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CASE STUDY : HYDROGEOCHEMICAL PROSPECTION IN A LEAD-ZINC MINE (VEDRIN, BELGIUM)

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ABSTRACT

The development of hydrogeochemistry applied to the search for metals was limited by the difficulties encountered during the routine chemical analysis (ppb order). Recent advances of some physical methods of analytical chemistry (Particle Induced X-ray Emission : PIXE method) enable water utilization to prospect new ore bodies as well as extensions of known mineralizations. The Vedrin deposit (Prov. Namur, Belgium) has been exploited until 1945 for Fe-Pb-Zn. The ore body was localised in carbonate rocks. From that time, the mine has been converted to piping of alimentary water. Many scientific reports let think that there are still unknown ore bodies. A sampling has been realised according two parameters : the space -15 water springs are taken into account- and the time -these springs are analysed once a week during 16 weeks-. HCO3, SO4, Cl, Mg, Na, K were analysed by classical analytical methods, whereas Fe, Zn, Mn, Br, Sr were quantified with the PIXE method. Different mathematical techniques have been applied : correlation between elements, correlation between springs, cluster analysis, principal component analysis. One of the principal results is that in spite of a short distance between sampling points, the water springs present distinct individual characteristics. The variation in time of these characteristics do not affect the statistical arrangement of the springs and thus do not mask their personality. Secondly, the most discriminant factor between the springs is a factor of mineralization which permits an use as prospection guide.

INTRODUCTION

Geochemical prospection of metals by water is a method whose development has been stopped for a long time by the difficulties met with the chemical analysis. Very recent advances of some sophisticated physical methods of analytical chemistry open new perspectives about water utilization to discover, if not new deposits, at least badly defined mineralizations.

The underground water contains metal tracks leached from mineral deposits and rocks by infiltrating into porosities and fractures. Rivers transport metals in real solution or in form of thin solid particles (Lang, 1976) whose equilibrium is governed by many complex factors like precipitation - dissolution, absorption - disorption, floculation - coagulation equilibriums (Bourg A., 1983). Like in geochemical prospection of soils and rocks, the usual procedure starts from anomalous contents to return to the origin of dispersions of some elements chosen as markers of the target mineralization according to their physical and chemical properties. The study of the water contents found in the fissures of the mine gallery is interesting as it can signal the proximity of mass or concentration which mine works would have failed to meet (Granier, 1973). Nevertheless, it is worth underlining the method complexity because of the numerous factors capable of acting upon the solubility and transport of elements by water. Among these, and without being exhaustive, we can mention :

- the physical and chemical properties of the elements migration forms,
- the mineralization composition,
- the climate,
- the topography,
- the composition and permeability of the formation containing or covering mineralization,
- the direction of the underground water flow,
- the geological environment, included the structure.

The prospection data interpretation usually reveals two aspects :
A statistical study of the contents distribution is considered. This study includes treatment by univariate method but also multivariate analysis technique which is more and more frequently used. The treatment by multivariate method aims at identifying properties of concentrations in characteristic elements of the kind of the planned mineralization, which move in the given chemical and physical environment. The multivariate analysis would enable a deeper interpretation of the water analysis; combined with thermodynamical data, it should be able to determine the geochemical cycle, the equilibrium or the metastability of the encountered associations.
The second aspect comes from this statistical and thermodynamical study. Taking into account the different factors, a local content unaltered by the searched target is estimated. Then, anomaly maps which represent geographically the more probable anomalous contents are drawn. The following step consists in discovering the different anomaly localizations and in prospecting further.

The Vedrin mine (Prov. Namur, Belgium) was exploited long ago for its iron and sulphurated lead-zinc ores appearing under the form of veins in a carbonate environment. As a result of the ore poverty and unwatering problems, it is closed in 1945. By that time, it was bought up by the "Compagnie Intercommunale Bruxelloise des Eaux" which converted it into water piping.

Several scientific works done on the spot suggest the existence of unknown remaining ore bodies. Conditions are thus fulfilled to consider an hydrogeochemical prospection in this area.
- The PIXE method was for us an efficient analysis instrument.
- There are many water springs in the mine providing an important sampling.

PROSPECTION IN VEDRIN

Sampling conditions.

The galleries net where the sampling was taken is on level 130 (130 meters under the mine bank). It looks like a Y which roughly follows the mineralized fault and meets Famenian rocks (shales and sandstones), Tournaisian rocks (dolomites) and Visean rocks (limestones) (see fig. 1)

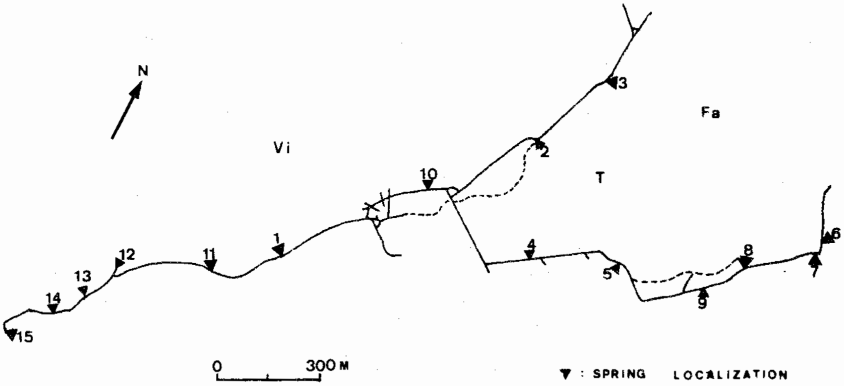

FIGURE 1 : MINE ON LEVEL 130

As many parameters could alter the contents of the elements dissolved in waters, a sampling was taken several times in 15 water springs spread in the mine. The number of water springs was limited for technical reasons of water conservation and analysis. In each water-spring, a sample was taken once a week for 16 weeks running. The sampling frequency and the spreading in the mine depended on the observations of the water exploitation society concerning the variations in contents.
Beyond the water sampling, the PH and the temperature of each water spring were measured in situ in order to discover possible physical and chemical variations. Among the chosen water springs, many of them presented concretions, as a result

of the precipitations when water comes out into the "open air", probably due to the PH and Eh modifications. Every time that they appeared, these concretions were also sampled as important complement of the contents studied in waters.

Taking and conservation of samples.

It is necessary to take good care of the samples operations in order to avoid contamination by some particles (pieces of rocks, deposits) which could come off the rocks and fall in the container.Yet it is impossible to prevent particles small enough from staying in suspension in the collected water. The water of the sampling place is used to rinse out the containers several times in order to keep them clean.

Because of the Eh modification at the taking, the water close to saturation for several elements is very unstable : it precipitates as soon as the sample is taken and produces a visible deposit after a few hours of conservation. It was therefore necessary to use special conservation methods of the sample : 20 ml of each sample was frozen before being analysed by neutronic activation; another fraction was acidified after "pipetting" the quantity required for the HCO3 determination with a view to the classical analysis. In spite of those cares, the water sometimes presented a precipitate in suspension. Analysis was carried out after the filtering of this precipitate considering the fact that this one was taken into account during the analysis of the water spring concretions.

Analysis methods.

Two analysis types were realized on the samples : HCO3, SO4, Cl, Ca, Mg, Na and K were analysed by classical chemical methods. We have to point out we did'nt want those elements to be quantified. A systematic error in the analysis isn't embarassing if it remains permanent from a measure to the other one. The obtained results can be useful to study the concentrations variations : corrections would be required for a precise chemical determination of the waters studied. Fe, Zn, Mn, Br and Sr were quantified by the PIXE method (Particle Induced X-ray Emission) by neutron activation. This method enables to work in routine very quickly, it is multielementary and accurate as soon as the quantities are sufficient. Table 1 shows the relative errors combined with different concentrations whose order of height is that of the Vedrin mine waters. Unfortunately, you can't (or it is difficult to do it) watch elements whose atomic number is lower than 18, and it is necessary to have a particle accelerator (cyclotron) at your disposal.

MATHEMATICAL TREATMENT.

We have mixtures of 12 elements on water samples coming from 15 water springs sampled 16 consecutive times once a week, which represents a considerable number of data. Table 2 shows an example of the results related to the first water spring and Table 3 shows the averages and the standard errors of analysis calculated on the analysis of 16 weeks, per water spring. In

TABLE 1 : RELATIVE ERRORS RELATED TO DIFFERENT CONCENTRATIONS, PIXE METHOD

K :	10 %	Mn : 5 to 10 ppb :	50 %	Sr : 50 to 100 ppb :	25 %	Zn : 20 to 100 ppb :	30 %
Ca :	3 %	10 to 50 ppb :	30 %	100 to 200 ppb :	20 %	100 to 200 ppb :	15 %
Br :	19 %	50 to 100 ppb :	15 %	200 to 400 ppb :	15 %	200 to 1000 ppb :	7 %
Fe :	12 %	more then 100 ppb :	10 %	more then 400 ppb :	10 %	more then 1000 ppb :	2 %

TABLE 2 : EXAMPLE OF RESULTS, SPRING 7

WEEK	HCO3 ppm	SO4 ppm	Cl ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Fe ppm	Zn ppb	Mn ppb	Br ppb	Sr ppb
1	207.4	728.2	38.92	187	85.16	10.75	5.25	57.7	2999	657	66	280
2	230.6	750.2	36.76	199	99.14	10.75	5.50	60.7	2991	669	76	246
3	284.3	757.5	36.30	213	83.49	12.75	5.50	63.8	3421	742	68	255
4	268.4	705.3	36.75	209	67.69	12.25	5.32	56.8	3422	449	66	354
5	268.4	582.7	35.25	202	76.55	10.63	4.90	44.8	3215	511	78	250
6	248.9	688.9	36.31	207	74.60	11.38	5.07	55.6	3313	460	129	284

TABLE 3 : MEAN AND STANDARD DEVIATION, CALCULATED OVER 16 WEEKS AND 1 SPRING

SPRING		HCO3 ppm	SO4 ppm	Cl ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Fe ppm	Zn ppb	Mn ppb	Br ppb	Sr ppb
1	m :	387.8	187.4	44.09	147	37.06	13.92	2.31	1.0	62	172	84	181
	s :	4.1	11.6	11.49	11	3.59	.99	.15	.6	54	32	27	51
2	m :	307.2	255.8	32.93	125	40.77	9.96	1.78	2.8	1093	338	80	201
	s :	5.1	4.7	1.40	9	7.61	.83	.15	2.6	294	30	28	41
3	m :	412.7	319.2	40.35	169	59.90	10.39	3.07	1.8	118	98	78	246
	s :	23.7	93.7	1.35	27	14.45	.88	.45	1.3	64	24	21	42
4	m :	344.9	76.4	27.64	105	21.63	9.64	1.68	.4	39	57	75	163
	s :	5.0	4.6	.91	10	3.86	.77	.17	.2	22	14	22	47
5	m :	358.2	87.6	24.86	109	23.43	9.52	2.19	.4	58	65	69	188
	s :	21.5	4.7	1.07	12	4.16	.72	.22	.2	40	15	24	38
6	m :	405.1	180.8	52.91	153	34.38	16.95	2.89	.5	20	148	89	291
	s :	9.3	9.9	2.35	16	4.95	2.48	.32	.2	10	27	30	60
7	m :	242.3	701.0	37.33	186	80.80	11.18	5.02	54.3	3384	514	91	314
	s :	20.8	36.6	1.44	18	8.57	1.05	.29	7.2	278	146	24	83
8	m :	350.3	369.7	39.95	148	70.05	14.94	3.41	15.9	1895	233	100	220
	s :	15.0	14.8	1.76	10	4.38	1.09	.22	4.6	293	19	27	54
9	m :	410.7	174.4	37.77	135	44.55	13.24	3.49	.3	164	28	84	185
	s :	5.6	3.5	1.43	9	6.77	.94	.15	.2	67	18	32	66
10	m :	370.8	183.7	46.69	154	29.46	14.39	1.66	1.1	300	181	91	183
	s :	6.1	38.4	1.96	14	4.89	2.58	.16	1.2	158	45	40	47
11	m :	347.5	188.7	55.44	173	17.84	11.63	1.28	.5	776	594	102	272
	s :	4.8	10.9	2.11	11	9.52	.71	.14	.2	170	55	39	62
12	m :	367.0	119.3	38.8	147	15.03	13.34	3.20	.4	298	83	88	226
	s :	5.8	3.4	1.4	11	5.46	.92	1.18	.4	105	108	35	48
13	m :	371.4	130.7	37.8	151	16.45	12.88	3.03	.4	255	74	67	217
	s :	9.1	5.7	1.9	13	5.59	.97	.24	.2	76	13	36	48
14	m :	363.0	102.3	38.0	136	18.11	12.88	2.82	.7	76	82	84	237
	s :	3.3	2.7	1.4	12	4.22	.86	.17	.7	43	20	41	86
15	m :	310.3	266.0	91.4	198	18.75	26.98	2.07	2.8	116	266	116	372
	s :	5.2	8.8	4.0	11	8.48	2.99	.15	.8	49	35	38	78

order to test a method for further prospection, it was interesting to watch if the analysis confirmed in general a few basis ideas about the water equilibrium.

Some results are illuminating would it be only for a treatment methodology.

Correlation.

It is very easy to implement the univariate correlation. But in this case, we can consider to do it on basis of different criteria. It is possible to calculate correlation coefficients
(1) between the different elements of a water spring,
(2) of the same element taken at the same time between the different water springs,
(3) between the different elements together whatever their belonging to a spring.

The coefficients calculated according to the first method don't give any results (see an example on Table 4). The coefficients obtained are characterized by a total lack of linkage between the different elements variations inside a spring. This phenomen is rather strange. The water equilibrium is expected to bring about some coherence in the variations between ions dissolved . By refering to table 3, we can see that the differences of contents inside the waters collected at one spring are in fact relatively small. A great part of the relative variation is due to the measuring precision and it constitues therefore a random term which masks the linked variations, which explains very low correlation coefficients.

The coefficients calculated according to the second method are of a greater interest. This interest depends nevertheless on the element taken into account. It expresses a simultaneous variation in time of the water composition in a particular element for two springs between which the coefficient is calculated. This correlation is worth considering for metals ions like Fe, Zn (Table 5). The springs varying in the same way show a kind of geographical logic. Springs not far from each other tend to behave in the same way. For a further understanding of the different springs, an hydrogeological study would be required, a much closer sampling would be useful in this case, which wasn't possible in the frame of this study. However, this analysis would be enable to precise a membership of the water between the springs. The hydrogeological study by identifying the reasons for the contents variations (resupplying of the watersheet, higher pression, higher flow and therefore a different leaching of the ,rocks) would make it possible to explain the temporial variations in contents according to physical and chemical properties of the different elements.

In this first approach by the simple correlation, the third method gave the most reassuring results open to direct interpretation (see Table 6). In the sedimentological environment of Vedrin (carbonate and evaporitical events) a right correlation between Na and Cl is expected. Indeed this correlation (0.853) is quite good. We have to point out that this

TABLE 4 : EXAMPLE OF CORRELATION BETWEEN DIFFERENT ELEMENTS OF A SAME SPRING
SPRING 6

HCO3	1.00											
SO4	.20	1.00										
Cl	-.45	-.18	1.00									
Ca	.03	-.24.	.04	1.00								
Mg	-.38	.17	-.17	-.52	1.00							
Na	.32	-.01	-.03	-.16	-.20	1.00						
K	.27	-.44	-.24	-.22	-.19	.40	1.00					
Fe	.46	.14	-.11	.11	-.50	-.09	.41	1.00				
Zn	.33	-.11	-.29	-.40	.22	-.05	.40	.37	1.00			
Mn	.23	-.06	.05	.61	-.20	-.05	-.12	.05	-.24	1.00		
Br	-.23	-.22	.08	.21	-.41	-.14	.04	.10	-.11	-.46	1.00	
Sr	-.04	-.53	.06	.43	-.33	-.27	.19	.10	-.34	.02	.36	1.00
	HCO3	SO4	Cl	Ca	Mg	Na	K	Fe	Zn	Mn	Br	Sr

TABLE 5 : EXAMPLE OF CORRELATION OF Zn BETWEEN THE DIFFERENT SPRINGS

1	1.00														
2	-.25	1.00													
3	-.27	.51	1.00												
4	-.11	.75	.48	1.00											
5	-.40	.76	.35	.86	1.00										
6	-.26	.25	.48	.47	.27	1.00									
7	-.15	-.44	.21	-.36	-.40	.07	1.00								
8	-.21	.80	.23	.77	.85	.28	-.44	1.00							
9	-.23	.85	.34	.86	.95	.28	-.47	.89	1.00						
10	-.19	.86	.50	.91	.91	.39	-.43	.86	.95	1.00					
11	.10	.28	.57	.18	.18	.02	.11	.12	.22	.28	1.00				
12	.04	.59	.37	.49	.49	.04	-.23	.52	.66	.57	.47	1.00			
13	-.29	.81	.57	.81	.81	.27	-.20	.73	.88	.83	.43	.78	1.00		
14	-.20	.87	.47	.85	.85	.29	-.57	.77	.91	.94	.33	.60	.85	1.00	
15	-.35	.88	.31	.88	.88	.19	-.51	.87	.89	.88	.14	.54	.78	.90	1.00
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

TABLE 6 : GENERAL CORRELATION BETWEEN THE ELEMENTS

Zn	1.00											
Fe	.92	1.00										
Br	.06	.05	1.00									
Na	-.14	-.08	.18	1.00								
K	.57	.69	-.07	-.03	1.00							
Cl	-.13	-.09	.32	.85	-.20	1.00						
HCO3	-.70	-.69	-.12	-.03	-.16	-.10	1.00					
SO4	.86	.90	.10	.06	.66	.11	-.56	1.00				
Ca	.32	.37	.22	.50	.28	.65	-.20	.57	1.00			
Mg	.68	.68	-.01	-.15	.63	-.18	-.23	.81	.20	1.00		
Mn	.63	.51	.16	.05	-.01	.30	-.61	.57	.51	.29	1.00	
Sr	.21	.26	.30	.45	.16	.53	-.29	.34	.52	.06	.34	1.00
	Zn	Fe	Br	Na	K	Cl	HCO3	SO4	Ca	Mg	Mn	Sr

pair of elements is badly related inside a spring (correlation type 1). This contradiction can be easily explained on figure 2.

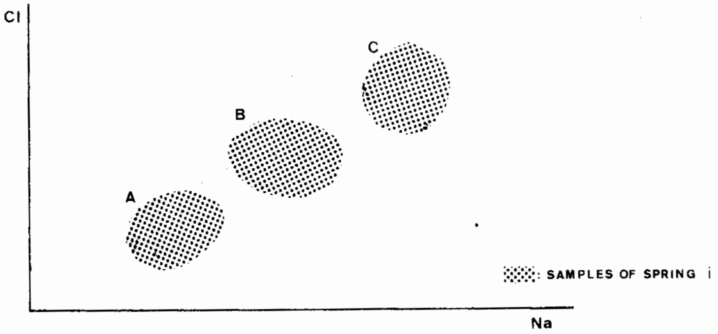

FIGURE 2 : CORRELATION (see text)

Variations inside a spring are too much affected by random terms (measurement error) and they can't be well understood without a thorough thermodynamical study. But the different springs have average contents which significantly part from each other, which results in a good correlation. The interpretation of the correlation matrix is rather simple. Correlated elements like Zn, Fe, SO4, ... present in pairs a high correlation coefficient (greater than 0.85) and a marked tendance (little than -0.56) towards an inverse correlation with HCO3. Those groups appear nevertheless more clearly thanks to the principal component analysis.

The Cluster Analysis.

The results of the different correlation calculation prompt us to ask ourselves wether each water spring has a typically feature in its trace elements. In order to verify this hypothesis samples without taking care of their origin were subject to a clustering program. This program distributes all the cases in an imposed number of clusters. In this case, a number of 10 clusters was chosen. The distance chosen to discriminate the cases from each other is the euclidian distance obtained after dividing each variable by its standard deviation. The results are simplified on Table 7. First it appears that the springs have a typical feature; in other words, the program reclassifies nearly complete ranks of the same spring in the same cluster which is not obvious at first sight. It always regroups at least several measures or the same spring in a cluster. One of the cluster seems nevertheless to be influenced in a greater part by a time parameter : cluster 8 takes into account the samples of the two last weeks of many springs. After checking, a Br important increase was noticed in permanence in the mine. The cause of this variation wasn't specified. There are also associations which can be explained by the space proximity of the springs (cluster 9) or by the resemblance of lithologies presumably met. The program results show that the different water springs have a strong personality. However, the distribution of water samples in cluster doesn't allow any interpretation in terms of a possible trend towards a mineralization or another aspect, and a more peculiar treatment must be used.

Principal Component Analysis.

A program of multivariate analysis was used to try to discover a possible trend of distribution of variables analysed in terms geologically explanable. The factors were extracted according to the correlation matrix, in accordance with the principal component method. Factor loadings are shown at Table 8.

The first factor, explaining 42% of the total variance seems to produce a kind of water more or less loaded in elements proving a mineralization. The Zn-Fe-SO4-Mg association is very strong. A negative factor for HCO3 is noticed as well as an association with other elements (Mn, K, Sr, Ca) which can perhaps been explained by a greater solubility in waters whose equilibrium is altered by the leaching of a mineralization. Like in the cluster analysis, the factor scores classified in an increasing order show an obvious trend towards a reclassifying per springs : most of the water samples of spring 7 have the highest factor scores followed immediately by the whole samples of springs 8. The mixed samples of the different springs can be found but they are obviously separated by other samples string of different springs. So it is possible to build a hierarchy between the different springs from the spring, which tends the most towards a mineralization leaching, to the one which has the most opposite feature. This result can thus be interpreted immediately on the spot, in terms of water combined with old works or water whose origin of mineralization feature is still unknown (capable of indicating the existence of a still unknown ore body).

The second factor, explaining 24% of the total variance produces very important factor loadings for the Na-Cl couple and Ca, Sr, Zn, Mg, Fe and K have in a lesser importance a negative factor loading. This factor is probably more connected with a lithological or sedimentological aspect. The carbonated environment is indeed characterized by evaporitical events. Once ranged, the factor scores related to this factor also tend to regroup the water samples of a same spring. Moreover, once spread over the map, the springs related to the highest factor scores are on the same side of the mine, which can correspond to either particular lithological series or a special feature of the mineralized fault followed by this gallery.

The third factor still explains 11% of the total variance. Its main feature is a K and HCO3 association (positive) contrary to Mn (negative). In a lesser importance, Na and Mg also form a positive association with the previous elements. The factor scores behaviour is similar to the factor 1 and 2 behaviour concerning the samples regrouping of a spring. It is surprising to note that the springs revealing the highest factor scores (springs 9,6 and 3) are also those which haven't or have only a few precipitates at the time at the arrival in the gallery. A thermodynamical study should enable to precise the causes of this particular phenomena.

CONCRETIONS.

Concretions (mainly iron hydroxides) next the springs were sampled and qualitatively analysed by arc atomic spectrometry. High contents in Mn can be noticed. On the other hand, some concretions have high contents in Pb or Zn. It is surprising to note that the springs 7 and 8, the most mineralized (according to the factor score 1) are springs whose concretions are in comparison very poor. Moreover, the spring 7 has poorer concretions in Zn than the spring 8 whereas the contents of the springs 8 water is poorer than spring 7 water. Everything happens as if a part of the dissolved metals precipitate as soon as they come near the spring. This situation should temper the Principal Component Analysis. Indeed, as the precipitated Zn was transported by water, this could mean that this water contains more Zn a little time before its reappearance in the gallery. From that, we can conclude that the water leaching the rocks is near saturation. The sulphurated mineralization produces most probably SO_4 ions by acidifying the water during the FeS_2 oxydation:

$$FeS_2 + 8\ H_2O \text{ --- } Fe^{++} + 2\ SO_4^{--} + 2\ H^+ + 7\ H_2$$

(Barnes & al., 1964). But the carbonated environment is a buffer agent of the water PH and consumes the H+. There is thus a competition between both phenomenous, presumably governing the water general equilibrium, which intensively alters the dissolution precipitation equilibrium. A general interpretation of the equilibrium could only happen on basis of a thermodynamical pattern taking into account many elements which are sometimes difficult to measure.

CONCLUSIONS.

In practice, the study shows that the springs have an obvious typical feature despite a rather short distance (100 to 500 meters) between the sampling points. Moreover, it enables to detect several springs able to leach a mineralization. Consequently, the carried out treatment reduces to a small number the springs the searcher is interested in. And after elimination of waters having possibly leached the old works, it is easy to represent on a map the springs which can possibly be used for further developments. A space organization of those springs in accordance with genetical hypothesis of the deposit provides another confirmation element.

The subsequent studies of prospection with other (physical) methods can thus been applied to the study of a confined region of the mine.

From methodological point of view, the consecutive measures

TABLE 7 : CLUSTERS (UNIT VARIANCE)

CLUSTER :	1	2	3	4	5	6	7	8	9	10
SPRING(S) : NUMBER	7	15	11	10 1	6 3	8	2	(15th and 16th week of spring :) 5 - 6 - 9 - 10 - 12 - 13 - 14	12 13 14 9	4 5

TABLE 8 : FACTOR LOADINGS

(loadings less than .25 have been replaced by zero)

	FACTOR 1	FACTOR 2	FACTOR 3
SO4	.963	.0	.0
Fe	.926	-.263	.0
Zn	.909	-.288	.0
Mg	.705	-.398	.313
HCO3	-.687	.0	.548
Mn	.676	.0	-.544
K	.623	-.396	.598
Ca	.595	.587	.0
Cl	.0	.937	.0
Na	.0	.827	.309
Sr	.451	.590	.0
Br	.0	.405	.0

TABLE 9 : SPRINGS CLASSIFIED BY INCREASING ORDER OF FACTOR SCORES

FACTOR 1 : 4 5 - 14 13 10 12 9 1 - 6 3 2 - 11 - 15 - 8 7

FACTOR 2 : 7 5 4 - 8 9 2 - 3 13 - 1 10 12 14 - 11 6 15

FACTOR 3 : 11 2 - 4 5 7 10 - 12 14 13 15 1 - 8 - 3 6 9

between hyphens : springs whose factor score of sample are mixed together

TABLE 10 : QUALITATIVE ANALYSIS OF CONCRETIONS (LIMONITES)

SPRING	Ba(ppm)	Sr(ppm)	Mn(%)	Pb(ppm)	Zn(%)	Ag(ppm)	Cu(ppm)	Ni	Co	Tl
1	600	>>300	>>3	100	.2	-	-	*	-	-
2	300	-	1.2-3	500	1.2	-	26	-	-	-
3	-	-	-	-	-	-	-	-	-	-
4	1000	>>300	>>3	900	.55	2	29	*	-	300
5	300	300	1.8-3	1000	.40	-	-	-	-	-
7	-	-	-	-	.45	-	-	-	-	-
8	-	-	-	3000	1.3	-	-	-	-	-
10	-	-	.4	150	.5	-	-	-	-	-
11	3000	>>300	>>>3	4700-13000	1.3-2.2	4-12	22	*	-	>300
12	-	-	-	-	1.2-1.8	4-12	22	-	-	-
13	1000	>>300	>>3	900	1.	2	25	*	>300	300
14	1000	300	>>3	300	.45	1.6	28	*	>300	300
15	1000	>>>300	>>>3	-	.26	3.1	29	*	>300	300

have contributed to a better identification of the springs and have enabled the realization of a profitable factorial analysis. The variation in time of the contents doesn't mask the springs personality because the waters keep their statistical range. The chemical analysis by the PIXE method are sufficiently applicable in routine and accurate for such a study. A thermodynamical study of basis of contents in waters but also in concretions near the springs would be of a great interest. The qualitative analysis doesn't make it possible to implement this accurate study, but opens up new perspectives about the possibilities of such a study.

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