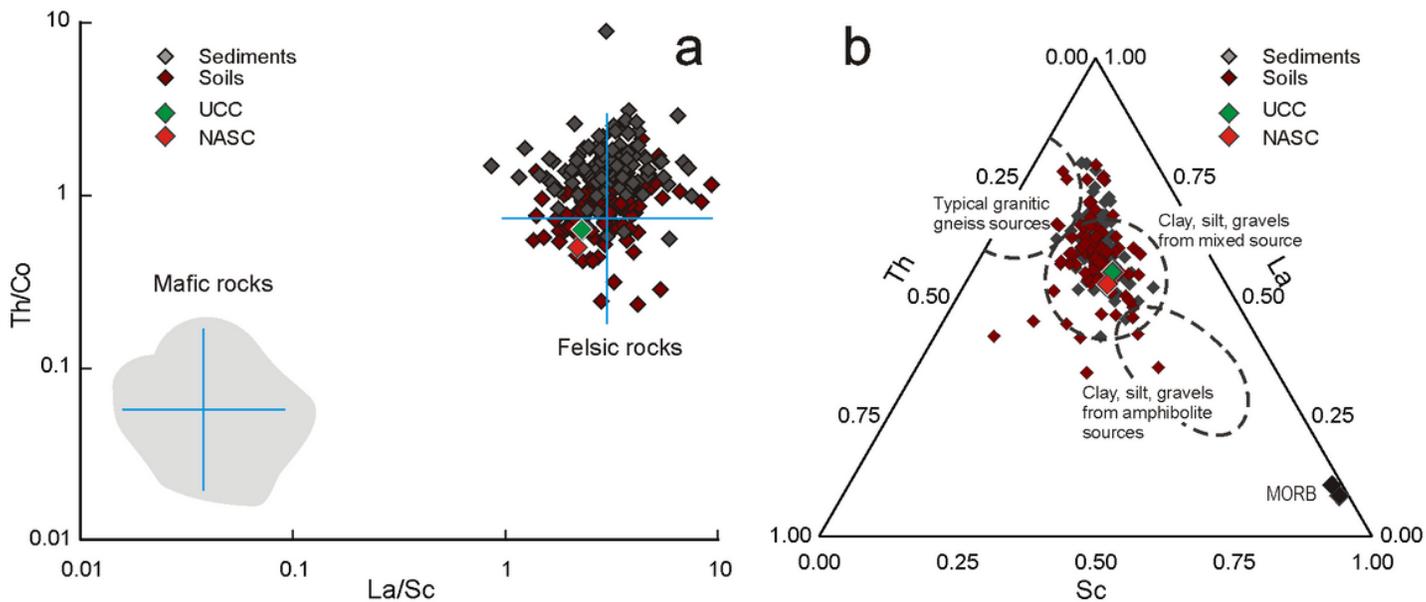


Figure 5

Discriminating bi-plot Th/Co vs. La/Sc (a) and ternary Sc-La-Th diagram (b) confirming the felsic origin of investigated sediment and soils.

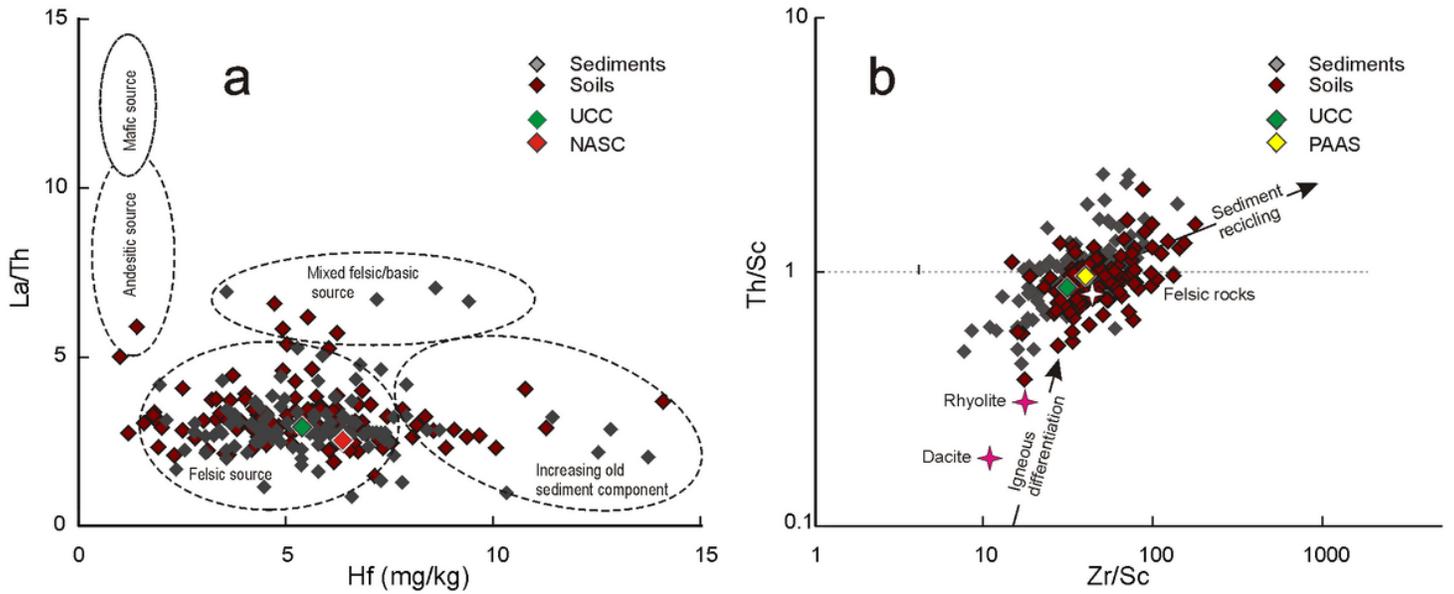


Figure 6

Discriminating bi-plots La/Th vs Hf (a) and Th/Sc vs. Zr/Sc (b) confirming the felsic origin of Zarafshon sediment and soils as well as the absence of a significant recycling of sedimentary material

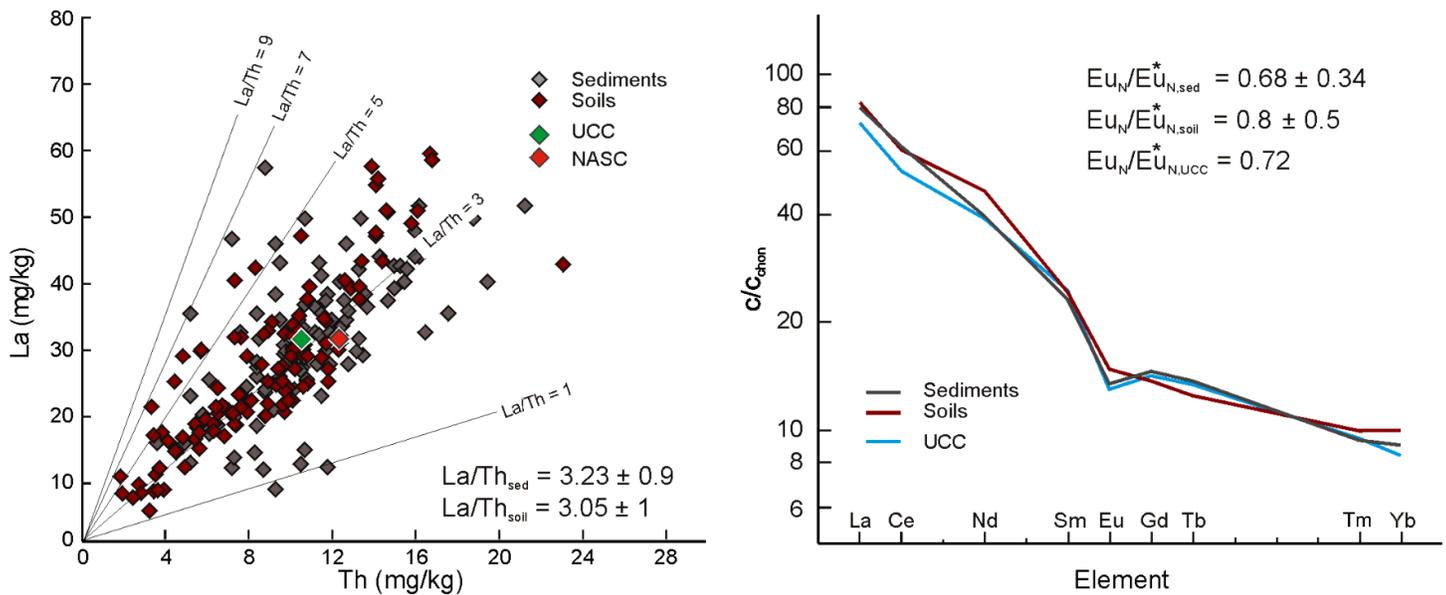


Figure 7

The La vs. Th bi-plot (a) proving that both Zarafshon sediment and soils are significantly closer to UCC (Rudnick and Gao, 2004) and NASC (Gromet et al. 21984) than to MORB (Allison et al., 1986) and the eight REE average values of Zarafshon sediment and soils normalized to chondrite together with the corresponding UCC data (b).

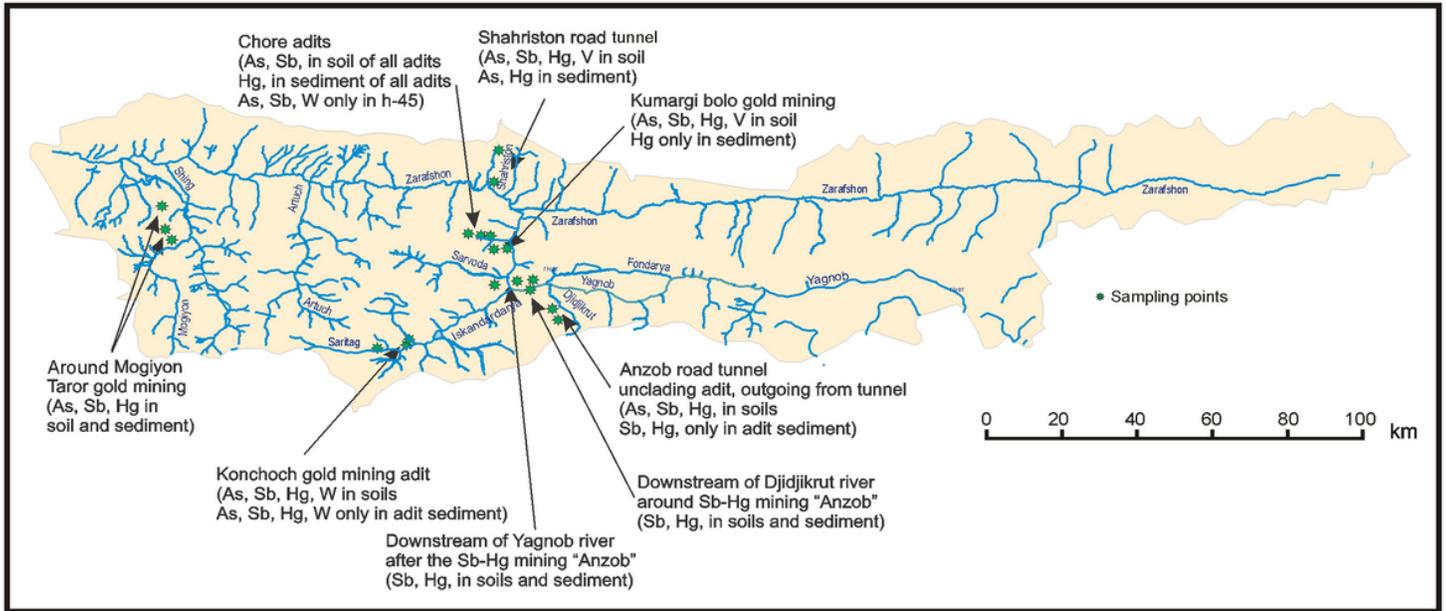


Figure 8

The Zarafshon basin showing the location of significant anthropogenic contamination.