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MINERALOGICAL INVESTIOGATION OF WEATHERING OF CRETACEOUS LIMESTONE. AN EXAMPLE OF PHENOMENON. PRACHODNA CAVE NERA OF ROMAN. NORTH BULGARIA

Badania mineralogiczne wietrzenia wapieni kredowych. Przykład zjawisk w Jaskini Prachodna, koło Roman. Północna Bułgaria.

Maciej Pawlikowski*, Piotr Bożęcki**, Urszula Buszkiwicz***, Sara Mandera***, Jakub Rędziak***.

*/ Katedra Mineralogii, Petrografii i Geochemii AGH, Kraków,
**/ Wydziałowe Laboratorium, Wydział Geologii, Geofizyki i Ochrony Środowiska AGH, Kraków,
***/ Studenckie Koło naukowe Geologów,Wydział Geologii, Geofizyki i Ochrony Środowiska AGH, Kraków

Abstract

Archaeological excavation of Prachodna and Temnata Cave conducted in 80tis of XX century had multidisciplinary character. The results of excavation are described in papers and books (Kozłowski, Laville, Ginter, 1992, Pawlikowski 1992, 2010, Sirakov 1992)). Presented publications is devoted process of weathering of limestone of mentioned caves and transformation of calcite into residuum called terra rossa. Mentioned investigation were conducted in field in 2014 and in lab. in 2015.

Described phenomenon explain the formation of karstic forms as for example caves system of caves –Prachodna - Temnata. Results document various rate od chemical dissolution of various petrographic kinds of limestone as well as the presence of poorly crystalline kaolinite as mine secondary mineral present in terra rossa.

Key words: Prachodna Cave, mineralogy, weathering of limestone, karst.

Streszczenie

Badania archeologiczne jaskiń Prachodna i Temnata prowadzone były w latach 80. XX wieku i posiadały charakter multidysciplinarny. Wyniki badań prowadzonych w trakcie ekspedycji zostały opublikowane w książkach i artykułach (Kozłowski, Laville, Ginter, 1992, Pawlikowski 1992, 2010, Sirakov 1992). Prezentowana publikacja jest poświęcona procesowi wietrzenia wapieni, w których występują wspomniane jaskinie oraz ich przeobrażeniu się w residuum zwane terra rossa. W 2014 roku prowadzono badania terenowe, natomiast laboratoryjne w 2015 roku. Na ich podstawie stwierdzono różne tempo chemicznego rozpuszczania różnych petrograficznych odmian wapieni, jak również obecność słabo krystalicznego kaolinitu jako głównego minerału obecnego w terra rossa.

Słowa kluczowe: Jaskinia Prachodna, mineralogia, wietrzenie wapieni, kras

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Materials and methods

Caves Prachodna-Temnata is located at northern part of Bulgarian (Fig. 1,) where one can see a lot of generations of caves formed at Cretaceous limestone.

Fig. 1. Locality of Cave Prachodna

One of the most interesting is system of two caves Prachodna-Temnata being result of separation of one big old cave (Fig. 2). Mentioned formation of two caves is the result of erosion and falling down of roof of primary, old cave. Continued erosion and karstic processes lead to formation of two separated caves known now as Prachodna and Temnata. Both caves were many times occupied by man. The stages of occupation are described at books (Kozłowski at all 1992).

Prachodna Cave is the tunnel like cave (Phot. 1) with two entrances. Karstic windows at the roof of cave (Photo. 2) makes cave light and at some places green and suitable for life of man as well as some kinds animals (of birds).

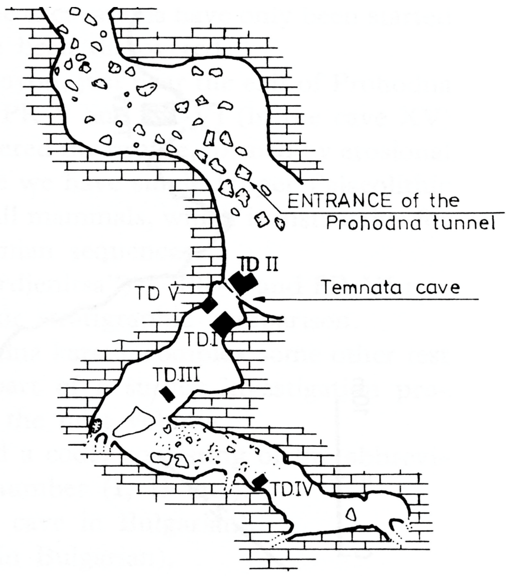


Fig. 2 Present situation. Area of roof destruction and separation of between entrance to Temnata and Prochodna caves. TD –IV archaeological trenches.(Pawlikowski 2010)

Geology

Caves are developed at Upper Createaceous limestone. They represent following petrographic kinds: organic- detrital, chemical and mixed types. They contain horizons of flint nodules. Bigger are represented by grey nodules up to 1,5 m in diameter. Second horizon is present below grey flints and is represented by black flint showing diameter up to 10 cm. Prochodna as well as Temnata Cave are developed mostly at organic and organic-detrital limestone (Pawlikowski 2010).

Mentioned caves were formed due to karstic phenomenon. Primarily formed as one cave were next separated as Temnata and Prachodna Caves because of falling down of roof of cave (Fig. 2).

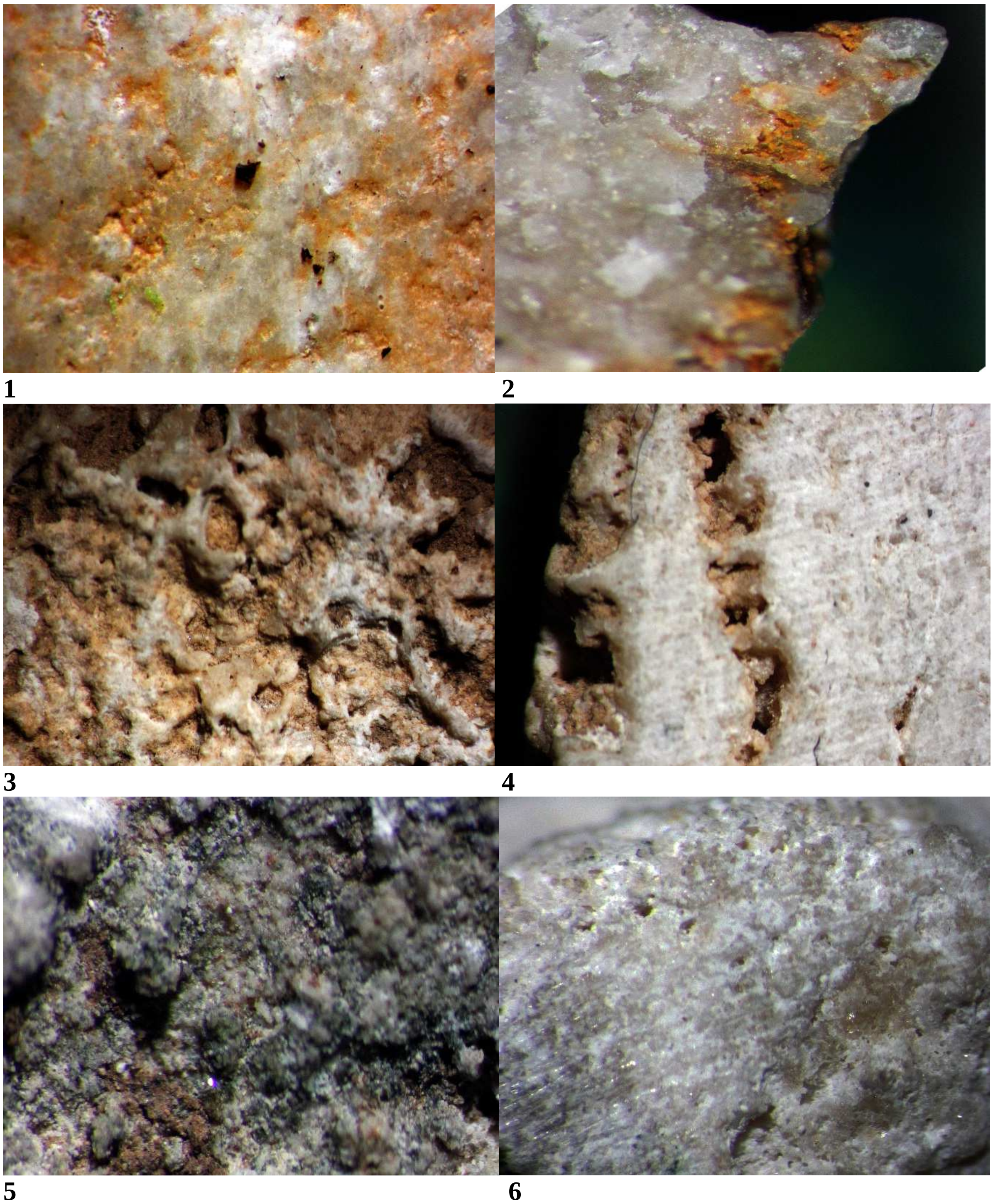
Prachodna Cave now is a big karstic tunnel (Phot. 1) with big karstic windows at some places of the roof.

A **B**

Phot. 1 A - The part of upper entrance into Prachodna Cave. B - big, karstic windows at the roof of Prachodna Cave

Investigation of micro karstic phenomenon present at limestone

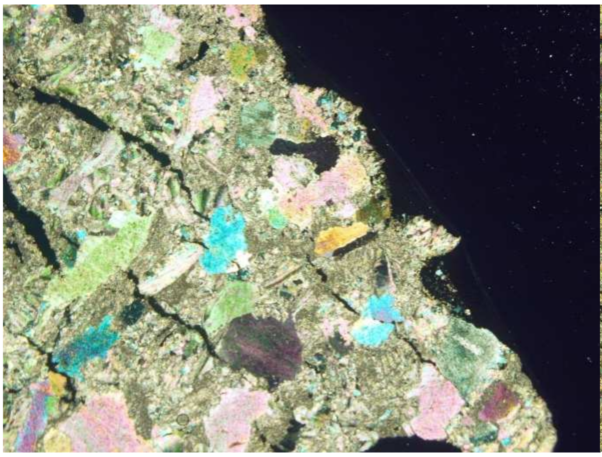
The process of limestone dissolution is well seen on walls of cave as well as under natural surface (Zalewski, Pawlikowski 2007). The degree of alternation of limestone is various i.e. surfaces show various alternation (Phot. 3, 1-6). Altered limestone is more porous . Karstic alternation starts between harder elements of limestone at spaces between fragments of calcite skeletons and bigger grains of calcite. Mentioned phenomenon leads to formation of uneven surface of limestone as well as to formation small fissures and holes just under the surface. Formed microholes and small depressions at surface of rocks are filled up with thin film of secondary products represented by poorly crystalline kaolinite stained with iron oxides for yellow-reddish color. These minerals are slowly removed form limestone by water present at cave. Next they are deposited out of cave making at some places 5-7 m thick layers of terra rossa.

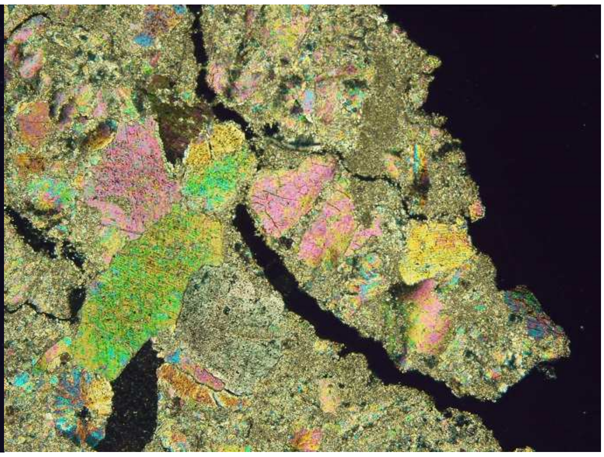


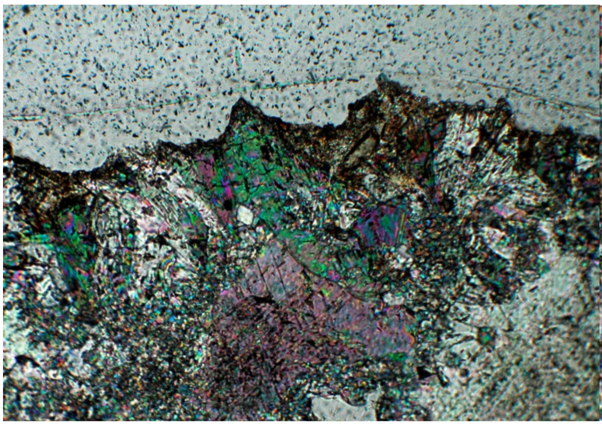
Phot. 2. 1-6 – Various stages of weathering of limestone. 1- Surface of limestone. Early stage of erosion of well crystalized limestone. One can see secondary red iron oxides mixed with poorly crystalline clay minerals. Black grain – Mn-oxide. 2 - cross section of sample showedat photo 1. One can see secondary minerals (red) at small, empty spaces just under natural erodes surface. 3 - advanced erosion of limestone surface. 4- small holes and empty spaces formed due to corrosion just under surface. 5 – altered surface of weathered limestone covered with secondary Mn-oxides. 6- the picture of

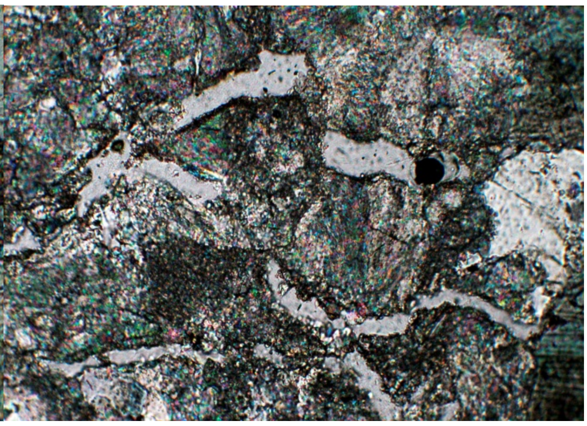
limestone showed at photo 5 just under surface. One can see small holes being result of limestone dissolution. Binocular microscope, magnification 5 x.

Microscopic observations performed using polarized light showed details of investigated phenomenon i.e. karstic process. Various empty spaces, holes, and fissures is observed just under corroded surface of limestone (Phot. 3, A-D).


A


B


C


D

Phot. 3 A, B - dark fissures present near of weathering surface of limestones. Polaroides X, magnification 80 x. C – micoroscopic picture of selected dissolution of surface of limestone. One can see protruding harder components of organodetrital limestone. D – system of light elongated holed developde due to process of carstic altern ation of limestone. Polaroides in part X, Magnification 80 x.

Examination of terra rosssa as secondry product of wethering of limestones using SEM-EDS methods.

Examinantion of fine fraction of red soil confirmed presence of quartz and traces of calcite (Fig. 3). Xraypattern of this material heat at 150° C confirmed presence of poorly crystlline kaolinite a (d_{hkl} =7.14 Ǎ) as mine clay mineral present in terra rosa.

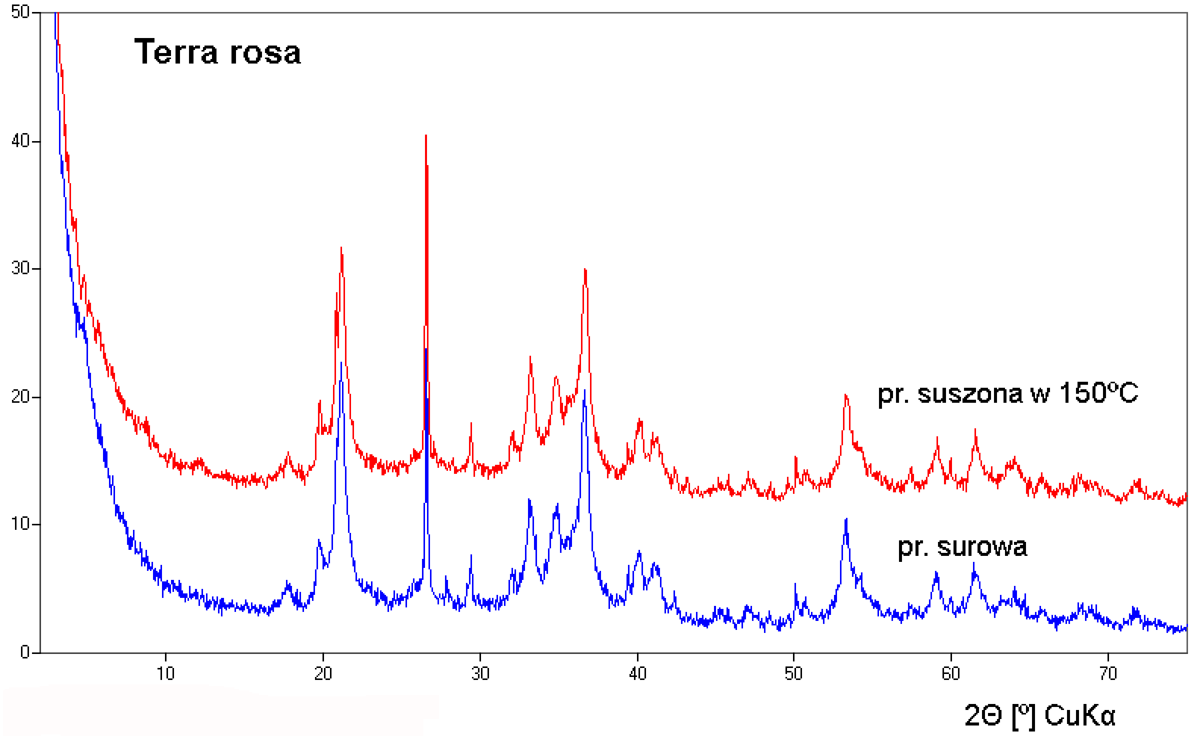
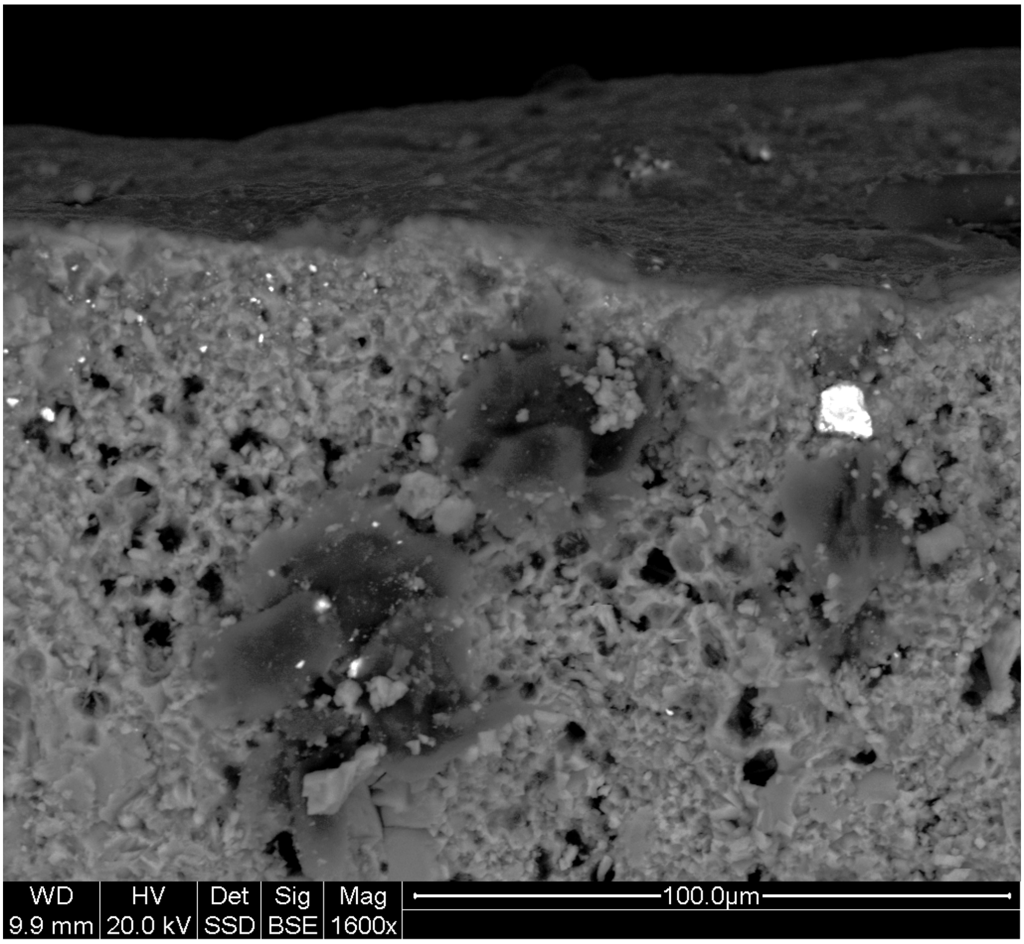


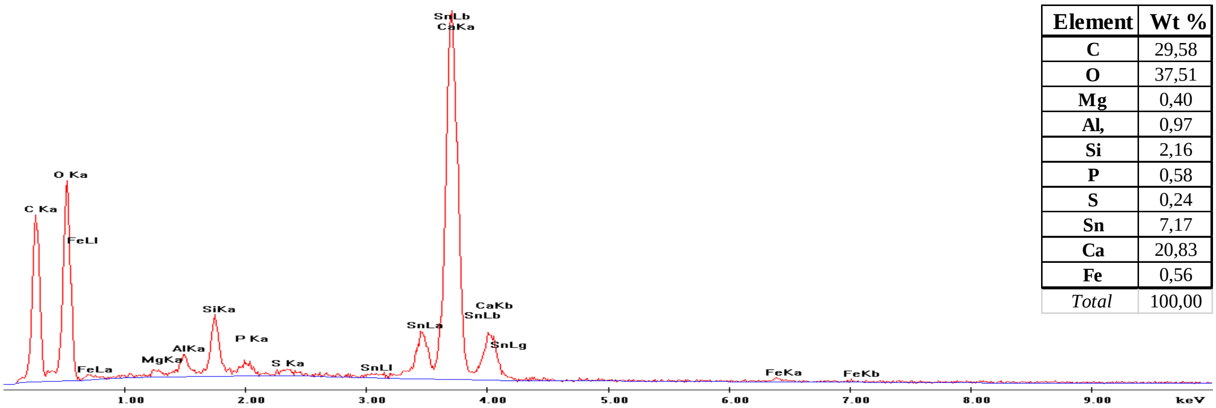
Fig. 3 X-ray patterns of terra rosa Lower (blue) – x-ray pattern of natural sample Upper (red) – x-ray pattern of terra rosa heated at 150° C.

Examination of early stages of karstic process present at limestone
Sample 1



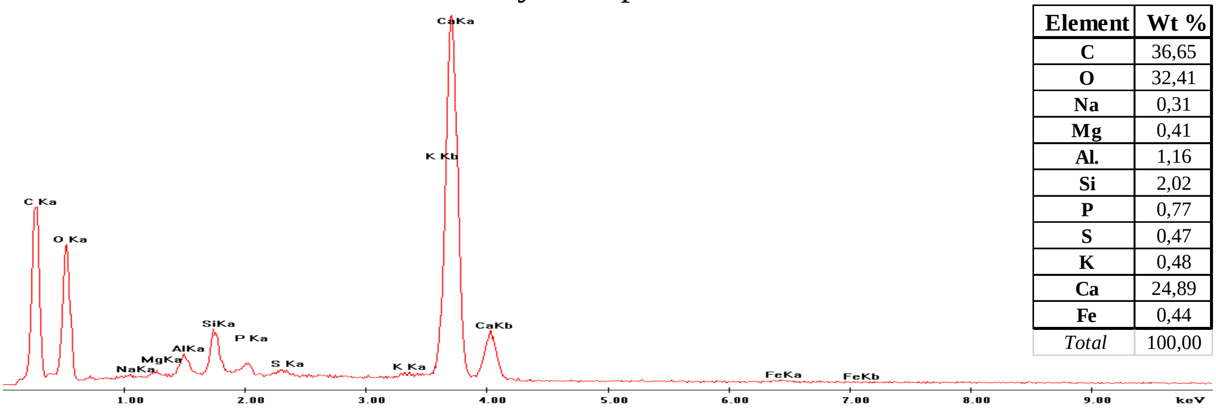
Phot. 4 SEM picture of porous structure of weathered organic - detrital limestone just under surface

Analysis of all surface



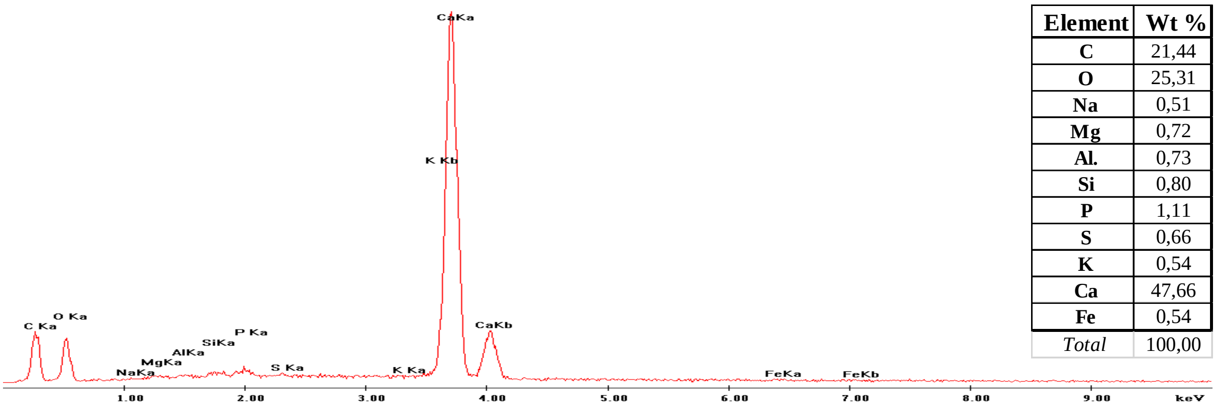
Element	Wt %
C	29,58
O	37,51
Mg	0,40
Al,	0,97
Si	2,16
P	0,58
S	0,24
Sn	7,17
Ca	20,83
Fe	0,56
Total	100,00

Analysis at point no 1



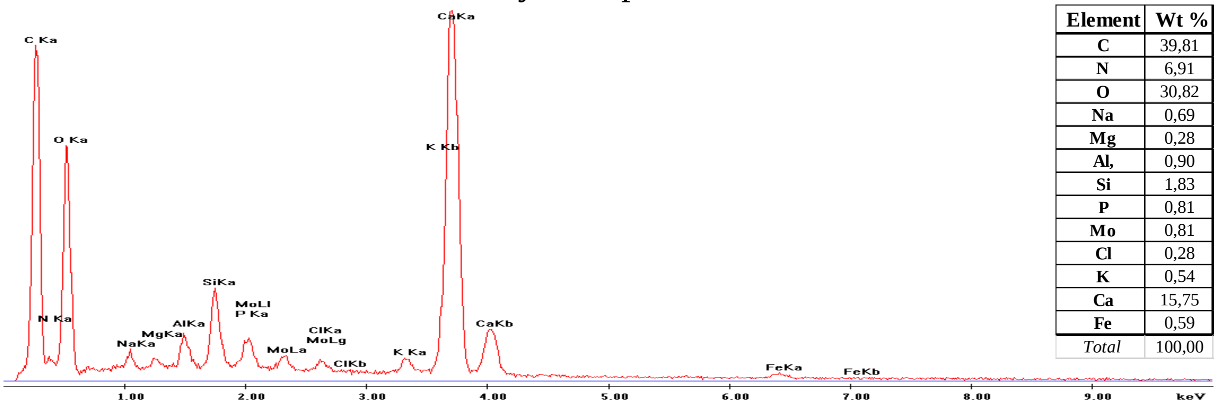
Element	Wt %
C	36,65
O	32,41
Na	0,31
Mg	0,41
Al.	1,16
Si	2,02
P	0,77
S	0,47
K	0,48
Ca	24,89
Fe	0,44
Total	100,00

Analysis at point no 2



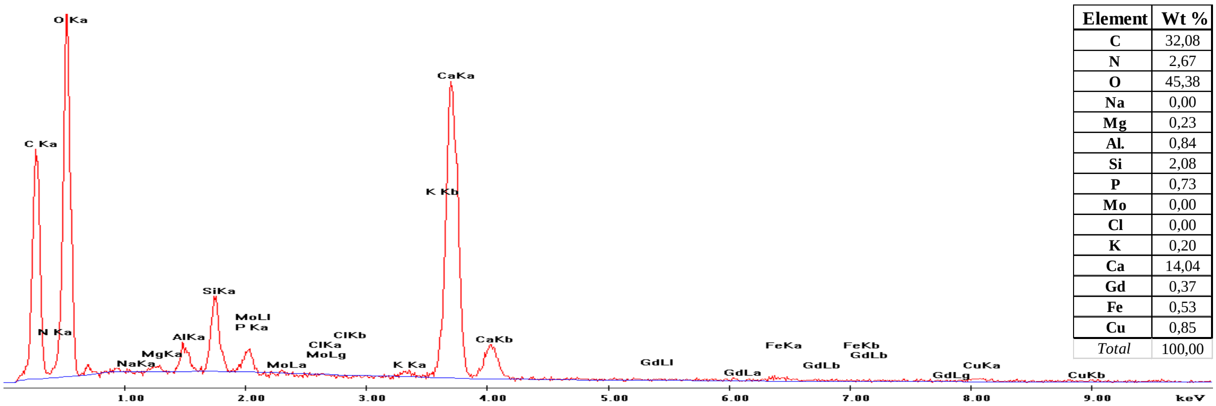
Element	Wt %
C	21,44
O	25,31
Na	0,51
Mg	0,72
Al.	0,73
Si	0,80
P	1,11
S	0,66
K	0,54
Ca	47,66
Fe	0,54
Total	100,00

Analysis at point no 3



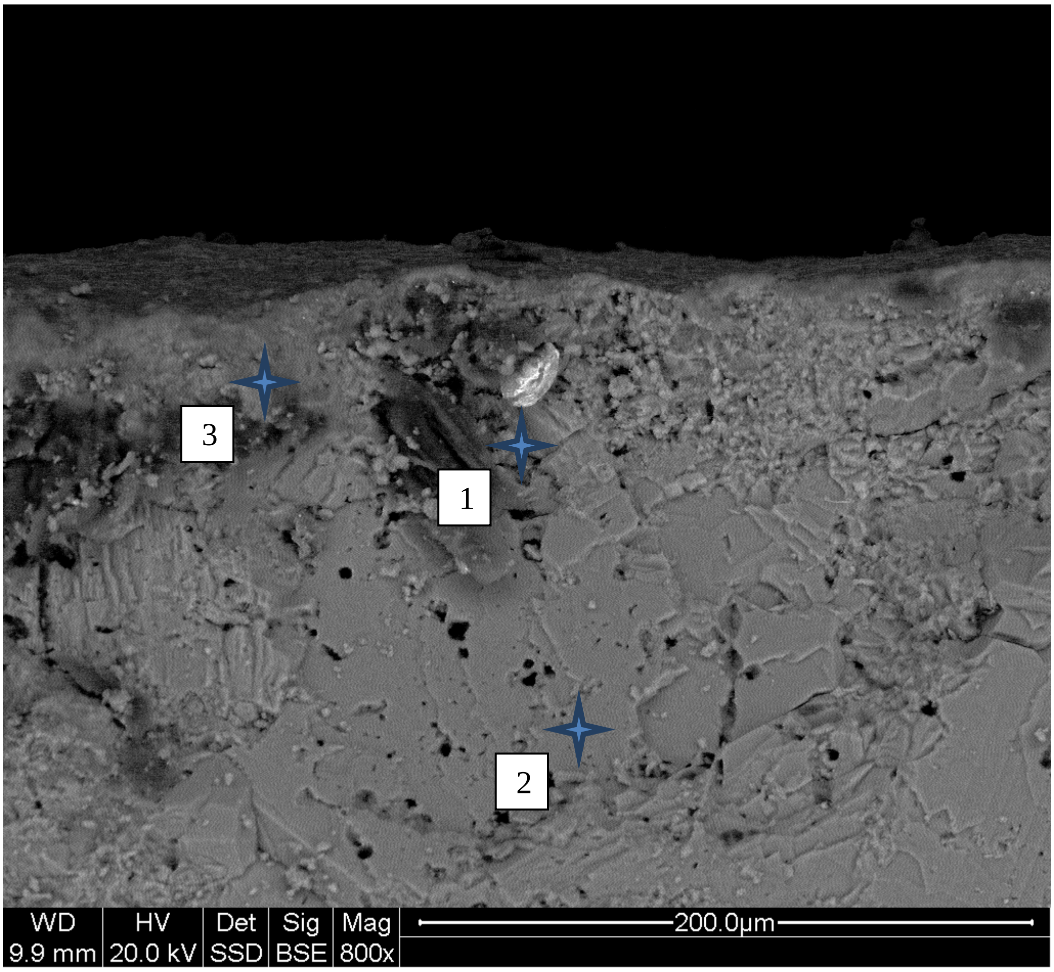
Element	Wt %
C	39,81
N	6,91
O	30,82
Na	0,69
Mg	0,28
Al,	0,90
Si	1,83
P	0,81
Mo	0,81
Cl	0,28
K	0,54
Ca	15,75
Fe	0,59
Total	100,00

Analysis at point no 4



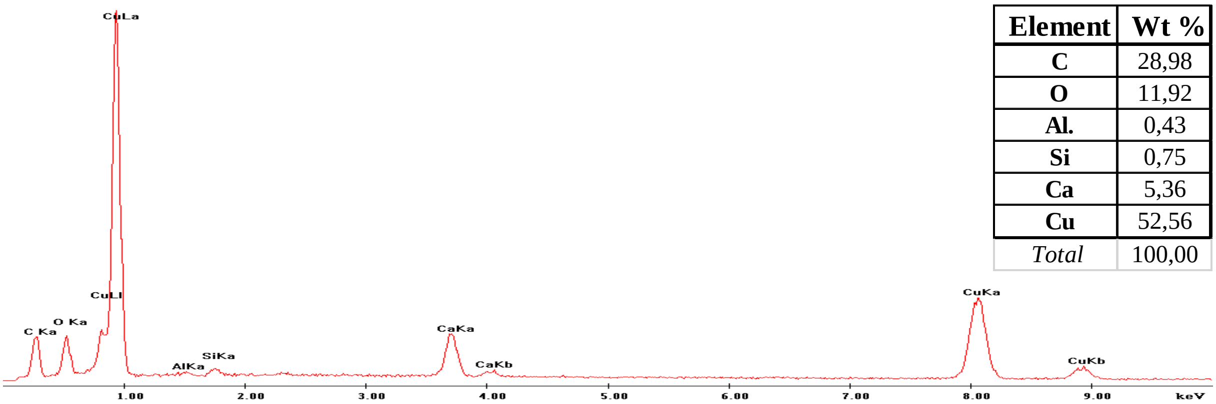
Element	Wt %
C	32,08
N	2,67
O	45,38
Na	0,00
Mg	0,23
Al.	0,84
Si	2,08
P	0,73
Mo	0,00
Cl	0,00
K	0,20
Ca	14,04
Gd	0,37
Fe	0,53
Cu	0,85
Total	100,00

Sample 2



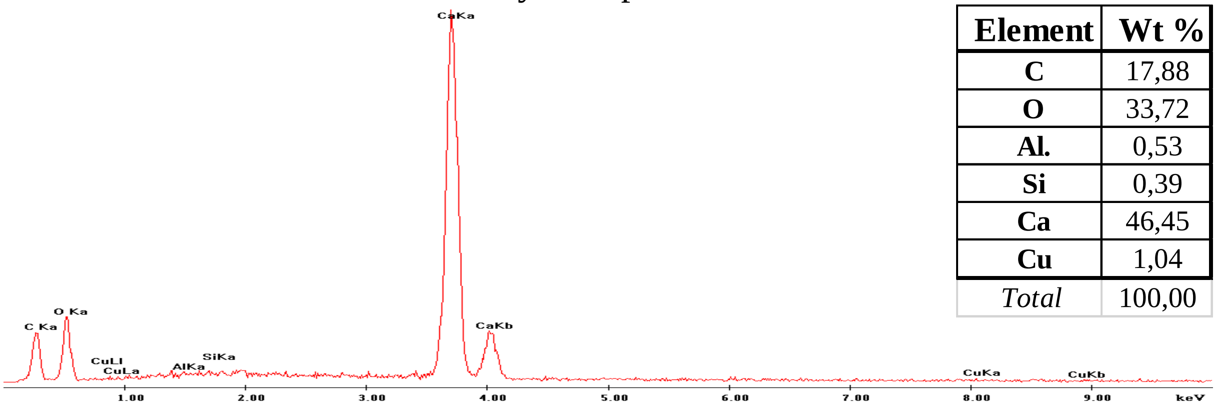
Phot. 6 SEM photo weathered of limestone of chemical origin. Structure just under weathered surface of rock.

Analysis at point no 1



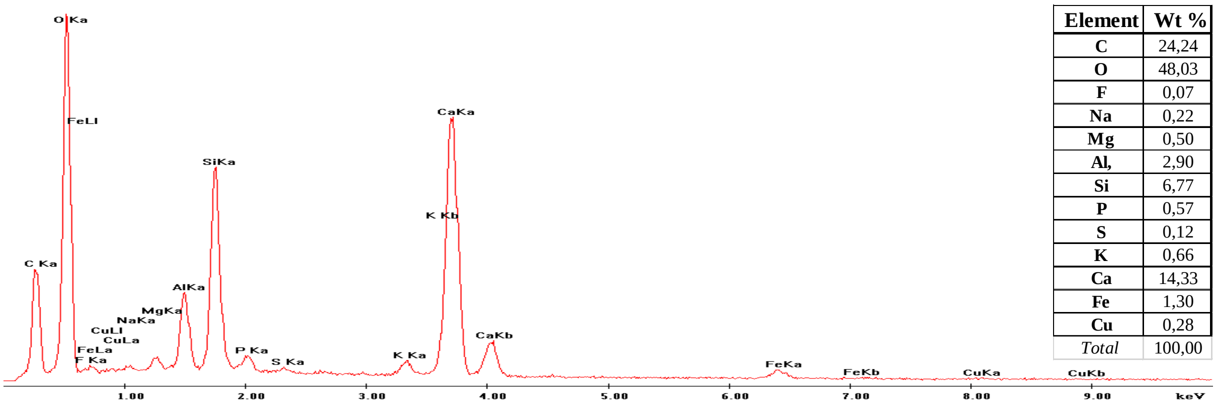
Element	Wt %
C	28,98
O	11,92
Al.	0,43
Si	0,75
Ca	5,36
Cu	52,56
Total	100,00

Analysis at point no 2



Element	Wt %
C	17,88
O	33,72
Al.	0,53
Si	0,39
Ca	46,45
Cu	1,04
Total	100,00

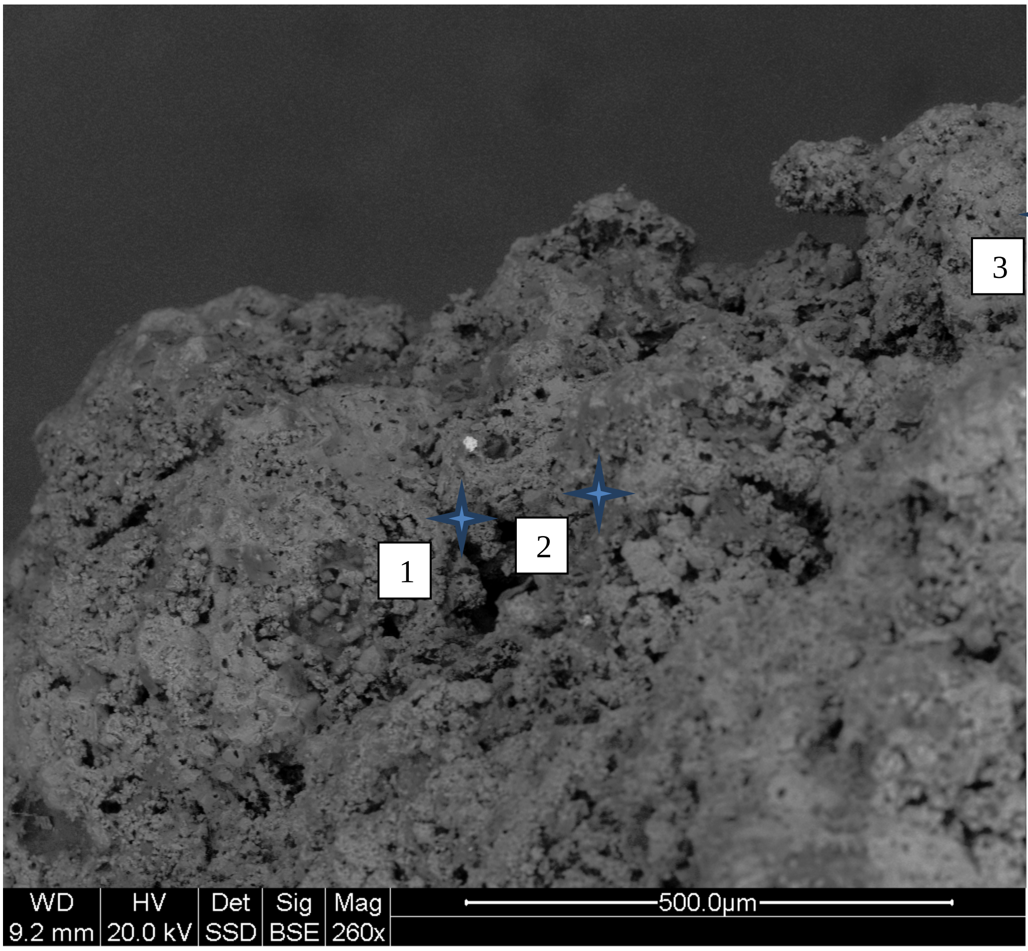
Analysis at point no 3



Element	Wt %
C	24,24
O	48,03
F	0,07
Na	0,22
Mg	0,50
Al,	2,90
Si	6,77
P	0,57
S	0,12
K	0,66
Ca	14,33
Fe	1,30
Cu	0,28
Total	100,00

Results of investigation of advanced karstic process

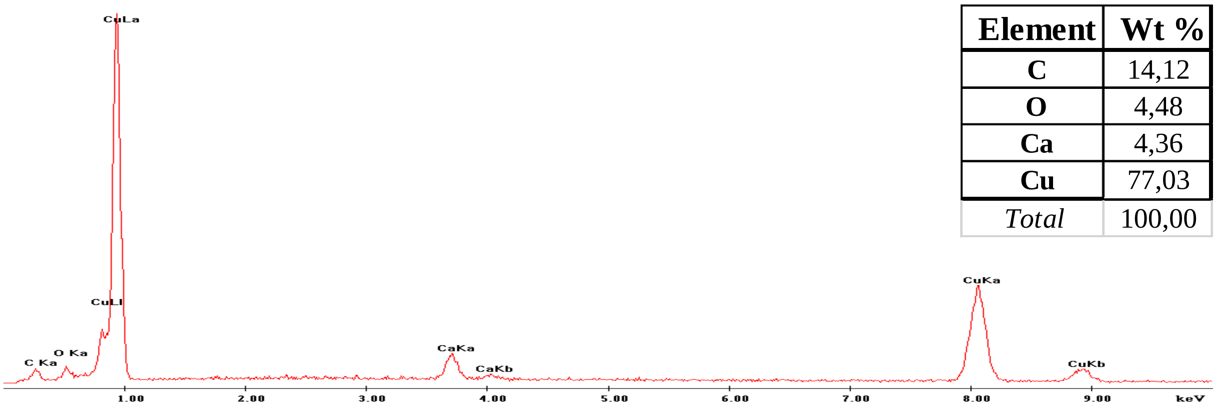
Sample 1. Porous limestone



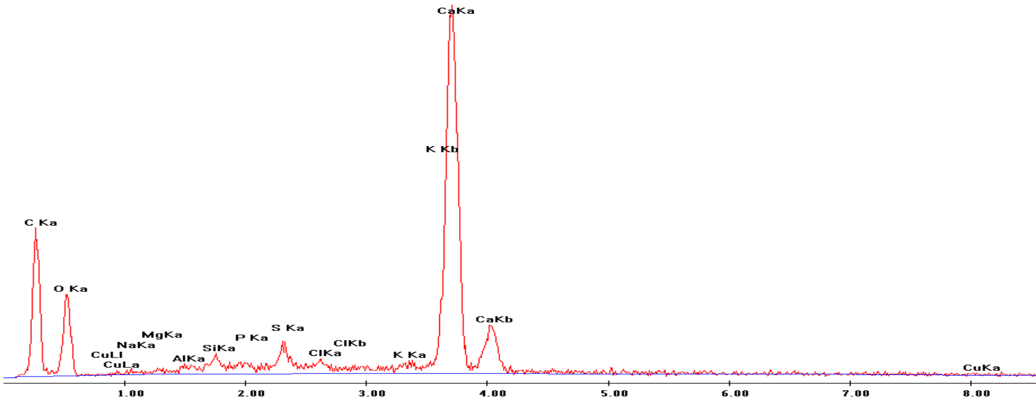
Phot. 7 Porous limestone containing concentration of seconadry Fe-Mn oxides. SEM

Analysis at point no 1

Element	Wt %
C	14,12
O	4,48
Ca	4,36
Cu	77,03
Total	100,00

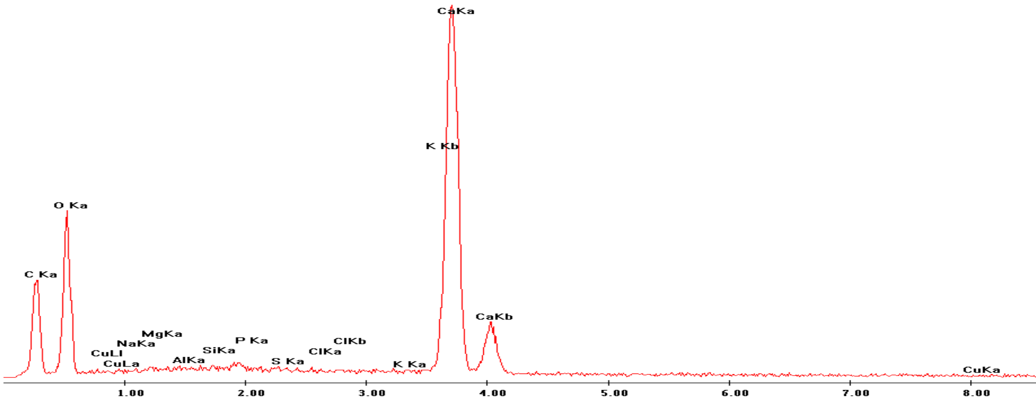


Analysis at point no 2



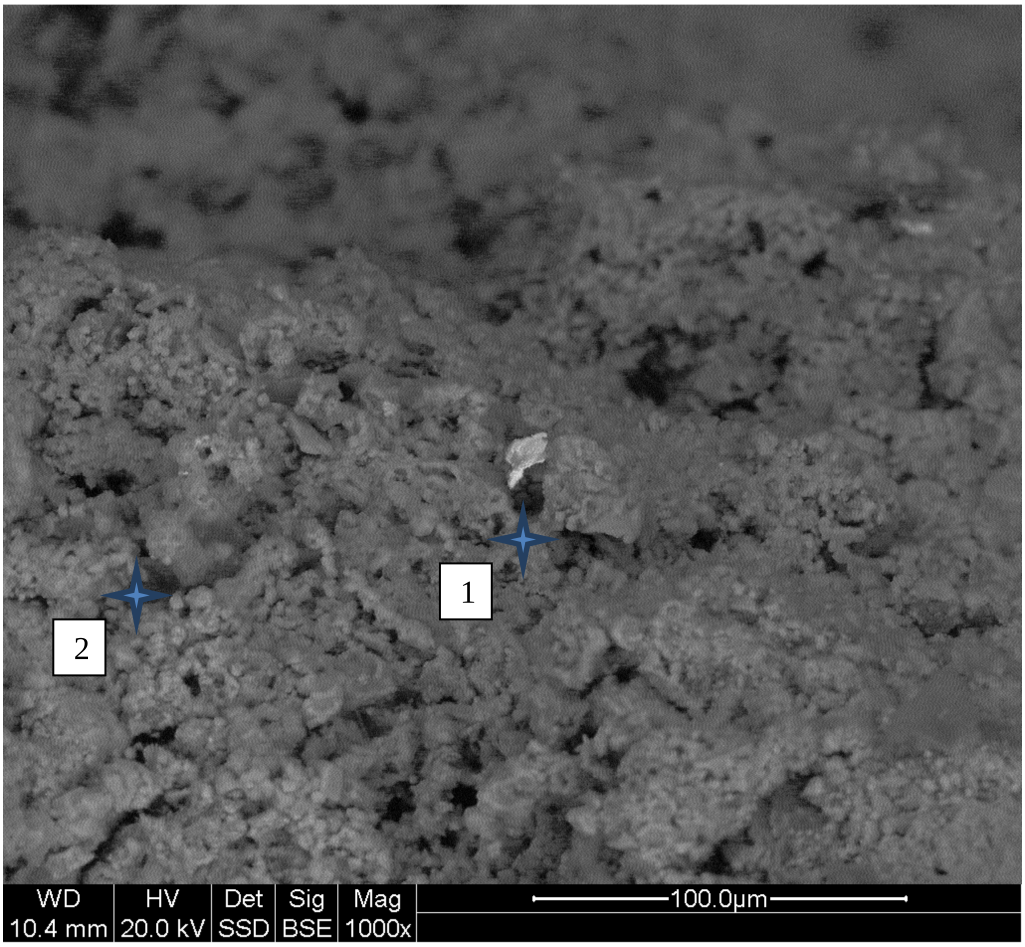
Element	Wt %
C	36,97
O	26,23
Na	0,39
Mg	0,32
Al.	0,54
Si	0,88
P	0,64
S	1,47
Cl	0,78
K	0,79
Ca	30,24
Cu	0,75
Total	100,00

Analysis at point no 3



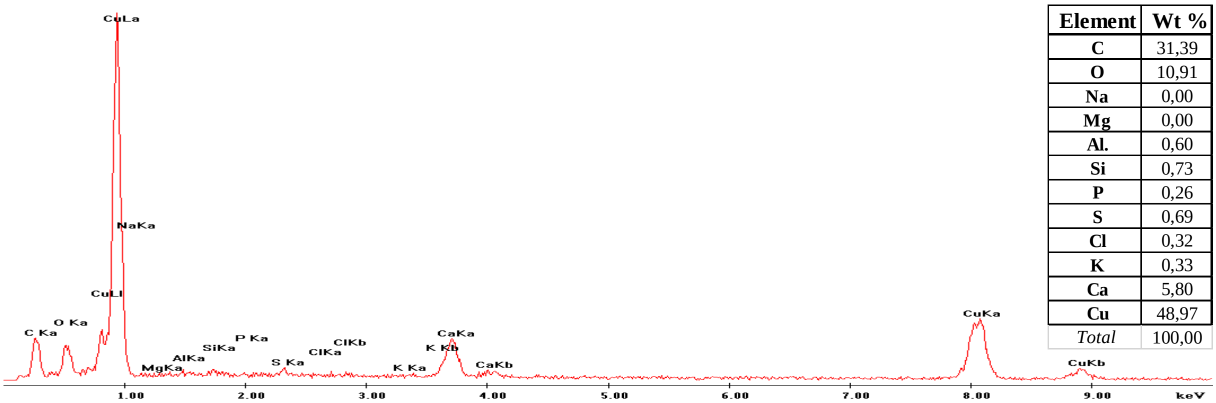
Element	Wt %
C	23,35
O	42,56
Na	0,58
Mg	0,57
Al.	0,51
Si	0,43
P	0,36
S	0,27
Cl	0,12
K	0,16
Ca	30,76
Cu	0,34
Total	100,00

Sample . Limestone showing advanced karstic alternation.



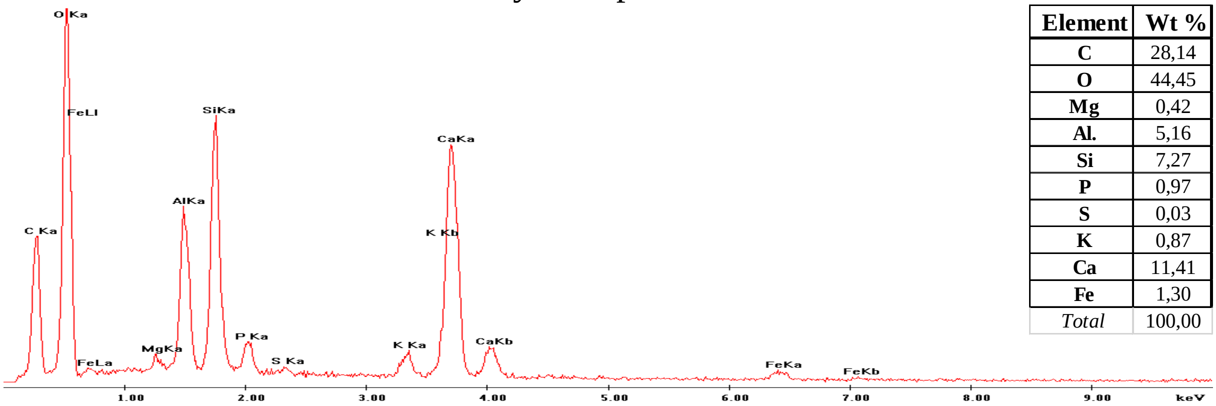
Phot. 8 Details of limestone structure. Small holes between relict of organic skeletons SEM.

Analysis at point no 1



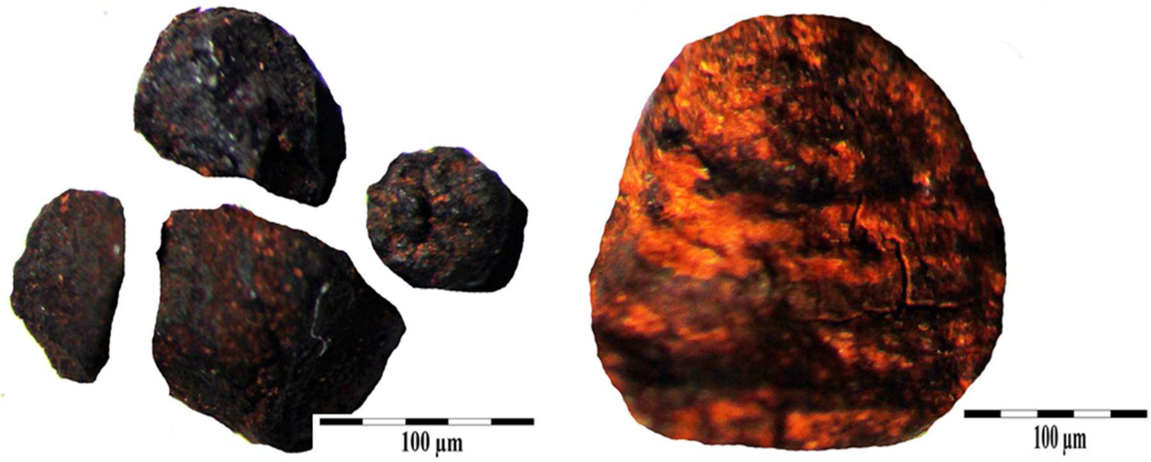
Element	Wt %
C	31,39
O	10,91
Na	0,00
Mg	0,00
Al.	0,60
Si	0,73
P	0,26
S	0,69
Cl	0,32
K	0,33
Ca	5,80
Cu	48,97
Total	100,00

Analysis at point no 2



Element	Wt %
C	28,14
O	44,45
Mg	0,42
Al.	5,16
Si	7,27
P	0,97
S	0,03
K	0,87
Ca	11,41
Fe	1,30
Total	100,00

Results of examination of secondary micro concretions present in residuum (terra rossa)

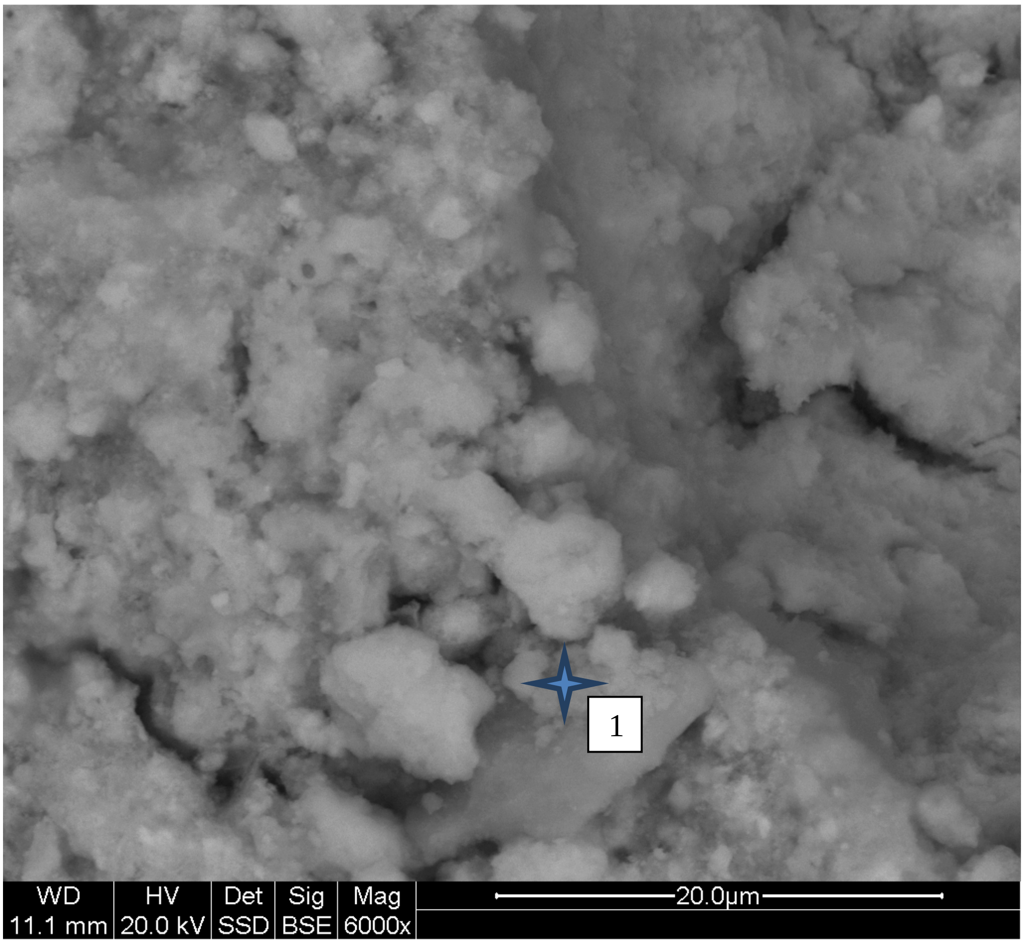


A **B**

Phot. 9 A –mixed Fe-Mn microconcretion. B – Fe miconceretion with lamina of Mn oxides.

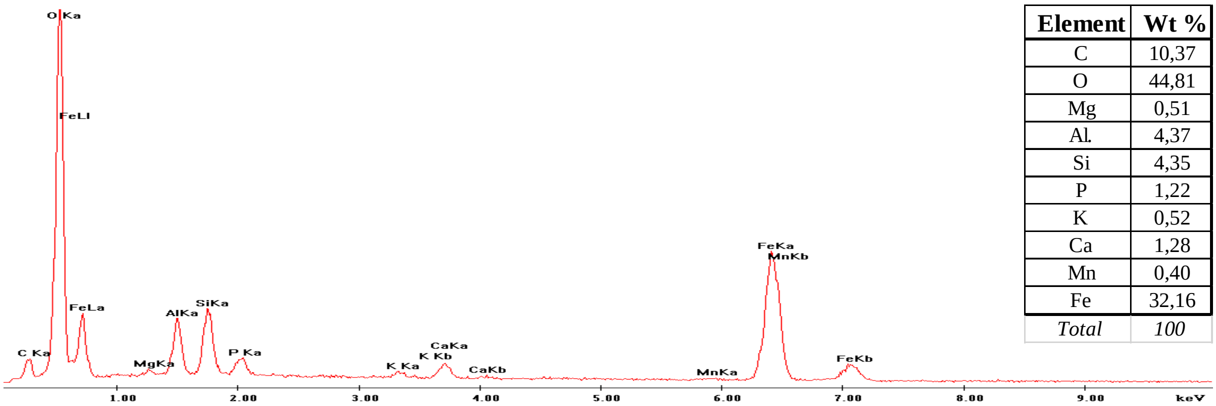
Red concretions

Concretion 1



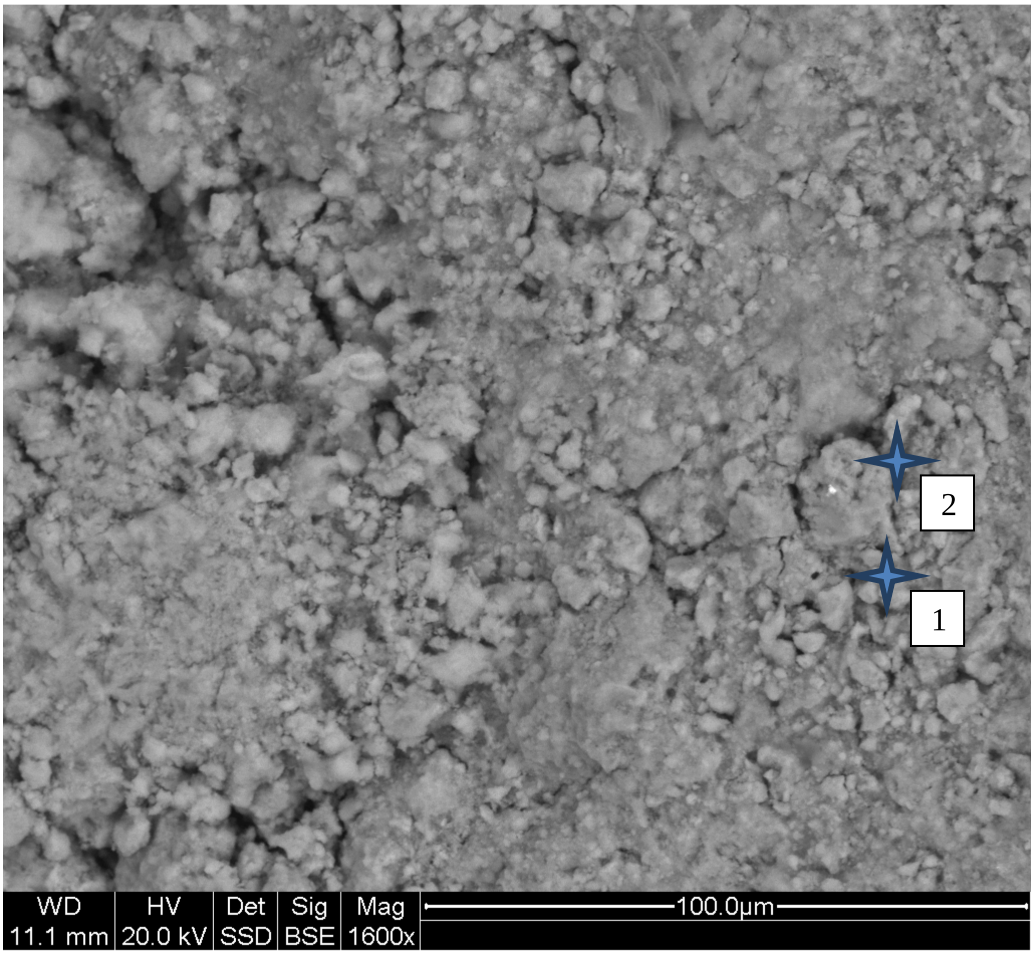
Phot. 10 Details of structure of concretion. SEM.

Analysis at point no 1



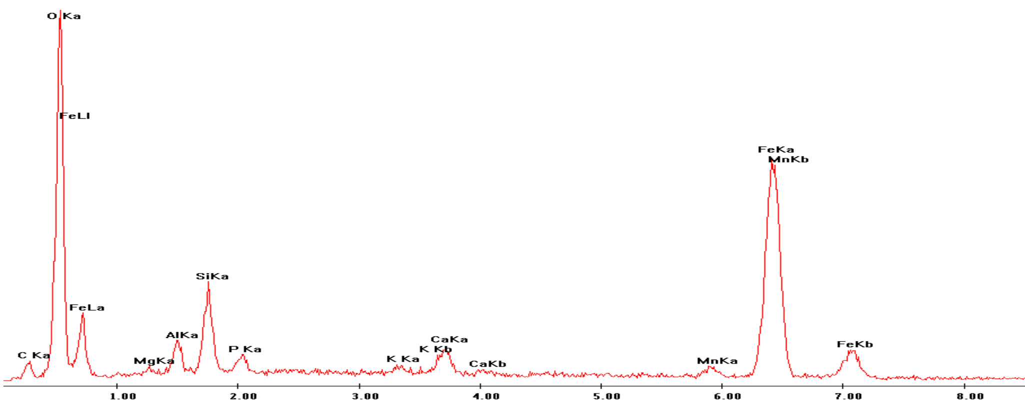
Element	Wt %
C	10,37
O	44,81
Mg	0,51
Al.	4,37
Si	4,35
P	1,22
K	0,52
Ca	1,28
Mn	0,40
Fe	32,16
Total	*100*

Concretion no 2



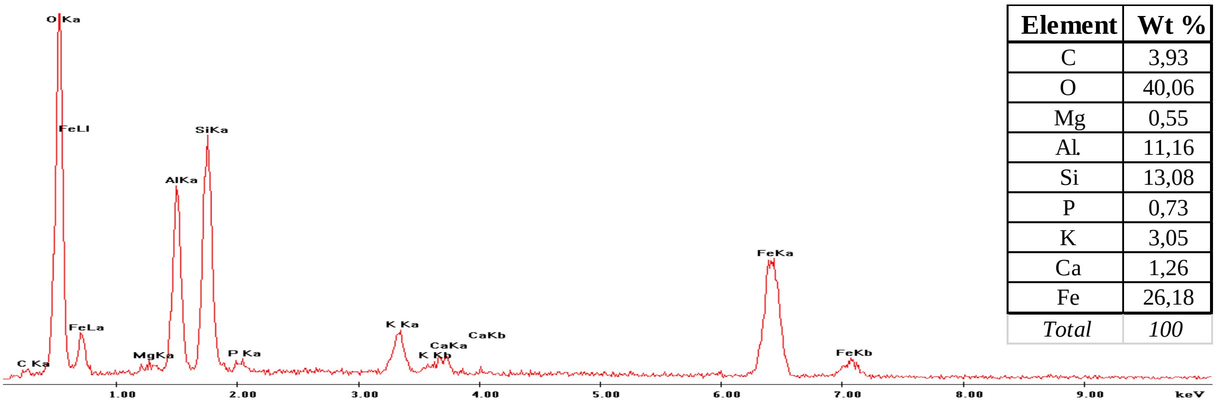
Phot. 11 Structure of surface of concretion showing semi grained character .
SEM.

Analysis of all surface of sample no 2



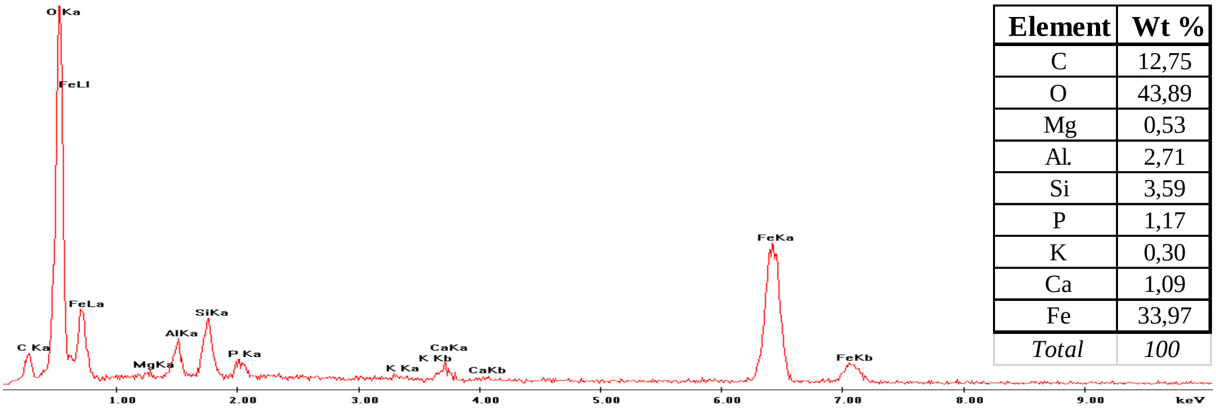
Element	Wt %
C	7,13
O	34,86
Mg	0,45
Al.	2,36
Si	4,50
P	1,07
K	0,57
Ca	1,90
Mn	1,77
Fe	45,40
Total	*100*

Analysis at point no 1



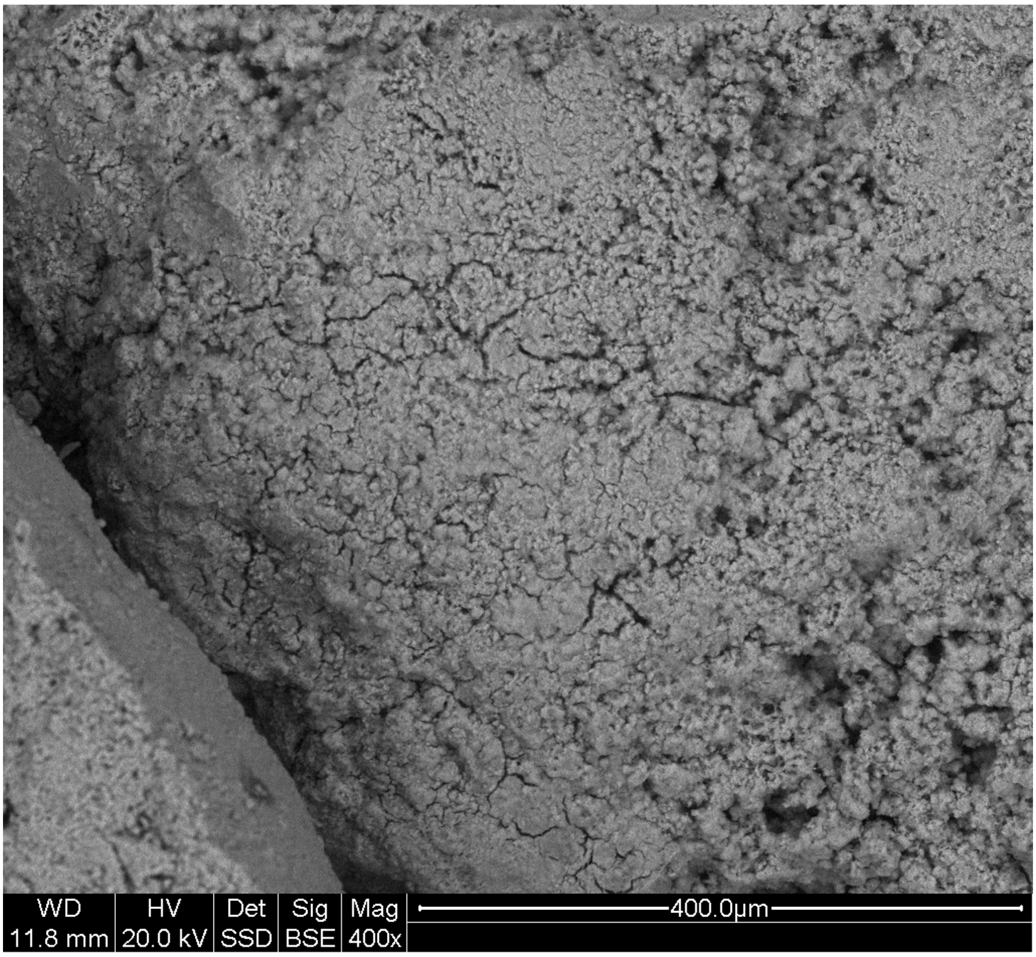
Element	Wt %
C	3,93
O	40,06
Mg	0,55
Al.	11,16
Si	13,08
P	0,73
K	3,05
Ca	1,26
Fe	26,18
Total	*100*

Analysis at point no 2



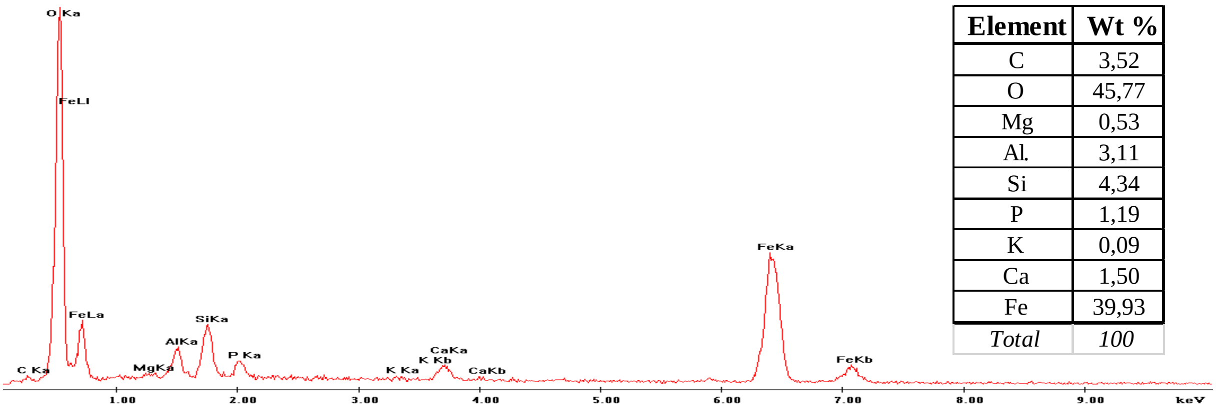
Element	Wt %
C	12,75
O	43,89
Mg	0,53
Al.	2,71
Si	3,59
P	1,17
K	0,30
Ca	1,09
Fe	33,97
Total	*100*

Sample no 3



Phot. 12 Cracked morphology of concretion. SEM.

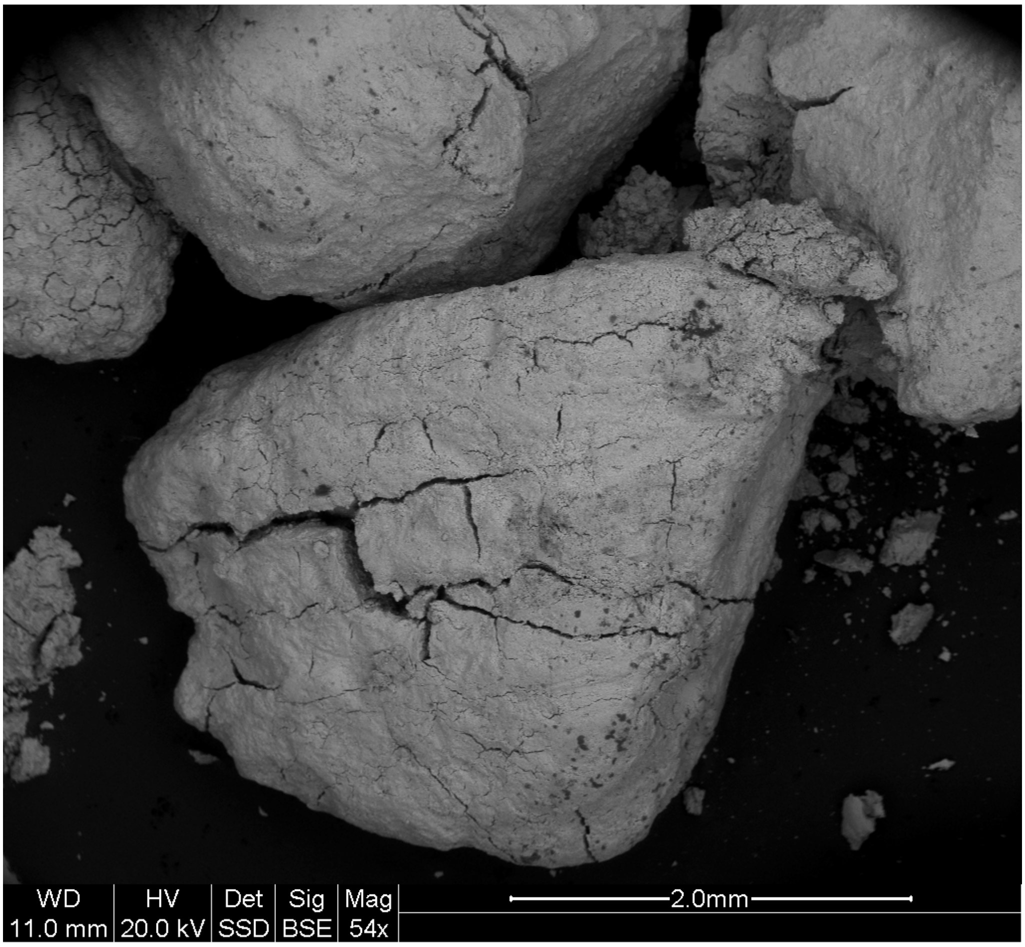
Analysis of all surface



Element	Wt %
C	3,52
O	45,77
Mg	0,53
Al.	3,11
Si	4,34
P	1,19
K	0,09
Ca	1,50
Fe	39,93
Total	*100*

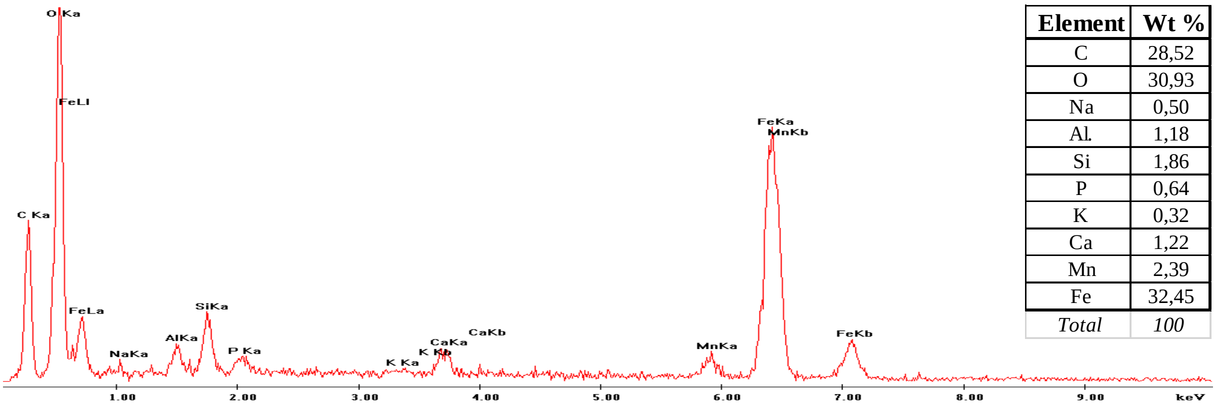
Examination of black micro concretions present et terra rosa

Concretion no 1



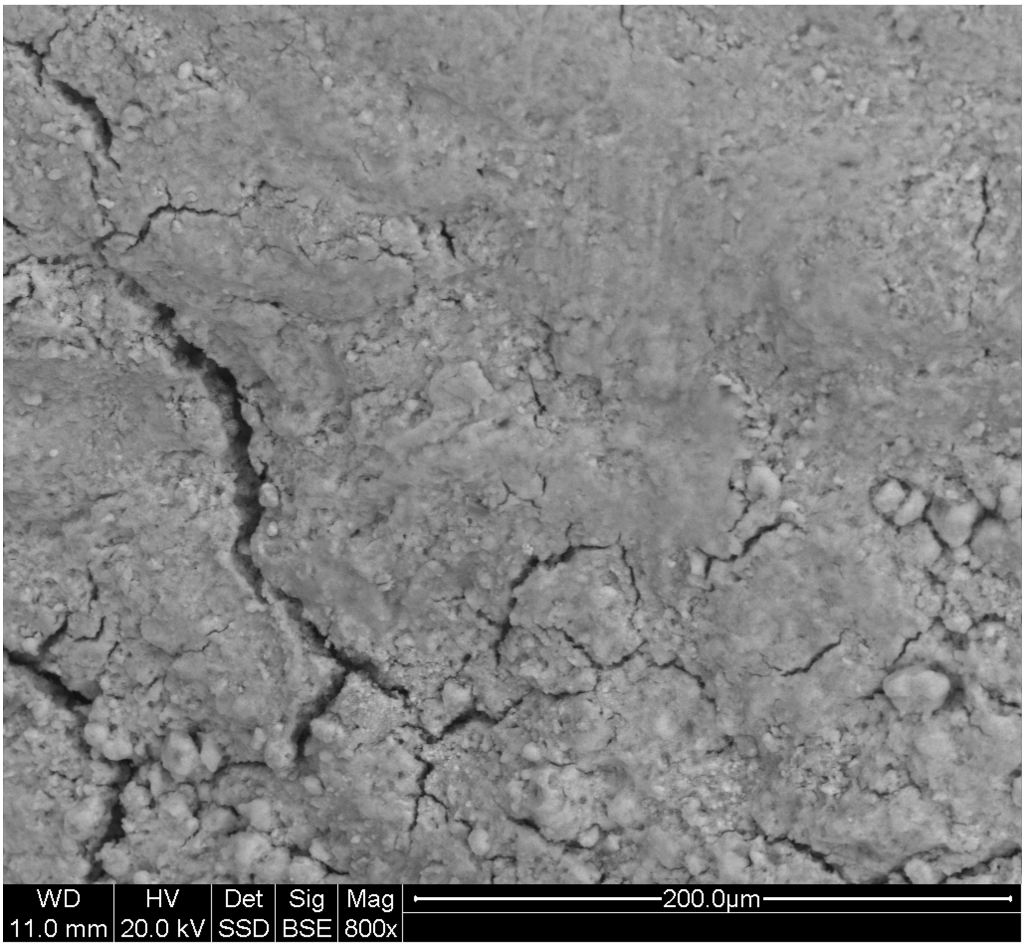
Phot. 13 Crack of micro concretion as result of drying after separation from terra rossa. SEM

Analysis of all surface



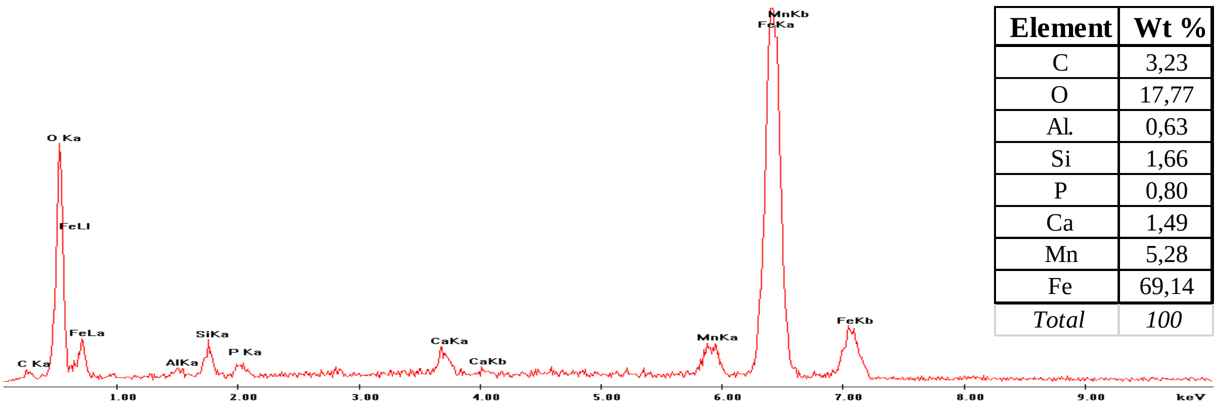
Element	**Wt %**
C	28,52
O	30,93
Na	0,50
Al.	1,18
Si	1,86
P	0,64
K	0,32
Ca	1,22
Mn	2,39
Fe	32,45
Total	*100*

Concretion no 2



Phot 14 Details of surface of dark concretion. SEM

Analysis of all surface



Element	Wt %
C	3,23
O	17,77
Al.	0,63
Si	1,66
P	0,80
Ca	1,49
Mn	5,28
Fe	69,14
Total	*100*

Concretion no 3

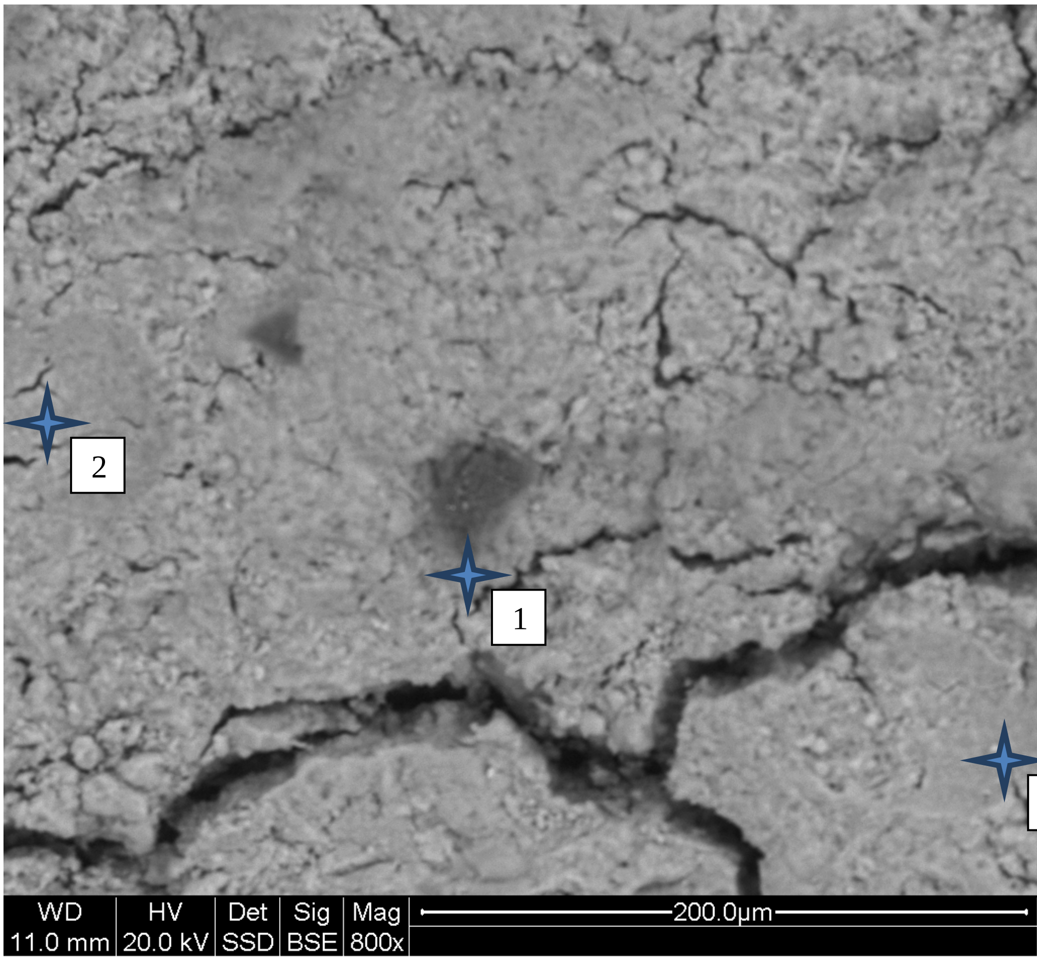
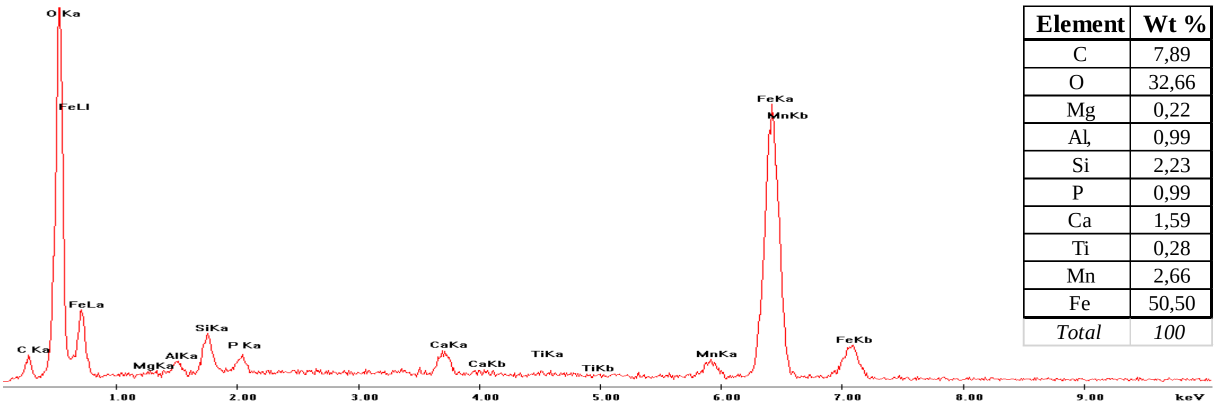


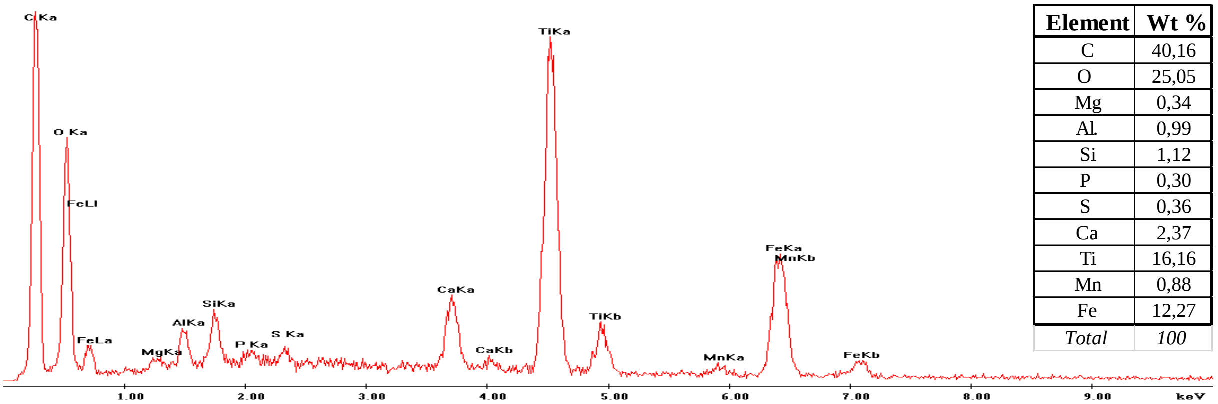
Photo 15 Details of surface of concretion near of crack. SEM.

Analysis of all surface



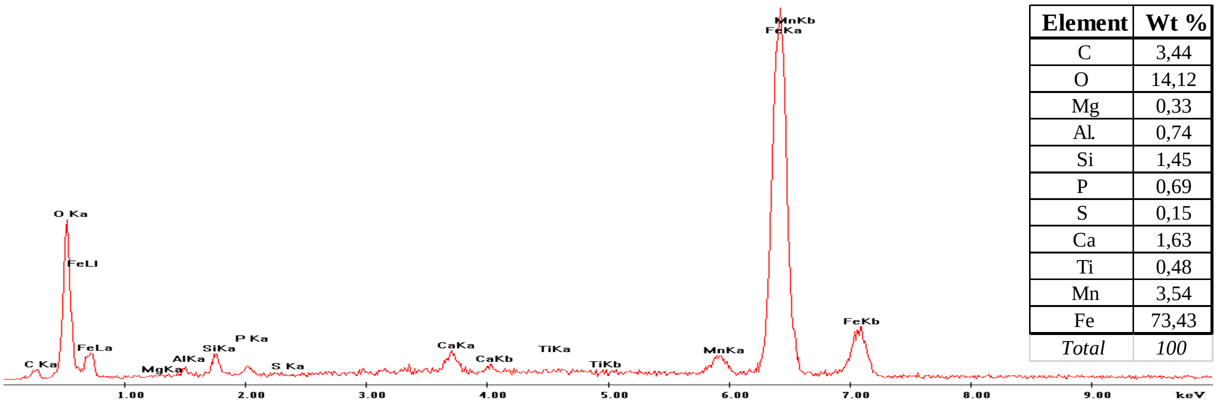
Element	Wt %
C	7,89
O	32,66
Mg	0,22
Al,	0,99
Si	2,23
P	0,99
Ca	1,59
Ti	0,28
Mn	2,66
Fe	50,50
Total	*100*

Analysis at point no 1



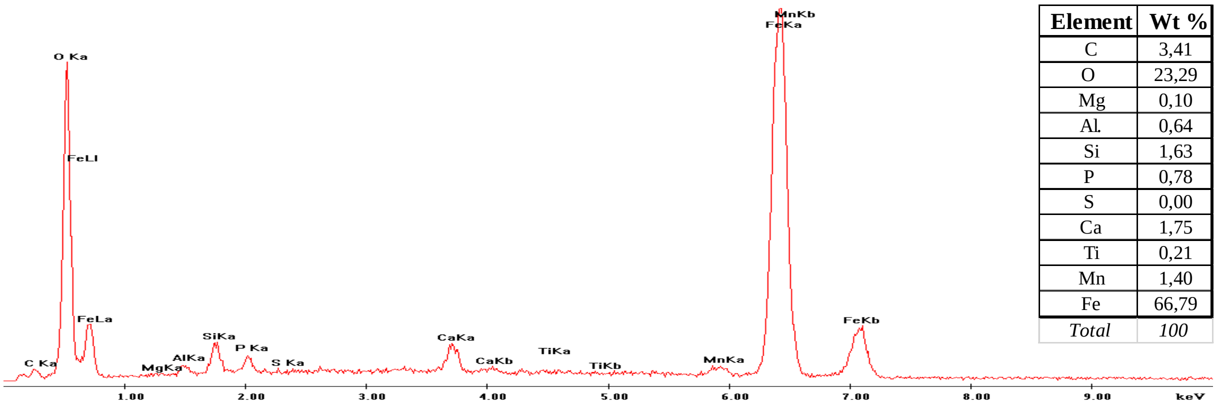
Element	Wt %
C	40,16
O	25,05
Mg	0,34
Al.	0,99
Si	1,12
P	0,30
S	0,36
Ca	2,37
Ti	16,16
Mn	0,88
Fe	12,27
Total	*100*

Analysis at point no 2



Element	Wt %
C	3,44
O	14,12
Mg	0,33
Al.	0,74
Si	1,45
P	0,69
S	0,15
Ca	1,63
Ti	0,48
Mn	3,54
Fe	73,43
Total	*100*

Analysis at point no 3



Element	Wt %
C	3,41
O	23,29
Mg	0,10
Al.	0,64
Si	1,63
P	0,78
S	0,00
Ca	1,75
Ti	0,21
Mn	1,40
Fe	66,79
Total	*100*

Conclusions

1. Light, light grey color of limestones is result of presence of small grains Fe sulfides dissemianted at calcitic background

2. During process of weathering of limestone sulphides are oxided into Fe-oxide due to reaction

$$FeS_2 + 2H_2O = FeOOH + H_2S + H^+ + S$$
$$4FeS_2 + 11O_2 = 8Fe_2O_3 + 8SO_2$$

3. This process leads to the change of color of product of weathering to red.

4. Prosess of oxidation is the reason of change of the volume of Fe - sulfides altered into Fe- oxides. This change leads to formation of micro fissures penetrated next by water. In consequence start be formed small holes, small fisures fissures next extending the size up to big carstic forms.

5. Disolution of calcuite present at limestones is selective. Faster is disloved calcite present between skeletons of organisms due to more prous structure. Structure of skeletions is much compact. The process od dissolution of calcite by rain waters one can describe as following:

$$CaCO_3 + H_2CO_3 = CaHCO_3 + CO_2 + H^+ +1/2O_2$$

6. Disolution of limestone and release Si and Al at acidic conditions create poorly cristaline kaolinite constituting main clay mineral of residum (terra rosa). The process goes as following reaction:

$$4\ Al.^{3+} + 4\ H_4SiO_4 + 2H_2O+ = Al_4[Si_4O_{10}](OH)_8 + 12\ H^+$$

7. Iron oxides containing admixture of Mn present at kaolinite (terra rosa) are during next processes concentrated in form of small nodules.

8. Mentioned phenomenon are the reason of Karst formation and deposition of red soils at area of Karst activity.

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