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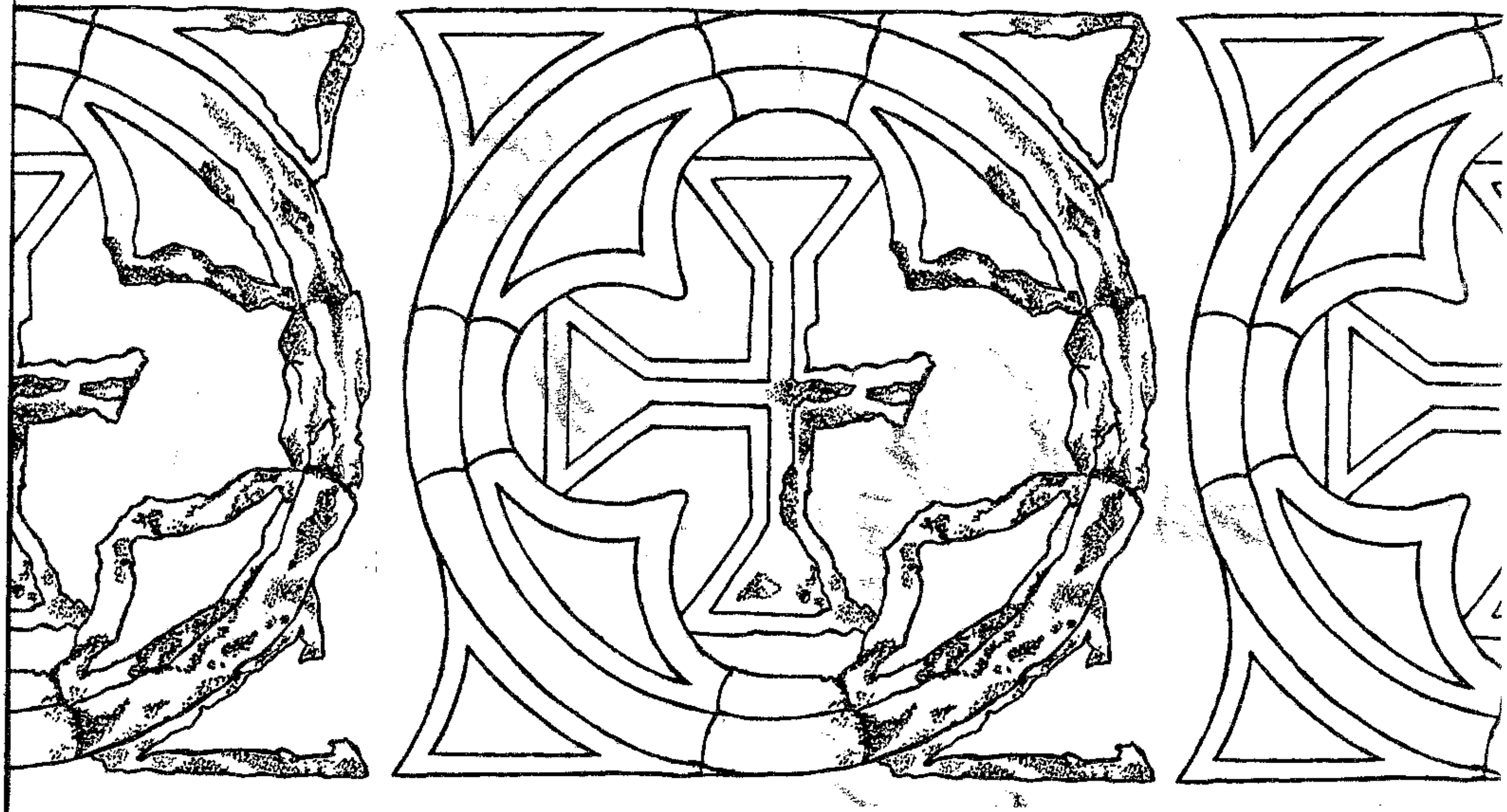

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MINERO-GEOCHEMICAL TRANSFORMATIONS INDUCED BY LICHENS IN THE BIO-CALCARENITE OF THE SELINUNTINE MONUMENTS

Transformations minero-geochimiques produites par des lichens dans la biocalcarenite des monuments de Selinunte

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SUMMARY
The stones of the monuments of the famous Greek Sicilian colony of Selinunte, as well as those of the ancient quarry fronts are extensively covered with various types of lichens. These organisms, among which the most common species are Dirina massiliensis, Verrucaria nigrescens, Lecanora pruinosa and Caloplaca aurantia, are not only aesthetically damaging but also cause the deterioration of the stone surfaces. The main effects produced are a strong corrosion, sometimes with the production of calcium oxalates and, after the lichen have died, the disintegration of surfaces. Further to stratigraphical microscopic studies of thin and opaque sections and mineralogical studies by X-ray diffraction and FTIR spectrophotometry, complete chemical analyses by X-ray fluorescence of major, minor and trace elements and their distribution in the lichen thalli and stone surfaces have led to an understanding of the mechanisms of attacks of the various species of the identified lichens.

RÉSUMÉ
Les pierres des monuments de la célèbre colonie grecque-sicilienne de Selinunte, de même que celles de l'ancienne surface d'exploitation de carrière, sont couvertes de différents types de lichens. Ces organismes, dont les espèces les plus communes sont Dirina massiliensis, Verrucaria nigrescens, Lecanora pruinosa et Caloplaca aurantia, défigurent non seulement esthétiquement la surface de la pierre, mais contribuent aussi à la détérioration de la pierre elle-même. Une corrosion prononcée de la surface, parfois avec formation d'oxalates de calcium, et l'époussetage des surfaces après la mort du lichen en sont les effects les plus importants. En complément aux études stratigraphiques par microscopie à lâme mince et polie et aux études minéralogiques par diffraction X et spectrophotométrie FTIR, des analyses chimiques complètes par fluorescence des rayons X des éléments majeurs, mineurs et en traces, leur distribution dans le thalli des lichens et des surfaces pierreux, ont permis de comprendre le méchanisme de corrosion des différentes espèces de lichens identifiés.

1. INTRODUCTION

Selinunte is the most westward ancient Greek town of Sicily. A subcolony of Megara Iblaea, it was founded around 628 B.C. from the sea at the end of a large calcareous plateau (1) very suitable for agricultural cultivation which was responsible for its prosperity.
Witness of this prosperity are the impressive ruins of the city which occupy a very large area and include an acropolis, the city itself, two harbours and two extramural sacred zones.
Among the most important monuments are ten temples, some of which are of enormous size and have been partially re-erected by modern restorations (2,3).
All the buildings of Selinunte have been made using a local stone, a biocalcarenite formed during the Sicilian period which was quarried in various localities (Cusa, Latomie Landaro, etc.), not far away from the city (4,5).
Selinunte reached its maximum splendour in the VI c. B.C., was then completely destroyed in 409 B.C. by the Carthaginians, later remaining a place of little importance in the Hellenistic and Roman times. In our era the site suffered for several earthquakes which completed the destructive action of man. It has been excavated by various teams of archaeologists since the last century, and is still under study and excavation by the University of Turin.
The environment of the Selinuntine area is a typical marine rural one. The only inhabited centre in the vicinity is the small fishermen's hamlet of S. Marinella which becomes a touristic resort in summer and produces, albeit low, a certain amount of air pollution.
All the ruins show a more or less strong lichen attack which in many cases is disfiguring the stone surfaces. This is particularly evident on the blocks of the buildings of the acropolis, and on the columns and other architectural elements of the F and G temples, all showing very frequent black spots and patches, sometimes large in size (several square cm).

2. SAMPLING AND ANALYTICAL METHODS

A few samples were taken from some of the blocks of the temple E lying on earth near the temple. Many others were removed from the quarries at Cusa, and some from the monuments of the acropolis.
The analytical method used was optical microscopy on thin and opaque cross sections to study the stratigraphy of lichen thalli and their interaction with the stone substrata. SEM observation proved very useful for the study of the morphology of the lichens and the stone layers near the surface. These studies were made on fracture surfaces and on polished cross sections, where EDS analyses were also performed. X-ray diffraction was used as an initial check for the presence of oxalates and other crystalline phases which may prove to be present in the lichens and on the attacked surfaces.

For a few samples FTIR spectrophotometry was also used to detect the presence of even very small amounts of oxalates in a measuring range of 350-4000 cm-1, with a resolution of 2 cm-1.
Chemical analyses were carried out by XRF in order to investigate any possible fractionations related to the lichen activity. For this purpose sampling was made at different levels: the whole thallus (samples A), the underlying substrate up to a depth of the order of 1 mm (samples B) and the internal part of the stone (samples C). Small-sized pellets (1 cm in diameter) were prepared with 0.15 g of sample on a boric acid support. Standardization was performed by using a large number of international reference materials of suitable composition (carbonates and sulphates).

RESULTS AND DISCUSSION

The stone of the Selinunte monuments is a biocalcarenite characterized by abundant bioclasts of micritic calcite, peloids and a detritic fraction rich in volcanic and metamorphic quartz (from 10 to 30 %), but also containing small amounts of chert, K-feldspars and plagioclases, biotite, opaque minerals and glauconite. The cement of the rock is also micritic and the degree of cementation varies considerably from place to place.
The lichen species considered in the present study were among the most common on the examined sites, e.g. Dirina massiliensis Dur. et Mont., Verrucaria nigrescens Pers., Caloplaca aurantia (Pers.) Hellb. and Lecanora pruinosa Chaub..
Dirina massiliensis has a white thallus which can reach a thickness of some mm, in this study to 3 mm. It is a lichen which is very common along the coasts and can also be found on siliceous substrates. It is common on monuments and can also survive on surfaces not in direct contact with rain, causing the deterioration of sculptures and frescoes in sheltered zones (6,7).
Verrucaria nigrescens has a brown-black areolate thallus, it is frequently found on limestone and prefers very light places; it is very common on monuments.
Caloplaca aurantia has a yellow-orange thallus and is very common on stone.
Lecanora pruinosa shows a whitish placodiomorphous thallus and grows on siliceous and silico-calcareous substrates. It has been reported several times on monuments.
The microscopic examination of the samples confirm the varying ability of the various lichen species to attack the Selinuntine biocalcarenite. In particular, four degrees of corrosion have been observed from the strongest, Dirina massiliensis, to the weakest one of Verrucaria nigrescens. This corrosion consists in the superficial dissolution of the calcite of the stone, with a tendency of quartz concentration towards the surface.
Isolated quartz and calcite granules are sometimes observed embedded in the thalli, or detached from the stone substrate, especially in Dirina massiliensis (fig. 1a). A consequence of this corrosion and the action of

the oxalic acid produced by the lichens results in the formation of calcium oxalates, which show up microscopically as very highly birefringent fine particles. These biogenic minerals are located in different parts of the thalli: in the whole thallus and even inside the stone down to the depth reached by fungal hyphae filling the pores in *Dirina massiliensis* (fig. 1a); at the surface and inside the thallus in *Lecanora pruinosa* (fig. 1b) and *Caloplaca aurantia* (fig. 1c), though much more concentrated in the former. The examination of thin sections of *Verrucaria nigrescens* does not show the presence of any trace of these minerals (fig. 1d). This distribution confirms the findings of previously reported literature (8,9,10) and further testifies to the peculiar behaviour of these species.

The oxalates identified by X-ray diffraction in most cases showed them to be composed of the dihydrated form weddellite, while whewellite, the monohydrated form, is present only in *Lecanora pruinosa* (Table 1). FTIR substantially confirmed the results obtained by XRD, also showing that the latter seems to be a sufficiently sensitive technique for detecting the presence of oxalate in lichens.

The distribution of elements (Ca, Si, Fe, Al) studied by SEM coupled with EDS indirectly confirmed the data resulting from the examination of thin sections for Ca and Si (fig. 2). No concentrations of Fe and Al were observed inside the thalli.

It is known that lichens may produce oxalic acid and many other "lichen acids" which together with the production of CO_2 are responsible for the decrease in pH and related attack of several minerals (11,12). In addition to this, other organic compounds may have a chelating capacity on a number

SAMPLES		XRD					FTIR	
		Quartz	Calcite	Feldspars	Weddellite	Whewellite	Weddellite	Whewellite
Lecanora pruinosa	A	++	+		+	+++	±	+++
	B	+++	++	±	±	+	+	+
Verrucaria nigrescens	A	+++	++					
	B	+++	+++	±				
Dirina massiliensis	A	+++	++	±	++		+++	
	B	+++	+++		+		+	
Caloplaca aurantia	A	+++	++		+		++	
	B	+++	+++		±		±	

Table 1 - XRD and FTIR analyses of lichen thalli (A) and the underlying substrate (B).

SAMPLES		MgO%	Al2O3%	SiO2%	P2O5%	K2O%	CaO%	TiO2%	MnO%	Fe2O3%
Lecanora pruinosa	A	0.095	0.18	7.5	0.172	0.265	31.0	0.066	0.046	0.820
	B									
	C	0.420	0.38	22.2	0.028	0.121	42.0	0.034	0.047	1.250
Caloplaca aurantia	A	0.290	0.52	12.7	0.560	0.430	29.0	0.108	0.038	1.200
	B									
	C	0.420	0.38	22.2	0.028	0.121	42.0	0.034	0.047	1.250
Verrucaria nigrescens S-2-4	A	0.150	0.36	9.0	0.550	0.540	29.5	0.093	0.026	1.038
	B	0.430	1.50	35.0	1.010	0.570	33.0	0.150	0.051	1.610
	C	0.350	0.51	28.8	0.029	0.188	38.1	0.038	0.051	1.400
Verrucaria nigrescens	A	0.380	0.21	6.6	0.410	0.240	38.0	0.032	0.044	0.760
	B	0.460	0.33	21.6	0.380	0.246	43.0	0.032	0.028	0.920
	C									
Dirina massiliensis S-2-37	A	0.190	0.23	16.5	0.063	0.205	30.7	0.043	0.031	0.760
	B	0.280	0.19	23.5	0.063	0.165	46.0	0.025	0.024	0.760
	C	0.450	0.35	22.3	0.026	0.140	42.1	0.030	0.025	0.850
Dirina massiliensis	A	0.165	0.24	4.9	0.095	0.226	35.0	0.050	0.018	0.620
	B	0.220	0.07	10.9	0.044	0.046	46.0	0.032	0.022	0.630
	C									

Table 2 - Compositional data referring to the different thalli (A), the underlying stone surface (B) and the internal stone (C).

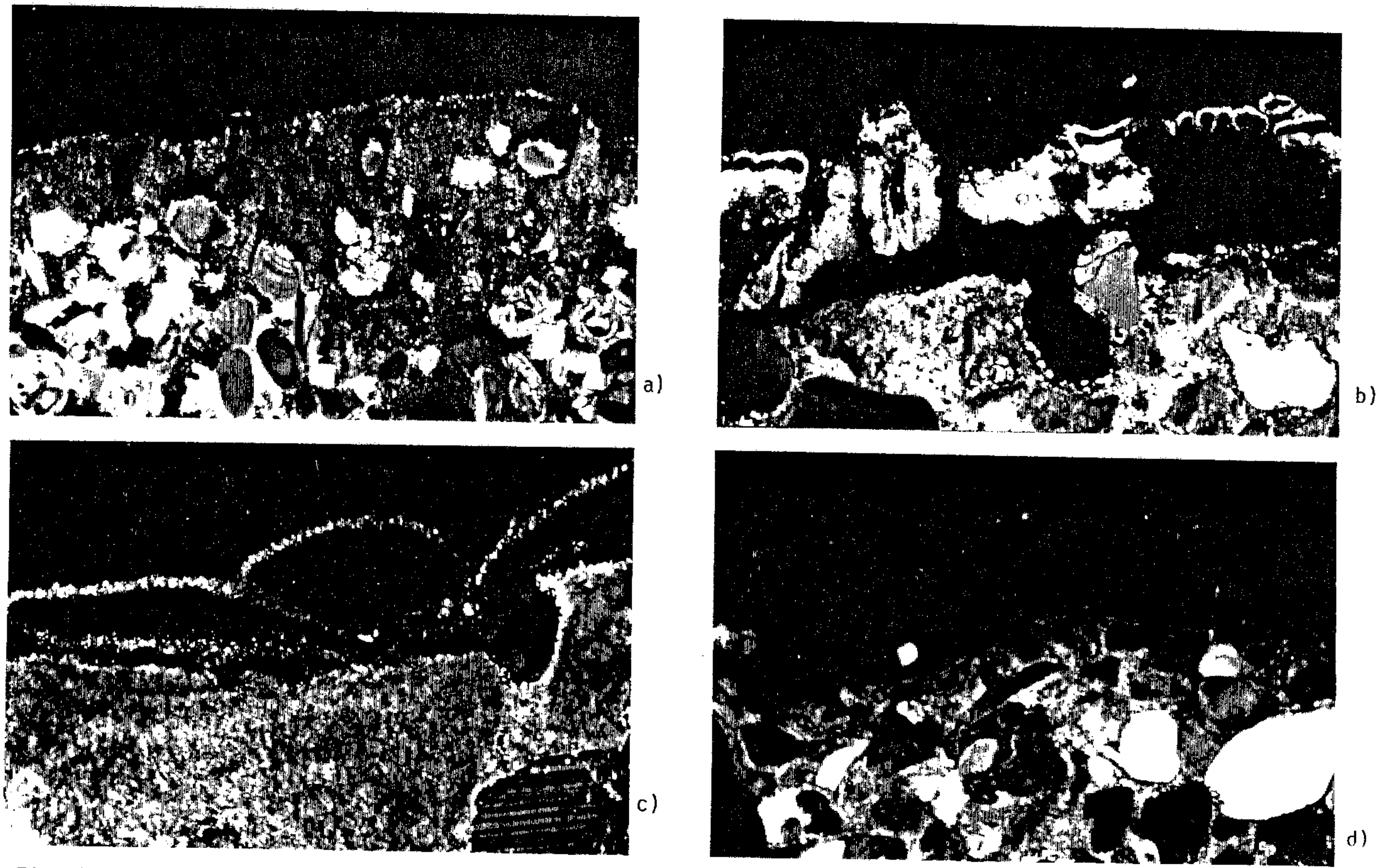
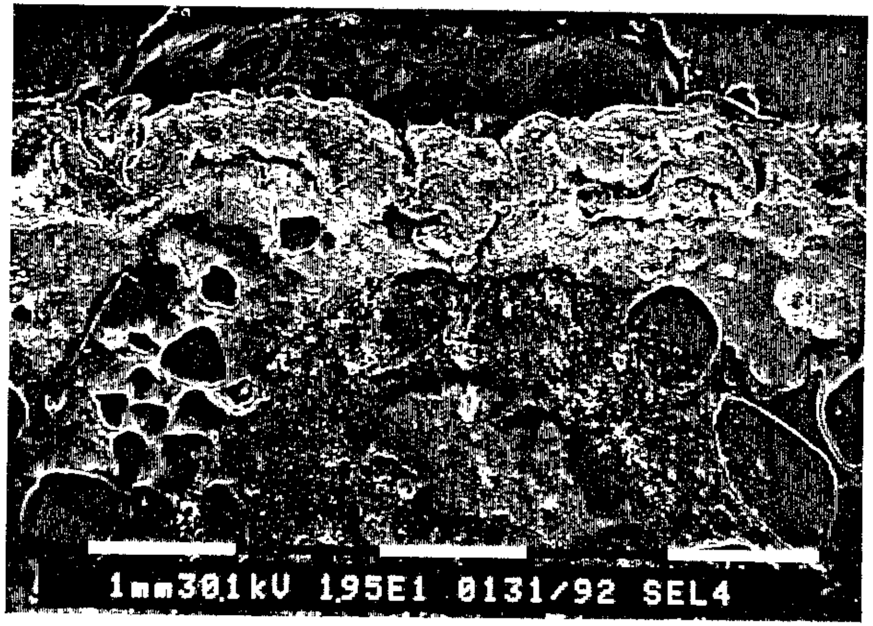


Fig. 1 - Photomicrographs of thin sections showing different quantities and location of Ca oxalates in lichen thalli: a) Dirina massiliensis (N+, 30x), b) Lecanora pruinosa (N+, 30x), c) Caloplaca aurantia (N+, 78x). Verrucaria nigrescens (d) does not show any oxalates (N+, 30x).



a)

b)

c)

Fig. 2 - SEM micrographs of polished cross sections of the biocalcarenite covered by Lecanora pruinosa (a). The distribution maps of calcium and silicon are respectively shown in b) and c).

of elements. These phenomena result in a complex of dissolution-neoformation processes and related biogeochemical fractionation.

From a chemical point of view, the compositional results collected in Table 2 obviously show a strong and homogeneous depletion for the elements characterized by a specific carbonatic affinity (Ca, Mg). Carbonates are in fact more easily solubilized through lichen activity. With specific reference to Ca, its re-precipitation as oxalate shculd only be partial, thus justifying a certain leaching of the element.

Silica has also been found generally to decrease from the inner part to the surface, but depletion should not be related to a direct chemical attack due to the highly unreactive nature of quartz, especially in this acid environment.

In this case, mechanical depletion is to be hypothesised as a consequence of the progressive solubilization of the carbonate matrix and related washing out of at least a part of the loose detrital grains. In addition to this, other important processes should be taken into account, such as the biological entrapment of loose particles (both of internal and external origin). Thus the very irregular trends shown by silica in one sample (Verrucaria nigrescens) and more in general by all the other elements having a specific detrital affinity can be explained as a consequence of the specific balance between these constrasting processes (washing out of loose detrital particles or their biological entrapment).

A different behaviour is shown by another group of elements characterized by a specific biogenic affinity (K,P), which tends to increase strongly along the surface.

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