GEOLOGIJA *65/2*, 225-235, Ljubljana 2022
https://doi.org/10.5474/geologija.2022.013

Statistical approach to interpretation of geochemical data of stream sediment in Pleše mining area

Statistični pristop k interpretaciji geokemičnih podatkov potočnega sedimenta na območju rudišča Pleše

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Prejeto / Received 25. 10. 2022; Sprejeto / Accepted 7. 10. 2022; Objavljeno na spletu / Published online 21. 12. 2022

Key words: ANOVA, t-test, correlation, cluster analysis, XRF, mineralization
Ključne besede: ANOVA, t-test, korelacija, clustrska analiza, XRF, mineralizacija

Abstract

The Ba, Pb and Zn ore deposit Pleše near Ljubljana is one of the formerly productive mines. The stream sediments were sampled and analysed by XRF to establish the effect of grain size, mineralization, and downstream location of sampling sites on geochemical composition based on various statistical analyses. Statistical analyses of the geochemical data confirm the impact of mineralization. The parametric t-test, non-parametric Mann-Whitney test and cluster analysis showed only minor differences in the geochemical composition of the samples with different grain sizes (< 0.063 mm and 0.063-2 mm). The parametric and non-parametric correlation coefficients as well as cluster analysis indicate that the contents of Si, Al, K, Rb, and Fe are associated with weathered rock forming minerals such as micas, and clay minerals, whereas Nb and Zr are associated with minerals resistant to weathering. Ca and Mg are associated with carbonates. S, Ba, Sr, Pb, Zn, and Mn indicate local mineralization with sulphates and sulphides. The results of the t-test and analysis of variance, Mann-Whitney tests and Kruskal-Wallis ANOVA of the groups established by the cluster analysis confirm that the contents of Ba, Pb and Sr have a statistically significant influence on the classification of the cluster group - i.e., the influence of sediment mineralization. There are no differences in elemental contents in the sediment samples downstream. The statistical approach to evaluate the geochemical data has proven useful and provides a good basis for further interpretation.

Izvleček

V rudišču Pleše v okolici Ljubljane so v preteklosti pridobivali Ba, Pb in podrejeno Zn. Vpliv velikosti zrn, mineralizacije in lokacije vzorčevanih točk dolvodno na geokemično sestavo sem določala v vzorcih potočnega sedimenta, katerega geokemična sestava je bila določena z metodo XRF. Statistična analiza podatkov geokemične sestave je potrdila mineralizacijo vzorcev potočnega sedimenta. Rezultati parametričnega t-testa, neparametičnega Mann-Whitney-jevega testa in clustrske analize so pokazali, da se geokemični sestavi vzorcev frakcij <0,063 mm in 0,063-2 mm skoraj ne razlikujeta. Tako parametrični kot neparametrični korelacijski koeficienti ter clustrska analiza so pokazali, da prvine Si, Al, K, Rb in Fe kažejo na prisotnost preperelih kamninotvornih mineralov (npr. sljud, glinenih mineralov), Nb in Zr na minerale odporne na preperevanje, Ca in Mg sta značilna za karbonate. S, Ba, Sr, Pb, Zn in Mn kažejo na lokalno mineralizacijo s sulfati in sulfidi. Razlike med skupinami, ugotovljenimi s clustrsko analizo, sem testirala s parametričnim t-testom, analizo variance in Mann-Whitney-jevim testom ter Kruskall-Wallis ANOVO. Na uvrstitev v skupine nabolj vplivajo vsebnosti Ba, Pb in Sr, kar potrjuje vpliv mineralizacije sedimenta. Razlik v geokemični sestavi vzorcev sedimentov dolvodno testi niso zaznali. Statistični pristop k interpretaciji geokemičnih podatkov predstavlja dobro osnovo za nadaljnjo interpretacijo.

Introduction

Nowadays, statistical analyses are very common and useful in many fields of geology (Swan and Sandilands, 1995; Davis, 2002), especially when dealing with geochemical data (e.g., Albanese et al., 2007; Grunsky et al., 2009). A statistical approach can also be useful in determining relationships between the geochemical composition of soils or stream sediments and mineral occurrences (e.g., Candeias et al., 2011; Carvalho et al., 2014; Levitan et al., 2015). There are some former mines and small ore deposits of Pb, Zn, Hg and Fe in the vicinity of Ljubljana (Dervarič et al., 2005). The Pleše Ba, Pb, and Zn ore deposit is one of the formerly productive mines (Mlakar, 2003). Barite, galena, and some sphalerite were mined here for at least 250 years. Between 1729 and 1963, when the mine was opened, more than 100,000 tons of barite, about 10,000 tons of Pb, and some Zn were mined (Žebre, 1955; Fabjančič, 1966; Mlakar, 2003). Today, water seeps and leaks from the formerly productive mine and transports mineralized sediments that may affect the local environment. Stream sediment chemistry is one of the indicators of local geology and also of mining activity (e.g., Hudson-Edwards et al., 1996; Ettler et al., 2006; Teršič et al., 2018). It can also be used as an indicator of potential contamination from mining materials (Baptista-Salazar et al., 2017; Potra et al., 2017; Gosar et al., 2020; Žibret & Čeplak, 2021; Miler et al., 2022).

Sediments from the stream of the abandoned mine tunnel in the Pleše area were sampled to evaluate their geochemical properties and the influence of grain size (0.063-2 mm and < 0.063 mm) based on statistical analyses. In addition, statistical tests were performed to evaluate the impact of the sampling site on sediment geochemical composition.

Materials and methods

The oldest rocks of the area are the Carboniferous clastites (Buser, 1974; Mlakar, 2003). The Permian rocks of the Val Gardena Formation are followed by Lower Triassic dolomites interbedded with fine clastites, red claystones, oolitic limestone and dolomite lenses. This is followed by Anisian and Cordevolian dolomites, and finally the upper Triassic Main dolomite. Stream and bog sediments with scree are the youngest rocks in the area (Buser et al., 1969; Buser, 1974; Mlakar 2003). The area has a complex tectonic history (Buser, 1974; Premru 1974, 1980; Mlakar, 1987; Placer, 1998; Dozet, 1999; Mlakar, 2003). The Upper Triassic dolomite is overthrusted by Paleozoic beds. In addition, several faults of different systems (e.g., cross-alpidic, dinaric, cross-dinaric) are observed. Mineralization with barite, galena and sphalerite occurs in both Paleozoic and Triassic beds (Buser, 1974; Mlakar 2003).

Stream sediment samples were collected at 10 sampling sites at a total distance of 250 m from the abandoned mining tunnel (Fig. 1). The upper 30 cm of the stream sediment was sampled. In the laboratory, all samples were dried at 40 °C. Sample size was reduced by quartering. Samples were sieved through sieves with a 2-mm and a 0.063-mm openings. A total of 15 samples were analysed - 5 samples of fraction 0.063-2 mm (samples designated PO1-2, PO3-2, PO5-2, PO7-2, PO9-2) and 10 samples with grain size of < 0.063 mm (samples designated PO1 to PO10). Geochemical composition was determined using a Thermo Fisher Niton XL3t GOLDD portable X-ray fluorescence (XRF) analyzer at the Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana. The accuracy was checked with several analyses of standard materials and found to be good for elements in question. The only exception is Ba, whose values were not standardised and therefore should be used with caution and only for relative comparison of the analysed samples. Relative percentage difference (%RPD) of duplicate measurements of sample PO1 showed very good precision (< 10 % error) for most elements, with the exception of S (< 12 % error). For further interpretation, the contents of Si, Al, Fe, Mg, Ca, K, S, Mn, Ba, Nb, Pb, Rb, Sr, Zn, and Zr were manipulated. The contents of the other elements were below the detection limit in the majority of the samples or were not of our interest. Statistical analysis was performed using Tibco Statistica software (2017).

Normality of data distribution was checked by comparison of medians, arithmetic and geometric means, by kurtosis and skewness, by visual inspection of histograms, by Kolmogorov-Smirnov and Lilliefors test, and by Shapiro-Wilk test. Because some of the variables aren't normally distributed and because of the small number of samples and for comparison, we applied parametric and non-parametric statistics (Swan and Sandilands, 1995; Davis, 2002). For comparision parametric t-test and non-parametric Mann-Whitney test were performed and correlations (Pearson` s product-moment and Spearman rank order correlation coefficients) were calculated. Cluster analyses of the variables and observations were performed using Ward's linkage rule method and the 1-Pearson correlation coefficient and Euclidean distance as a distance measure.

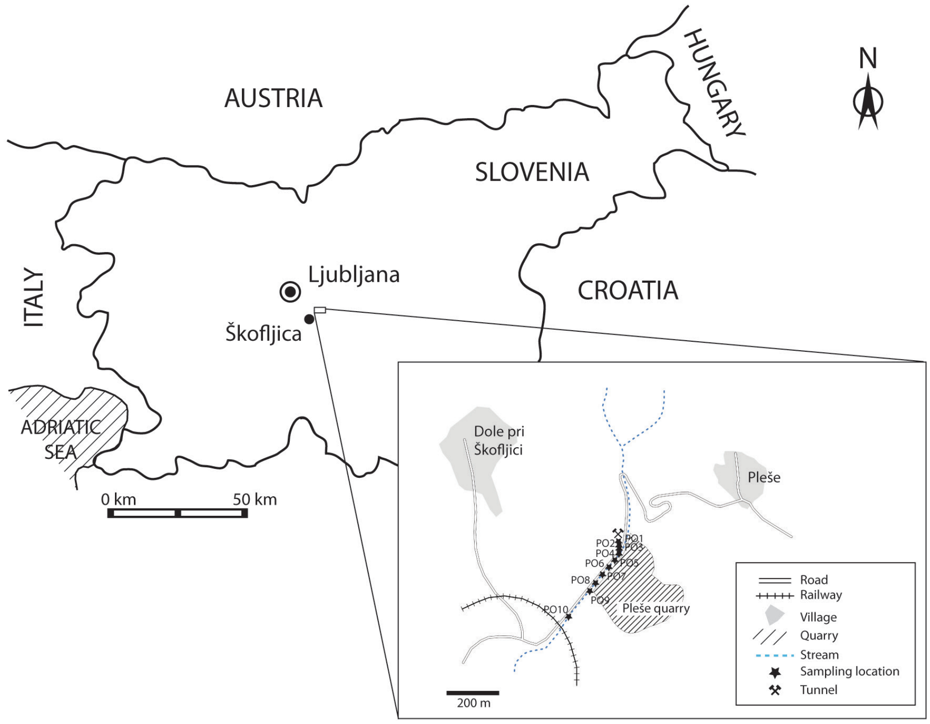

Fig. 1. Map of the area with sampling locations.

Results and Discussion

Ba-Pb-Zn mineralization is clearly evident in the geochemical compositions of the stream sediment samples (Table 1). In some samples, the contents of Ba (the values reported should be used with caution and for relative comparison only), Pb, and Zn exceed the intervention values of 625, 530, and 720 mg/kg, respectively, in soils (Ur. list RS 68/96) and in soils and sediments (VROM, 2000). The contents of Ba and Pb above intervention values were also established by others (Gosar et al., 2014; Miler et al., 2022). For comparison, median values for Ba, Pb and Zn in stream sediments analysed by XRF in Europe are 370, 21 and 71 mg/kg (Salminen et al., 2005).

The presence of silicate and carbonate minerals in sediment samples is also evident (Table 1). The variations in geochemical composition is the result of complex geological composition of the area (Buser, 1974; Mlakar, 2003).

The effect of grain size on the distribution of elements was examined using the parametric t-test and the non-parametric Mann-Whitney test. The parametric t-test revealed statistically significant differences (95 % probability) in the studied fractions (0.063-2 mm and < 0.063 mm) with respect to the content of Mg ($t = -2.53$, $p = 0.025$), Nb ($t = 2.26$, $p = 0.041$), and Zr ($t = 2.35$, $p = 0.036$). The results of the Mann-Whitney test were very similar, with statistically significant differences at the 95 % probability level for the contents of Nb ($Z = 2.02$, $p = 0.043$) and Zr ($Z = 2.88$, $p = 0.004$) in the studied grain size fractions.

The results are also confirmed by box and whisker plots (Fig. 2) - the geochemical composition is very similar in both fractions. Some samples are more mineralized than others, with no clear trend as a function of grain size. Minor differences are observed only in Mg content, which is almost twice as high in the coarse-grained fraction, with a mean of 9.01 % and a median of 9.73 % (in the < 0.063 mm samples, the mean is 5.44 % and the median is 5.98 %). The Mg content can be attributed to the presence of dolomite. Niobium and Zr are more abundant in the fine-grained fraction. For Nb, the mean is 16 mg/kg and the median is 15 mg/kg in the < 0.063 mm fraction, while it is lower in the coarser fraction at 9 mg/kg and 7 mg/kg, respectively. The difference in Zr content is even greater: mean and median are 251 mg/kg and 150 mg/kg in the finer fraction, while 42 mg/kg (mean) and 41 mg/kg (median) in the coarser fraction. Niobium and Zr are bound in weathering resistant minerals.

The small number of samples and the (non-)normality of the distribution clearly affect the differences between mean and median values (Swan & Sandilands, 1995). In the present case, the number of samples (10 vs. 5 samples) also affects the range - the ranges of the fine-grained samples (< 0.063 mm) are generally larger than the ranges of the 0.063-2 mm samples for most elements. The exceptions with wide ranges for S, Ba, Pb, Sr, and Zn in the coarser fraction are probably due to the mineralization of the sediments.

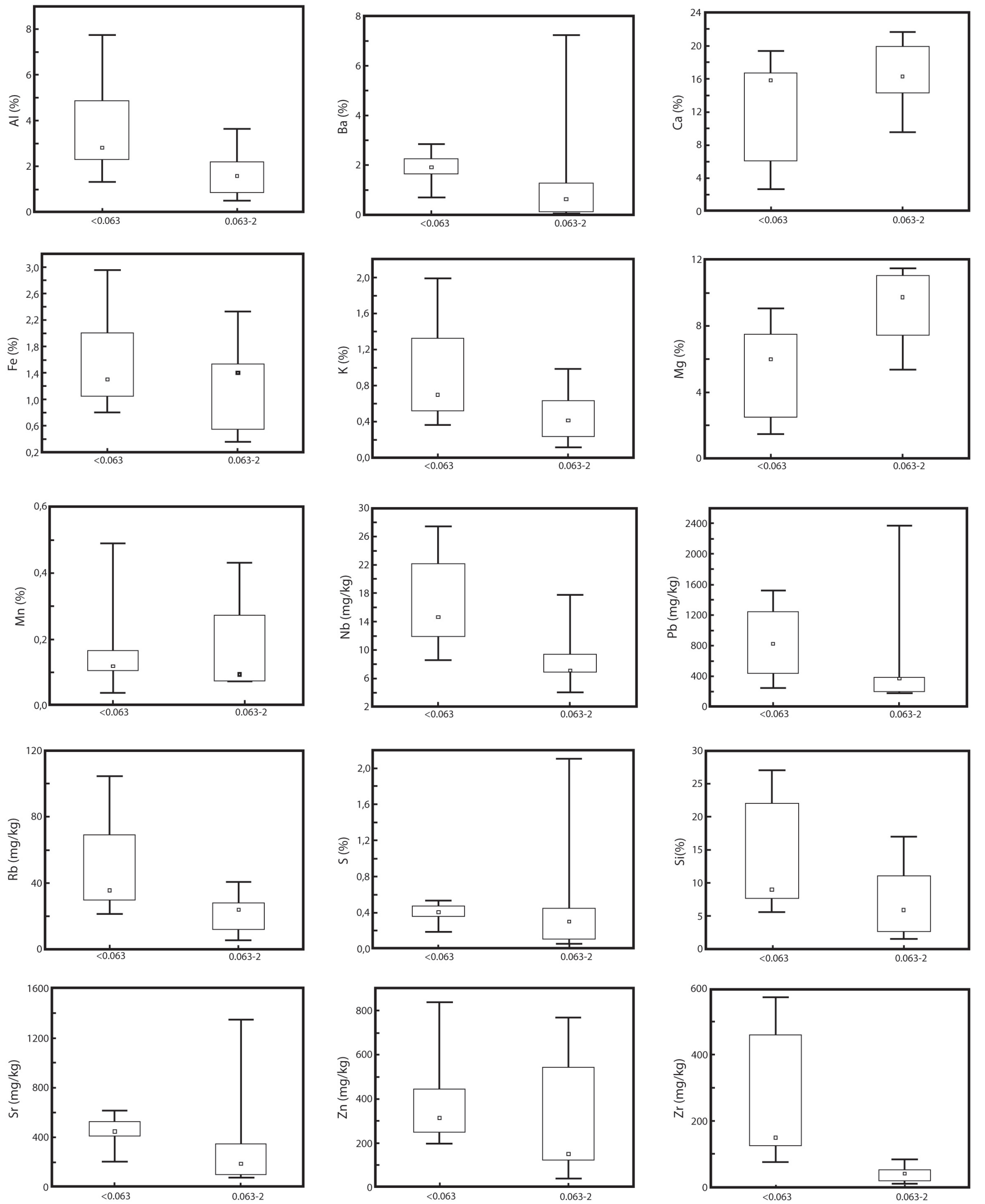

Fig. 2. Medians, interquartile ranges (boxes) with minimum and maximum values (whiskers) of measured elements in finer (<0.063 mm) and coarser (0.063-2 mm) fractions.

The relations between elements have been determined by calculation of correlation coefficients and by cluster analysis. Care should be taken when comparing parametric and non-parametric correlation coefficients calculated using Tibco Statistica software. The software requires all data to calculate the parametric correlation coefficient. If one or more variable values are missing, the entire observation is excluded from the analysis. As Mn content in sample PO9-2 was not detected by XRF, the entire observation was eliminated from the analysis. Therefore, when comparing the two correlation coefficients, some data are "lost" - regardless of whether we omit the entire observation or the variable with the missing data. Consequently, the results may differ to some extent and may also be biased.

First, the coefficients were calculated without the sample PO9-2 data. For most elements, there are almost no differences in the statistically significant correlation coefficients calculated with the parametric Pearson`s product-moment correlation coefficient (Table 2) or with non-parametric Spearman rank order correlation coefficient (Table 3). Exceptions are Si-Nb, Fe-Zr, and Mn-Pb, for which parametric correlations were determined to be statistically significant, and Si-Pb, Mn-Nb, Mn-Rb, and Ba-Zn with statistically significant non-parametric correlation coefficients. The results look slightly different if we omit the Mn values (Tables 4 and 5) instead of PO9-2 observation. In this case, the differences are in S-Zn, Ba-Nb, Ba-Zn, Nb-Sr, and Sr-Zn correlations, where non-parametric correlation coefficients are statistically significant, and Pearson`s product-moment correlation coefficients aren`t. The Pearson`s product-moment correlation coefficient is based on the agreement and direction of the linear relationship between two variables, while the non-parametric correlation is based on the ranking of the data values rather than the values themselves (Swan & Sandilands, 1995). Therefore, scatter plots with a distinct trend line may have a low non-parametric correlation even though the parametric correlation is statistically significant because the positive and negative deviations from the line almost cancel each other out. The non-parametric correlation is also less sensitive to extreme values (Swan & Sandilands, 1995). On the other hand, the calculation of Pearson`s product-moment correlation coefficient requires a larger number of samples and normality of the distribution. Therefore in presented case, the results of non-parametric correlations are more trustworthy, while parametric Pearson`s product-moment correlation coefficient should be used with caution.

The results of cluster analysis of the variables show two main groups (Fig. 3). The first group consists of Si, Al, K, Rb, Fe, Nb, and Zr, while the second group can be divided into two subgroups, with Ca and Mg in one and Zn, Pb, Mn, Sr, Ba, and S in the other subgroup. Cluster analysis confirms the results of correlation coefficients. Namely, members of the groups have in general higher correlation coefficients. The contents of Si, Al, K, Rb, and Fe can be attributed

Table 1. Results of geochemical analysis.

Sample	Grain sizes (mm)	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	K (%)	S (%)	Mn (%)	Ba (%)	Nb (mg/kg)	Pb (mg/kg)	Rb (mg/kg)	Sr (mg/kg)	Zn (mg/kg)	Zr (mg/kg)
PO1	<0.063	26.989	7.750	2.950	1.470	2.680	1.988	0.188	0.128	1.188	27	245	105	302	308	460
PO2	<0.063	22.058	4.882	2.124	2.482	5.475	1.323	0.389	0.106	1.650	22	376	69	409	319	554
PO3	<0.063	24.015	5.296	2.009	2.493	6.104	1.450	0.475	0.159	2.061	24	435	71	459	445	574
PO4	<0.063	10.240	2.920	1.531	5.989	15.450	0.765	0.482	0.188	2.275	15	1454	44	525	664	161
PO5	<0.063	7.665	2.561	1.269	5.967	19.352	0.697	0.465	0.489	2.838	14	1520	37	615	839	138
PO6	<0.063	9.201	3.060	1.341	6.843	15.970	0.700	0.531	0.166	2.564	15	954	34	584	342	138
PO7	<0.063	8.790	2.720	1.124	7.503	16.394	0.595	0.410	0.108	1.928	12	688	32	425	281	126
PO8	<0.063	5.591	1.324	0.967	4.655	15.639	0.456	0.400	0.104	1.908	13	567	26	482	199	124
PO9	<0.063	5.997	1.767	0.803	9.051	18.715	0.363	0.213	0.037	0.703	9	1248	21	206	215	76
PO10	<0.063	8.531	2.299	1.045	7.907	16.742	0.521	0.356	0.071	1.727	12	1193	30	436	250	162
PO1-2	0.063-2	16.970	3.643	2.330	5.356	9.565	0.984	0.056	0.112	0.117	9	177	41	77	150	83
PO3-2	0.063-2	11.080	2.183	1.535	7.438	14.274	0.633	0.300	0.074	0.634	7	371	24	186	769	53
PO5-2	0.063-2	5.910	1.580	1.401	9.726	16.284	0.416	2.106	0.432	7.239	18	2369	28	1350	544	41
PO7-2	0.063-2	2.649	0.853	0.549	11.482	19.940	0.235	0.453	0.071	1.285	7	387	12	347	122	19
PO9-2	0.063-2	1.553	0.510	0.361	11.044	21.651	0.116	0.107		0.055	4	197	5	102	40	11

Table 2. Pearson s product-moment correlation coefficients (red marked correlations are significant at p <0.05).

Si (%)	Si (%)														
Al (%)	0.96	Al (%)													
Fe (%)	0.92	0.91	Fe (%)												
Mg (%)	-0.87	-0.84	-0.80	Mg (%)											
Ca (%)	-0.97	-0.91	-0.92	0.86	Ca (%)										
K (%)	0.97	0.99	0.93	-0.88	-0.94	K (%)									
S (%)	-0.30	-0.29	-0.16	0.36	0.22	-0.28	S (%)								
Mn (%)	-0.15	-0.07	0.03	0.04	0.20	-0.05	0.64	Mn (%)							
Ba (%)	-0.27	-0.22	-0.14	0.24	0.22	-0.22	0.97	0.76	Ba (%)						
Nb (mg/kg)	0.77	0.82	0.71	-0.76	-0.76	0.83	0.17	0.25	0.28	Nb (mg/kg)					
Pb (mg/kg)	-0.52	-0.43	-0.38	0.46	0.54	-0.46	0.74	0.69	0.80	-0.04	Pb (mg/kg)				
Rb (mg/kg)	0.93	0.98	0.88	-0.87	-0.91	0.98	-0.19	0.01	-0.11	0.90	-0.35	Rb (mg/kg)			
Sr (mg/kg)	-0.29	-0.23	-0.17	0.24	0.24	-0.23	0.95	0.75	1.00	0.29	0.80	-0.11	Sr (mg/kg)		
Zn (mg/kg)	-0.02	-0.01	0.08	-0.06	0.12	0.03	0.28	0.64	0.34	0.10	0.43	0.02	0.34	Zn (mg/kg)	
Zr (mg/kg)	0.87	0.84	0.67	-0.84	-0.84	0.86	-0.20	-0.10	-0.12	0.86	-0.38	0.87	-0.11	-0.03	

Table 3. Non-parametric Spearman rank order correlation coefficients (red marked correlations are significant at p <0.05).

Si (%)	Si (%)														
Al (%)	0.93	Al (%)													
Fe (%)	0.89	0.81	Fe (%)												
Mg (%)	-0.72	-0.75	-0.70	Mg (%)											
Ca (%)	-0.85	-0.74	-0.89	0.80	Ca (%)										
K (%)	0.93	0.96	0.88	-0.85	-0.82	K (%)									
S (%)	-0.30	-0.15	-0.20	0.24	0.27	-0.13	S (%)								
Mn (%)	0.25	0.41	0.45	-0.32	-0.21	0.47	0.60	Mn (%)							
Ba (%)	-0.26	-0.04	-0.16	0.09	0.26	-0.04	0.91	0.73	Ba (%)						
Nb (mg/kg)	0.48	0.63	0.55	-0.62	-0.55	0.64	0.35	0.64	0.50	Nb (mg/kg)					
Pb (mg/kg)	-0.56	-0.39	-0.50	0.48	0.61	-0.45	0.65	0.37	0.76	0.11	Pb (mg/kg)				
Rb (mg/kg)	0.82	0.93	0.79	-0.81	-0.71	0.94	0.01	0.59	0.17	0.79	-0.23	Rb (mg/kg)			
Sr (mg/kg)	-0.33	-0.13	-0.20	0.07	0.27	-0.09	0.87	0.68	0.98	0.49	0.77	0.11	Sr (mg/kg)		
Zn (mg/kg)	0.29	0.24	0.37	-0.16	-0.17	0.34	0.48	0.67	0.54	0.38	0.39	0.32	0.49	Zn (mg/kg)	
Zr (mg/kg)	0.68	0.80	0.48	-0.71	-0.54	0.77	0.02	0.29	0.20	0.73	-0.10	0.83	0.17	0.25	

Table 4. Pearson`s product-moment correlation coefficients (without Mn; red marked correlations are significant at p <0.05).

Si (%)	Si (%)												
Al (%)	0.96	Al (%)											
Fe (%)	0.93	0.92	Fe (%)										
Mg (%)	-0.88	-0.86	-0.83	Mg (%)									
Ca (%)	-0.98	-0.92	-0.93	0.88	Ca (%)								
K (%)	0.98	0.99	0.93	-0.90	-0.95	K (%)							
S (%)	-0.20	-0.19	-0.06	0.24	0.13	-0.19	S (%)						
Ba (%)	-0.14	-0.09	0.01	0.09	0.09	-0.09	0.96	Ba (%)					
Nb (mg/kg)	0.80	0.85	0.76	-0.80	-0.80	0.85	0.24	0.36	Nb (mg/kg)				
Pb (mg/kg)	-0.38	-0.29	-0.22	0.29	0.39	-0.32	0.76	0.81	0.08	Pb (mg/kg)			
Rb (mg/kg)	0.94	0.98	0.90	-0.89	-0.92	0.98	-0.10	0.01	0.91	-0.21	Rb (mg/kg)		
Sr (mg/kg)	-0.15	-0.10	-0.02	0.08	0.10	-0.10	0.95	1.00	0.37	0.81	0.01	Sr (mg/kg)	
Zn (mg/kg)	0.11	0.12	0.23	-0.20	-0.03	0.15	0.33	0.42	0.24	0.49	0.16	0.41	Zn (mg/kg)
Zr (mg/kg)	0.88	0.85	0.69	-0.85	-0.85	0.86	-0.14	-0.04	0.86	-0.29	0.88	-0.03	0.07

Table 5. Non-parametric Spearman rank order correlation coefficients (without Mn; red marked correlations are significant at p <0.05).

Si (%)	Si (%)												
Al (%)	0.94	Al (%)											
Fe (%)	0.91	0.85	Fe (%)										
Mg (%)	-0.77	-0.79	-0.75	Mg (%)									
Ca (%)	-0.88	-0.79	-0.91	0.83	Ca (%)								
K (%)	0.95	0.96	0.90	-0.88	-0.86	K (%)							
S (%)	-0.10	0.03	-0.03	0.08	0.07	0.04	S (%)						
Ba (%)	-0.02	0.15	0.06	-0.10	0.02	0.16	0.92	Ba (%)					
Nb (mg/kg)	0.58	0.70	0.63	-0.68	-0.64	0.71	0.46	0.60	Nb (mg/kg)				
Pb (mg/kg)	-0.30	-0.17	-0.26	0.25	0.35	-0.21	0.71	0.80	0.26	Pb (mg/kg)			
Rb (mg/kg)	0.85	0.95	0.83	-0.84	-0.76	0.95	0.16	0.33	0.83	-0.04	Rb (mg/kg)		
Sr (mg/kg)	-0.12	0.05	-0.03	-0.08	0.07	0.08	0.90	0.98	0.57	0.81	0.24	Sr (mg/kg)	
Zn (mg/kg)	0.43	0.38	0.49	-0.31	-0.33	0.46	0.57	0.63	0.50	0.50	0.45	0.58	Zn (mg/kg)
Zr (mg/kg)	0.74	0.84	0.58	-0.76	-0.63	0.81	0.19	0.35	0.78	0.09	0.86	0.31	0.39

to secondary minerals (e.g., clay minerals, micas) or oxides (hematite; Mlakar 2003), Nb and Zr to weathering-resistant minerals, and Ca and Mg to carbonates. Ba, Pb, Zn and S indicate local mineralization with sulphates and sulphides, while Sr might be attributed to trace elements in barite (Mlakar, 2003) and Mn in galenite and sphalerite (Drovenik et al., 1980) or to secondary minerals formed with ore mineral weathering (Miler et al., 2022).

When clustering the observations without sample PO9-2 (using Ward's method as a linkage rule and Euclidean distance measurement), three groups are distinguished (Fig. 4): the first group with samples PO1, PO1-2, PO2, PO3, PO3-2, PO7-2; the second group with samples PO6, PO7, PO8, PO9, PO10; and the third group with samples PO4, PO5, and PO5-2. We checked the differences between the groups obtained by cluster analysis using analysis of variance and Kruskal-Wallis

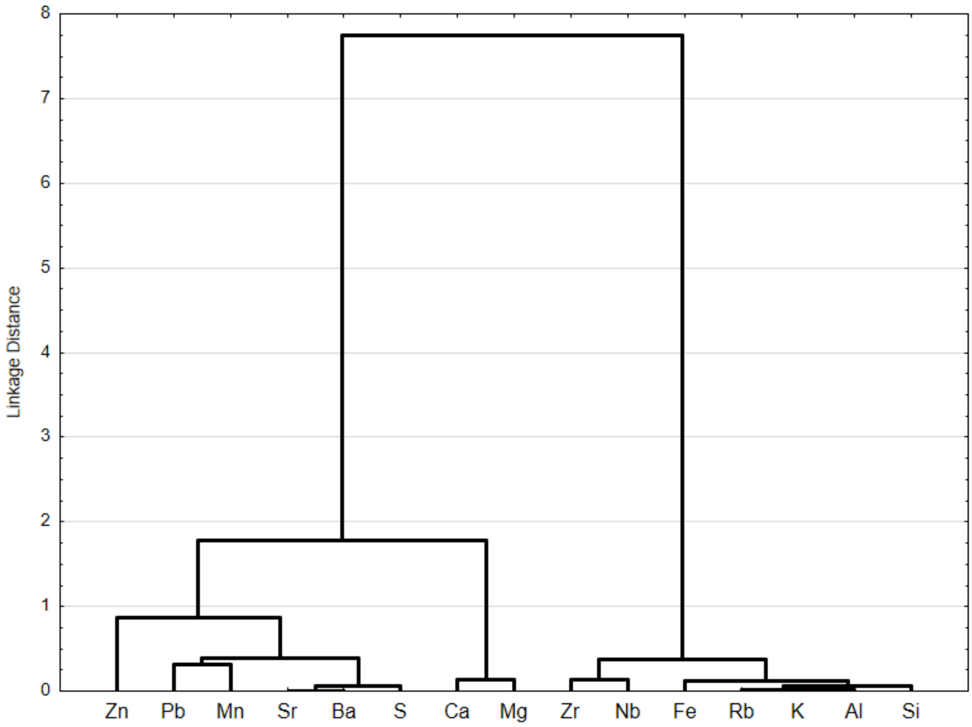

Fig. 3. Cluster analysis of measured elements (calculation is based on Ward's method as a linkage rule and 1-Pearson r as a distance measurement).

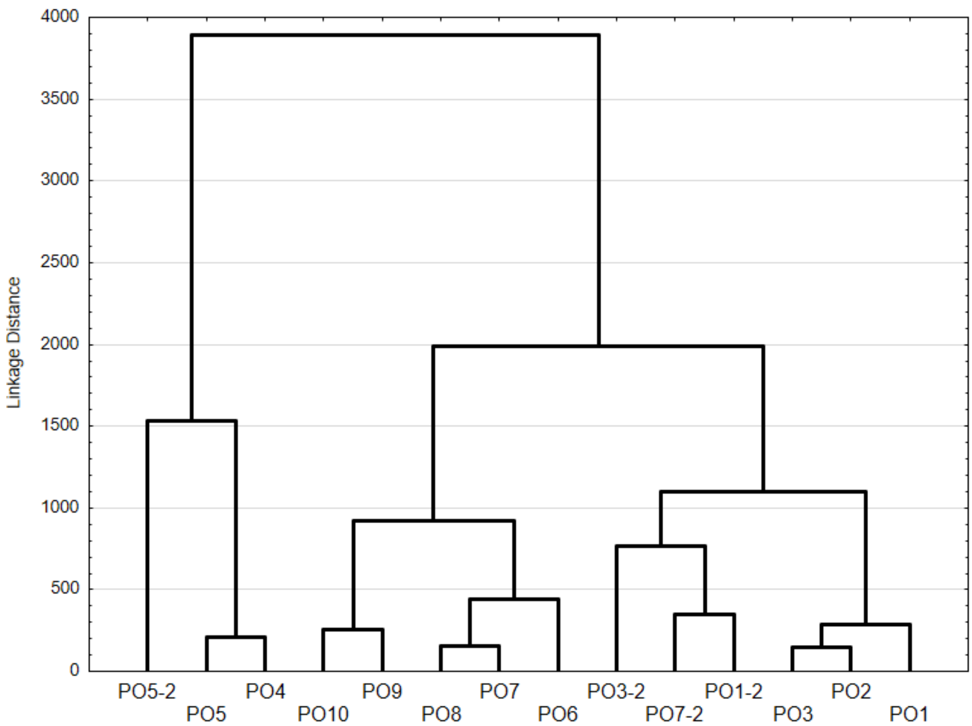

Fig. 4. Cluster analysis of investigated samples without PO9-2 (calculation is based on Ward's method as a linkage rule and Euclidean distances as a distance measurement).

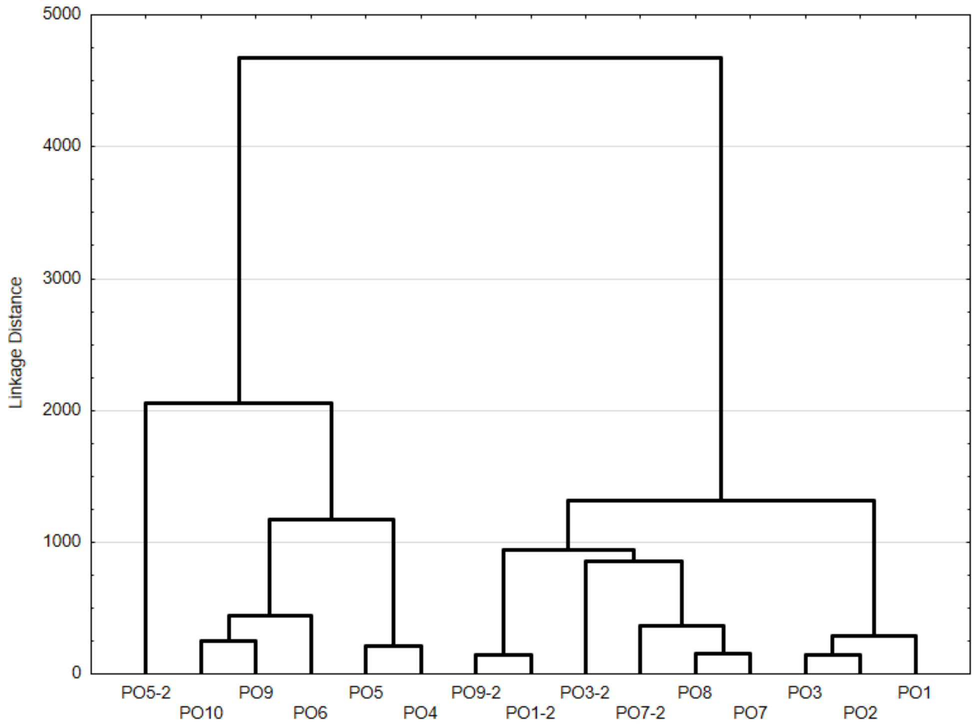

Fig. 5. Cluster analysis of investigated samples without Mn content in all samples (calculation is based on Ward' method as a linkage rule and Euclidean distances as a distance measurement).

ANOVA test. The results show that the content of Pb, Ba, Mn, and Sr (i.e., the mineralization of the sediment) has the greatest influence on the classification into these three individual groups. If we exclude the Mn content from the analysis (it was not detectable in one sample) and manipulate all 15 sediment samples, the result of the cluster analysis looks somewhat different (Fig. 5). Only two groups can be distinguished: PO1, PO2, PO3, PO7, PO8, PO7-2, PO3-2, PO1-2 and PO9-2 form one group, PO4, PO5, PO6, PO9, PO10 and PO05-2 form the second. According to the results of the parametric t-test for independent groups, the contents of Pb and Sr have a significant effect on the grouping. Due to the results of the non-parametric Mann-Whitney test, the contents of Pb, Ba and Sr have a statistically significant influence on the grouping of observations. The statistical analysis clearly shows the different contents of ore minerals of the samples and its effect on the clustering of observations. However, the grain size has no influence on the geochemical composition of the studied samples (< 0.063 mm and 0.063-2 mm; Figs. 4 and 5) as geochemical composition is practically the same in both fractions. Cluster analysis of the samples also shows no significant differences in the geochemical composition regarding the downstream location of sediment samples.

Conclusions

Mineralization with barite, galena and sphalerite in the Pleše area is clearly demonstrated in the geochemical composition of stream sediments. The contents of Ba (the values given should be used with caution and only for relative comparison), Pb and Zn in some samples exceed the intervention values of 625, 530 and 720 mg/kg, respectively (Ur. list RS 68/96; VROM, 2000).

The parametric t-test and the non-parametric Mann-Whitney test showed only minor differences in geochemical composition between samples with different grain sizes, whereas cluster analysis shows no differences. The Mg content is statistically significantly higher in samples of 0.063-2 mm, and the contents of Nb and Zr are higher in < 0.063-mm samples. The number of observations (sediment samples) influence the ranges of the variables as the ranges of fine-grained samples are generally larger than ranges of coarse-grained samples. The diverse composition is the result of the complicated geological composition of the area (Buser, 1974; Mlakar, 2003). Ba, Sr, Pb, Zn, Mn and S indicate local mineralization with sulphide and sulphate minerals and their weathering products.

Pearson`s product-moment correlation coefficients, non-parametric Spearman rank order correlation coefficients and cluster analysis indicate that Si, Al, K, Rb, and Fe contents are associated with weathered rock forming minerals such as mica, and clay minerals, whereas Nb and Zr are associated with weathering-resistant minerals (oxides, silicates). Ca and Mg are characteristics of carbonates and S, Ba, Sr, Pb, Zn and Mn of local mineralization with sulphides and sulphates. The results of the parametric t-test, analysis of variance, and non-parametric Mann-Whitney and Kruskal-Wallis ANOVA tests of the clustered sediment samples confirm that the contents of Ba, Pb and Sr have a statistically significant influence on the clustering of the sediment samples, i.e., the statistical analyses confirm the influence of sediment mineralization. Cluster analysis of the observations also shows no significant differences in the geochemical compositions regarding the downstream sampling position.

Although the number of sediment samples was relatively small, the combination of various statistical tests and analyses shows results that have a geologic basis and significance. The statistical approach to evaluating the geochemical data has proven useful and provides a good basis for assigning elemental data to parent rocks and for identifying potentially contaminated areas.

Acknowledgments

The author gratefully acknowledges financial support from the state budget through the Slovenian Research Agency (Programme No. P1-0195). Special thanks to Ema Hrovatin, Primož Miklavc, Miran Udovč and Gašper M. Volk for preparation of the samples and technical support, and to Prof. Dr. Nina Zupančič for her comments and suggestions.

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