

Geochemical classification of oxidized Mn-ores from Úrkút (W Hungary) and its consequences for ore genesis

Lóránt Bíró
Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Szeged

Márta Polgári
*Institute for Geochemical Research
Hungarian Academy of Sciences, Budapest*

Tivadar M. Tóth
Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Szeged

Analytical data of primary oxidized manganese ores were processed by statistical methods. Six hundred and twenty-one samples were measured (Mn, Fe, Si, and P); thus 2,426 assay data were available. The statistical pointer numbers, the distribution of the elements and the results of the correlational analysis showed the heterogeneity of the ore samples where the measured elements correlated weakly. The samples were grouped by the 4 elements to decrease the heterogeneity and the concentration of elements, and these relationships in the groups were examined. Very few and weak relationships were proved in the groups by the results of the correlational and regression analysis. It is possible that not the heterogeneity of the samples but one or more syngenetic or postgenetic processes caused the absence of relationships. The multivariate statistical processes (principal component analysis, discriminant analysis) allow the determination of the background factors, namely which are the effects that produced the ore. Consequently – with high probability – the ore was formed by two processes. The most likely are hydrothermal and microbial ones (on the basis of geochemical results), but supergene enrichment processes can also be taken into consideration. Both hydrothermal and microbial processes played a significant role in the majority of the samples (81%), which are the ferruginous manganese ores. In the smaller group of samples (19%) the hydrothermal process predominates but the microbial one is also influential, namely for the low iron-bearing manganese ores of excellent quality.

Key words: manganese ore, Csárda Hill, multivariate statistical methods, cluster analysis, principal component analysis

Addresses: L. Bíró, T. M. Tóth: H-6701 Szeged, P. O. Box 651, Hungary, e-mails: birolori@gmail.com, mtoth@geo.u-szeged.hu
M. Polgári: H-1112 Budapest, Budaörsi u. 45. Hungary, e-mail: rodokrozit@gmail.com
Received: November 17, 2011; accepted: November 30, 2011

Introduction

Research on the Csárda Hill manganese ore deposit is a key to understanding the genesis of the Úrkút manganese ore. The primary oxidized, tuberous, siliceous, ferruginous manganese ore is located in a small area (Csárda Hill, Nyíres open pit) in Úrkút, and similar ore was known from Eplény. This ore type was mined in both areas up to 1980, so archive data of reports were used for examination, except for the collection of a few samples. It has been proven in many cases that the archive data are very important for reappraisal, and with modern methods new results can be obtained from them.

Recent work was based on research reports (Cseh Németh 1960; Szabó 1970), within the framework of which the steps of drilling exploration and production operations were presented. There are successive layers from 99 boreholes, 5 investigation shafts and the samples obtained from these (621 piece of samples were analyzed for Mn, Fe, Si, P); thus 2,426 data were available.

The aim of our study was to process these sample analyses with advanced statistical methods, which may impact the understanding of the genesis of the ore deposit and the potential of future exploration.

Geologic setting

The Mn deposits embedded in sedimentary rocks are located at Úrkút-Csárda Hill in the central Bakony Mountains (Transdanubia), in the North Pannonian Unit of the Alps–Carpathians–Pannonian (ALCAPA) region (Fig. 1). The Transdanubian Range, as a part of the Periadriatic region of the Southern Alps, is an allochthonous domain, which escaped northeastward from the continental convergence (collision) zone between Africa (Apulian Microplate) and Europe (Kázmér and Kovács 1985; Fodor et al. 2003).

The largest Mn mineralization (70 million tons of Mn ore with 14 million tons of metal content) occurs in the Úrkút Basin, which was formed by the NW–SE trending block faulting that characterized the Late Triassic and the Jurassic of this region. The deposits are Early Jurassic (Late Liassic) in age and are within marine sedimentary rocks composed mainly of bioclastic limestone, radiolarian clay marlstone and dark-gray to black shale (Polgári et al. 2000). In the Tethyan Realm the Jurassic was an important epoch of Mn mineralization; Mn deposits with variable reserves and Mn-bearing chert are distributed from southern Spain to Greece and Oman.

The Csárda Hill mineralization in the Úrkút area is of very special importance in genetic studies of the huge Úrkút Mn deposit. The Csárda Hill mineralization differs from Mn carbonate and secondary oxide mineralizations, as it is very cherty and Fe-rich. The ore occurs in karst-like holes which are the result of submarine dissolution of underlying limestone. The idea that the accumulation of the entire ore body is the result of the alteration and transportation of the Úrkút carbonate deposit is still commonly accepted, in spite of the different

characteristics of the secondary oxide ore and the so-called Csárda Hill-type, cherty Fe-Mn oxide ore which most probably represents primary formation. The Mn-oxide ore of Csárda Hill area was exploited in an open pit; mining of Mn-oxide ore was abandoned in the 1960s.

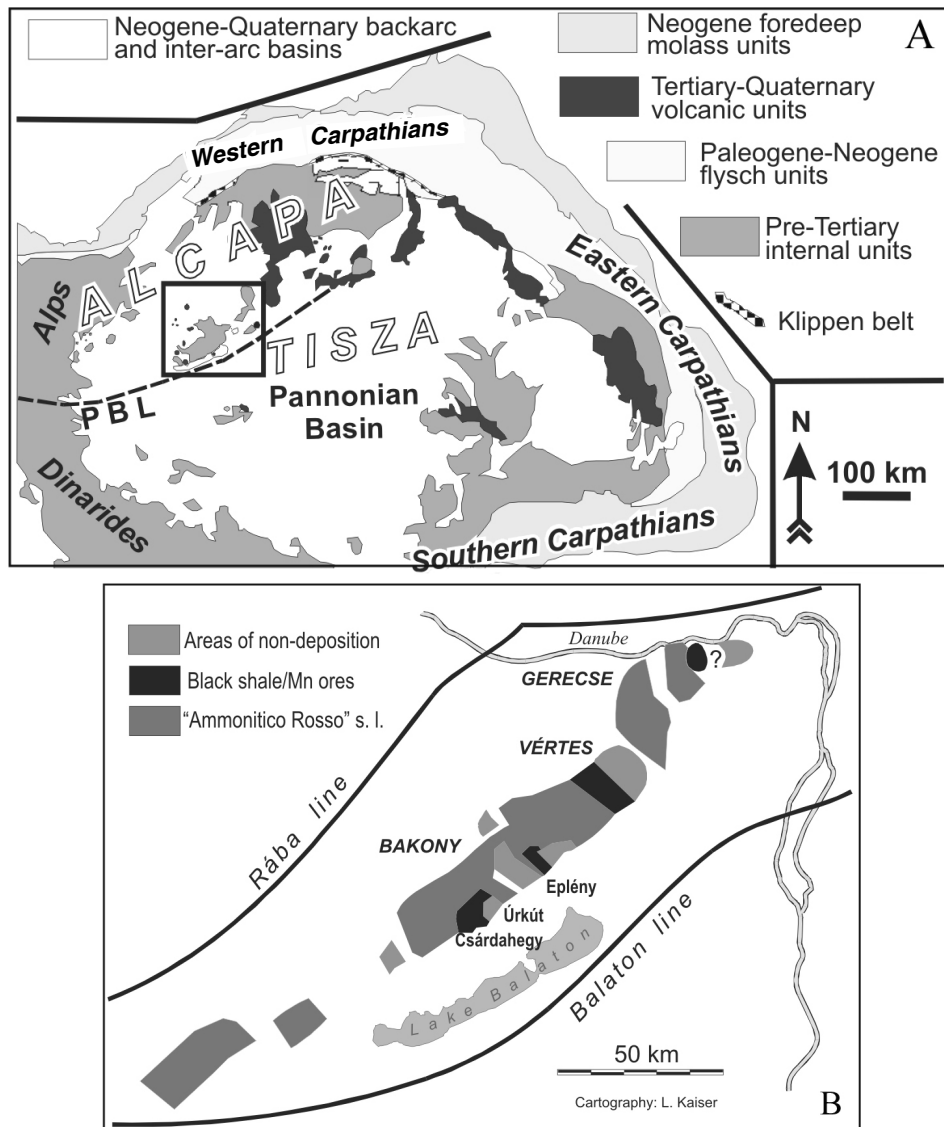


Fig. 1 Location of Jurassic manganese deposits (A), and indications in the Transdanubian Range, Central Europe. (B) Early Toarcian paleogeographic sketch map, modified from Vörös and Galács (1998)

Materials and statistical methods

The samples were obtained from the ore deposit during the deep drilling exploration and were analyzed for Mn, Fe, Si, and P (concentrations were given in weight per cent). Thus the dataset consisted of 2,426 analytical data (620 Mn and Si, 621 Fe and 565 P).

The statistical examination of element concentrations began with univariate statistical methods because by this preliminary work, insight into the structure of chemical parameters can be obtained. The purpose of using these methods is the examination of position indicators (mean, median, and mode), deviation (range, relative deviation) and other (minimum, maximum) statistics to detect the heterogeneity of distribution of the elements.

Following the application of univariate methods, multivariate ones are applied in the interest of revealing the deeper relationships between the components. The classification of the samples and the correlational analysis in the groups can be more precise than the relationships between the chemical components. Classification on the basis of sample descriptions is ambiguous. In the earlier exploration report (Cseh Németh 1960) there were no uniformly detailed sample descriptions, while Szabó (1970) included such information. For this reason the samples could not be classified uniformly on the strength of their descriptions alone. The analytical data of the samples were used for classification with the help of cluster analysis (hierarchical cluster analysis using Ward's method). The quality of the cluster analysis is checked by discriminant analysis in all cases.

After classification of the sample analyses the effects which drove the chemical components were studied. While in the course of examination of the samples, at first the measured chemical components (Mn, Fe, Si, and P) were used for classification, during the more recent process principal component analysis was performed first, followed by classification through the resulting principal components. Principal component analysis serves to reduce and summarize the data and can indicate the independent processes. During principal component analysis the relationships between each mutually connected variable are examined and then presented on the basis of some interpreted principal components. Thus it can determine the background factors which influence the concentration of chemical components and can classify the samples on the basis of these factors.

Results

On the basis of the elements' concentration distribution test Mn showed Gaussian distribution, while in the case of the other elements a robust estimator was used in the statistical pointer numbers because of a different type of distribution.

In the examination of the pointer numbers (mean, median, mode) it could be seen that the modes do not correspond to the means; all elements have outlier

concentrations which modify the means (Table 1). It was shown that the parameters do not show a Gaussian distribution. This is visible in the value of the relative deviation (standard deviation/mean). The high value of Si supported this (such material cannot be considered an ore with such a high Si content). In the case of relative deviations, it seems that the relative deviation is higher than other pointer numbers only in the case of P, which occurs in the ore with very heterogeneous distribution, and is concentrated locally. The maximum values of Mn and Fe indicate the premium ore grade (manganese ore, iron ore). A box-plot diagram was used to study the outlier values (Fig. 2).

Table 1
Univariate statistical pointer numbers of the elements (for the complete oxide sample set)

Pointer numbers	Mn	Fe	Si	P
Average	17.90	15.18	8.14	0.15
Median	17.23	15.43	8.95	0.16
Mode	18.40*	11.31*	1.50*	0.11
Relative deviation	0.53	0.35	0.68	1.21
Range	48.37	37.14	36.78	4.36
Minimum	0.10	2.23	0.19	0.02
Maximum	48.47	39.37	36.97	4.38

* The least among more modes

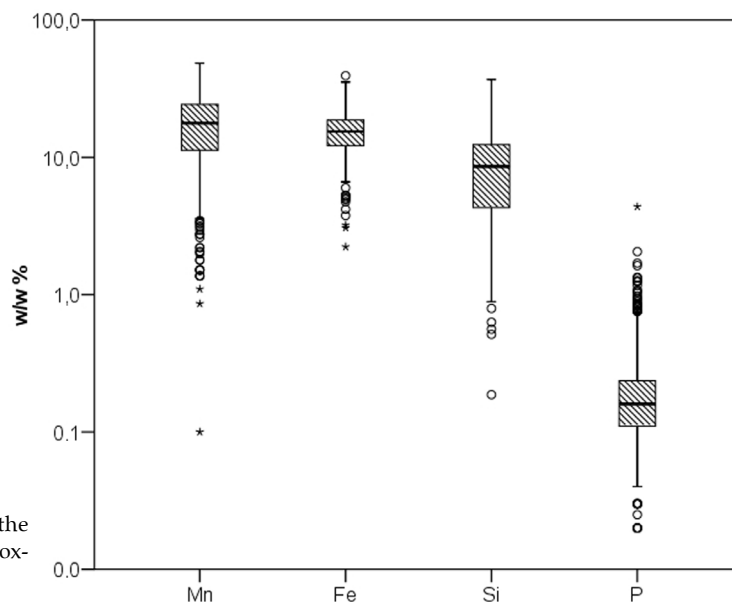


Fig. 2
Diagram of the concentration's box-plot

The case of P indicates that the relative deviation is very high (Table 1). Comparing it to the box-plot (Fig. 2) it can be stated that the concentrated occurrence of P in the ore would increase the deviation.

During the correlational analysis very few linear relationships were typical between the elements. A presumed relationship was seen between Mn and Si (Table 2).

Table 2
Correlational matrix of the elements in the case of linear connection

	Mn	Fe	Si	P
Mn	1.00			
Fe	0.10	1.00		
Si	-0.69	-0.49	1.00	
P	-0.75*	-0.15	0.06*	1.00

* Not significant ($\alpha = 0.05$)

The results of the univariate pointer numbers, the element distribution, and the correlational analysis showed that the ore layers can be characterized by heterogeneous composition. The elements are correlated weakly with each other. Five groups could be distinguished by cluster analysis from application of the four-element database (Mn, Fe, Si, and P) but the classification of the groups did not give

suitable results. It is possible that the presence of P causes discrepancies, so it must be taken into consideration that the P distribution is very inhomogeneous (local P enrichments occur as accumulations of fish fossils and/or phosphorite crusts) which can cause disturbances in the classification of elements. For this reason the three-element database (Mn, Fe, and Si) was used for classification, which also resulted in five groups. The classification of the groups by the formations was proved by the chemical parameters, which were amplified by discriminance analysis as well (Fig. 3). This method was able to classify the samples into one of the five groups at 93.5%, at a 0.05 confidence interval level.

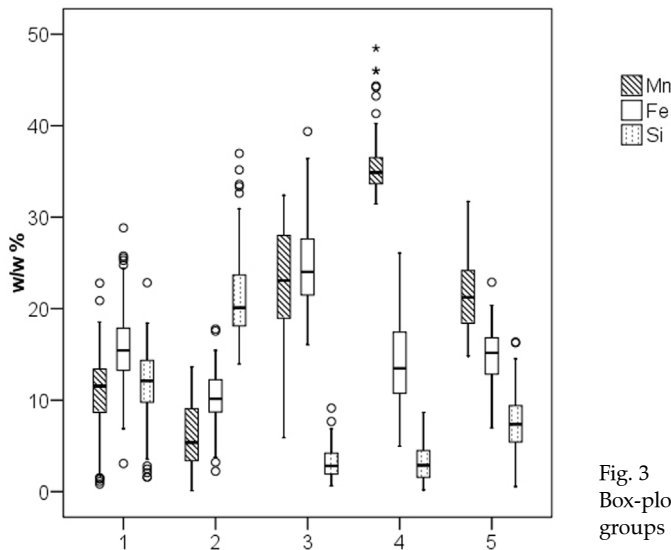


Fig. 3
Box-plot diagram of the resulting groups

Summarizing the two exploration reports' descriptions, and comparing them with the results obtained from the clustering, the resulting groups were the following:

1. Group: clay with manganese ore, brown, red – varicolored clay (lower Si-content) – 191 samples
2. Group: clay with manganese ore, brown, red – varicolored clay (higher Si-content) – 76 samples
3. Group: manganese and iron oxide ore, brown, black, blueish-gray, tough, shatter fracture, tuber oxide ore – 97 samples
4. Group: ferruginous manganese oxide ore and manganese oxide ore, black, brown, red, yellow-varicolored manganese oxide ore – 58 samples
5. Group: clayey manganese ore, brown, red, yellow, varicolored, pisolitic, clastic, Mn-oxide-bearing granular clay – 198 samples

Among the data in the groups, the linear relationships could not be improved (Table 3).

Table 3
Correlation matrix of the groups

Element / Group	Mn					Fe					Si					
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	
Fe	1	-0.25														
	2		-0.03*													
	3			-0.53												
	4				-0.32											
	5					-0.23										
Si	1	0.19				-0.67*										
	2		-0.07*				-0.68									
	3			-0.52				0.10*								
	4				-0.25*				-0.49							
	5					-0.24				-0.17						
P	1	-0.09*				-0.29					-0.10*					
	2		-0.06*				-0.02*					0.16*				
	3			-0.22				0.10*					0.32			
	4				0.08*				-0.15*						-0.01*	
	5					-0.08*				-0.19						0.16

* Not significance ($\alpha = 0.01$)

While a weak negative correlational relationship occurred between Mn-Si in the complete data set, in the case of groups a weak negative correlational relationship was determined between Fe-Si in Group 2.

It can be stated that the formed groups contain well-defined formations. High quality ores belong to Groups 3, 4, and 5 (these groups represent 57% of samples) while Groups 1 and 2 contain clay-rich manganese ores (43% of the samples). These groups are separated from each other but the relationships of the elements in the groups are very weak. It is possible that the heterogeneity of the samples is caused rather by one or more syngenetic or postgenetic processes than the absence of linear relationships between the elements.

During examination of the background processes (applied to the previously shown methods) principal component analysis resulted in 3 principal

components. These principal components change the chemical parameters by the following measure (Table 4):

The 1st principal component seems to be preferred by both Mn and Fe while this effect decreases the Si (the values express relative strength). These attributes

Table 4
Correlational matrix of the principal components and analyses

	1 st principal component	2 nd principal component	3 rd principal component
Mn	+ 0.8	+ 0.3	- 0.4
Fe	+ 0.6	- 0.5	+ 0.6
Si	- 0.9	- 0.2	- 0.1
P	- 0.2	+ 0.8	+ 0.5

are characteristic for hydrothermal systems where ore-forming processes move Mn and Fe together (Balogh 1992). In submarine hydrothermal mixing zones Fe precipitates very quickly as oxide by autocatalytic processes (Humphris et al. 1995) and Fe oxide would provide the active surface to precipitate Mn (active oxide surface precipitation model; Morgan 2005).

In the case of the 2nd principal component, Fe and P behave in opposing ways; while the concentration of P is strongly increased, the Fe grade decreases. This background process seems to enrich the primary sediment with organic matter, which can be identified as a basic process. The fishes and other fossils are a part of this process, which is responsible for the enrichment of P (Polgári et al. 2000; Polgári et al. 2004).

Finally, the 3rd principal component is explained by the effect of the similar attitude and relative enrichment of Fe and P, or absorption of P on an active surface of Fe oxi-hydroxide in a submarine environment.

Spatial distribution of the above-mentioned components is important, and for this reason the 3D geologic model was created which helps to show the changes of the principal components in space. The key question was the behavior of the principal components in the submarine dissolved holes. Certain effects showed craggy changes in the southern part of studied area (the surroundings of Holes 3 and 4) while these cannot be found around Holes 1 and 2). This is in harmony with the previously studied element profiles, during which it came to light that the element distribution is more homogeneous around Holes 1 and 2 than near Holes 3 and 4. The results of the two investigations seem to be in harmony with each other, assuming that the element distributions are determined by geologic processes. There are boreholes (for example Cs-66) where the changes of the principal components are unambiguous. This can be supported by the explained effects in accordance with a probable hydrothermal effect dominating toward depth, while the primary sediment accumulation has not been changed. But there are other boreholes (for example Cs-76) where the result was very

disturbed. The intensity of effects was changed in time; therefore changes of these ratios were compared to each other and to the sediment, and have been very variable. This does not disregard the fact that the redeposited ore occurrences and ores which formed *in situ* from primary ores are known where the postgenetic processes modified the original character. So it is possible that zones exist where more effects jointly originated different effect profiles.

The samples can be classified by the 3 principal components. Cluster analysis thus helps to clarify how the samples can be classified according to the interpreted processes in space and time. Placing these groups onto maps, the dominant effects in the presented area will be visible. This creates a more exact picture of the spatial distribution of effects, as not only are the geologic models visible on the basis of the distribution of effects, but the results of effects as well, namely that the samples formed by the given effect show the kind of spatial distribution of the effects.

Two supergroups were created during the cluster analysis of the principal components. According to the box-plot diagram of the principal components (Fig. 4A) the two supergroups genetically differ from each other.

The No. 1 supergroup contains 81% of all samples. These were formed by the three principal component effects in equal degree. It can be seen that in the case of the No. 1 supergroup the three effects resulted in the formation of ferruginous-manganese ore (Fig. 4B).

On the other hand, the samples of the No. 2 supergroup (19% of all samples) could have been = formed by the 1st principal component, namely the hydrothermal effect, which could have controlled the formation (Fig. 4A). In the high grade ore the Mn content is high, while the Fe and Si contents are much lower (Fig. 4B). The P concentration cannot be bound to the primary ore formation, so its concentrations do not differ between the supergroups.

The investigation of No. 2 supergroup is more interesting from a genetic point of view, because in this group the hydrothermal effect occurs as the dominant background effect. For this reason the group was investigated in greater detail. On the dendrogram of cluster analysis it is easily visible that the No. 2 supergroup is divided into 2 subgroups (subgroups 2A and 2B; Fig. 5A). Accordingly the 2A and 2B subgroups differ in the strength of the 3rd principal component. Looking at the box-plot diagram of the elements' concentrations of the two subgroups (Fig. 5B), the highest grade manganese ores belong to the 2A subgroup, while in the 2B subgroup the iron concentration is already about 20%. The spatial distribution of these groups was examined and subgroup 2A, which represents the better quality, low iron-bearing manganese ore, occurs in the holes or directly around them. The samples of the 2B subgroup (samples with higher iron concentration) can be found around the holes but they occur at a much greater distance as well.

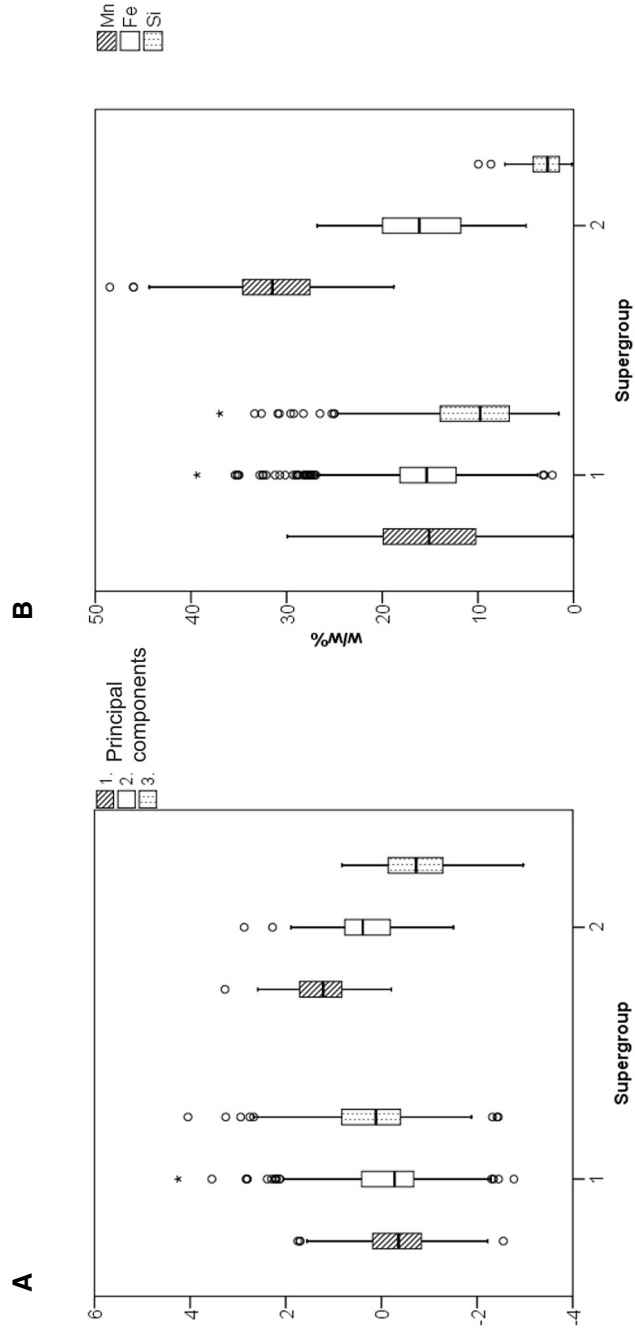


Fig. 4 Strength of the supergroups' principal components on box-plot diagram (A), element concentration of the supergroups on box-plot diagram (B)

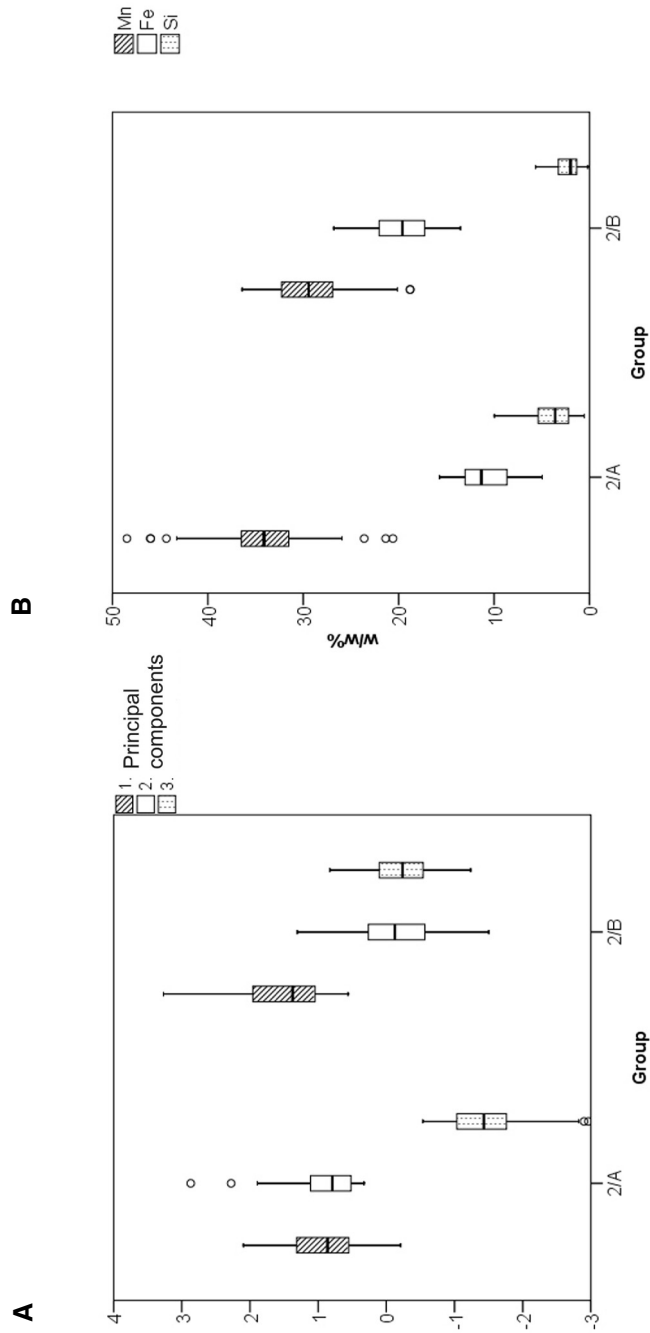


Fig. 5 Strength of the No. 2 supergroup's principal components on box-plot diagram (A), element concentration of the No. 2 supergroup on box-plot diagram (B)

Acknowledgements

The authors thank Zoltán Szabó and Tamás Vigh (Mangán Ltd. Úrkút) for their help and advice, and József Kovács (Eötvös Loránd University) for his help in the initial steps. Helpful comments from János Földessy and Zoltán Unger improved the text. The study was supported by the grant of Pro Renovanda Cultura Hungariae "Students for Science".

References

- Balogh, K. 1992: Sedimentology III. – Akadémiai Kiadó, Budapest.
- Cseh Németh, J. 1960: Research report and reservoir estimation of the Csárda Hill area. – Manuscript, Archive, Hungarian Geological Institute. (In Hungarian.)
- Fodor, L., B. Koroknai, Kad. Balogh, I. Dunkl, P. Horváth 2003: Nappe position of the Transdanubian Range Unit ("Bakony") based on structural and geochronological data from NE Slovenia. – Bulletin of Hungarian Geol. Soc., 133/4, pp. 535–546.
- Humphris, S.E., R.A. Zierenberg, L.S. Mullineaux, R.E. Thomson (Eds) 1995: Seafloor hydrothermal systems. Physical, chemical, biological, and geological interactions. – American Geophysical Union, Washington, DC, USA, 466 p.
- Kázmér, M., S. Kovács 1985: Permian–Paleogene paleogeography along the eastern part of the Insubric-Periadriatic Lineament system: evidence for continental escape of the Bakony-Drauzug Unit. – Acta Geologica Hungarica, 28/1–2, pp. 71–84.
- Morgan, J.J. 2005: Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. – Geochimica et Cosmochimica Acta, 69, pp. 35–48.
- Polgári, M., Z. Szabó, T. Szederkényi (Eds) 2000: Manganese Ores in Hungary – In commemoration of professor Gyula Grasselly. – MTA Szegedi Akadémiai Bizottsága. Szeged. 675 p.
- Polgári, M., M. Szabó-Drubina, Z. Szabó 2004: Theoretical model for the Mid-European Jurassic Mn-carbonate mineralization Úrkút, Hungary. – Bulletin of Geosciences, Czech Geological Survey, 79/1, pp. 53–61.
- Szabó, Z. 1970: Research report on the geological exploration of the Csárda Hill area, 1970. – Manuscript. Archive, Hungarian Geological Institute. (In Hungarian.)
- Vörös, A., A. Galács 1998: Jurassic palaeogeography of the Transdanubian Central Range (Hungary). – Rivista Italiana di Paleontologia e Stratigrafia, 104, pp. 69–84.