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INFLUENCE OF WEATHERING OF IRON SULFIDES CONTAINED IN AGGREGATES ON CONCRETE DURABILITY

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Abstract

The oxidation of pyrrhotite and pyrite initiates a series of weathering reactions in aggregates extracted from the Mont Palau quarry (Barcelona, Spain). The lithotypes enclosing the sulfides, however, play an important role in controlling the progress of weathering: whilst expansive hydrated Fe-sulfates characteristic of acidic environments formed in the black shales, the neutralizing capacity of calcite dissolution prevents the formation of these harmful mineral phases in the limestones.

Introduction

The concrete used in some buildings and public works in Maresme, a region near Barcelona (NE Spain), during the period 1970-1972 underwent considerable degradation due to the development of fissures. All the affected concretes contained aggregates from the Mont Palau quarry, which have high contents of iron sulfides, mainly pyrrhotite.

Several authors related to the building industry have studied these problems (1,2). The Spanish code regulating the use of aggregates with iron sulfides in concrete (3) was called into question in these studies, given that an anlytical process is used which apparently underestimates the amount of sulfides (and consequently accepts unsuitable aggregates). Nevertheless, a detailed description of the mineralogical aspects of the materials and processes that explain the weathering products has not been carried out until now.

In this paper we study the relation between the mineralogy of aggregates and the mineralogy of the weathering products observed in the quarry.

Mont Palau quarry: Location and Description of Rock Units

Mont Palau quarry is located close to Pineda de Mar township in the Maresme region, 60 Km NE from Barcelona, Spain (Fig. 1). The rock units, which occur at the northern edge of the Subunidad Litoral Catalana, are Paleozoic metasediments intruded by Hercynian granitoids.

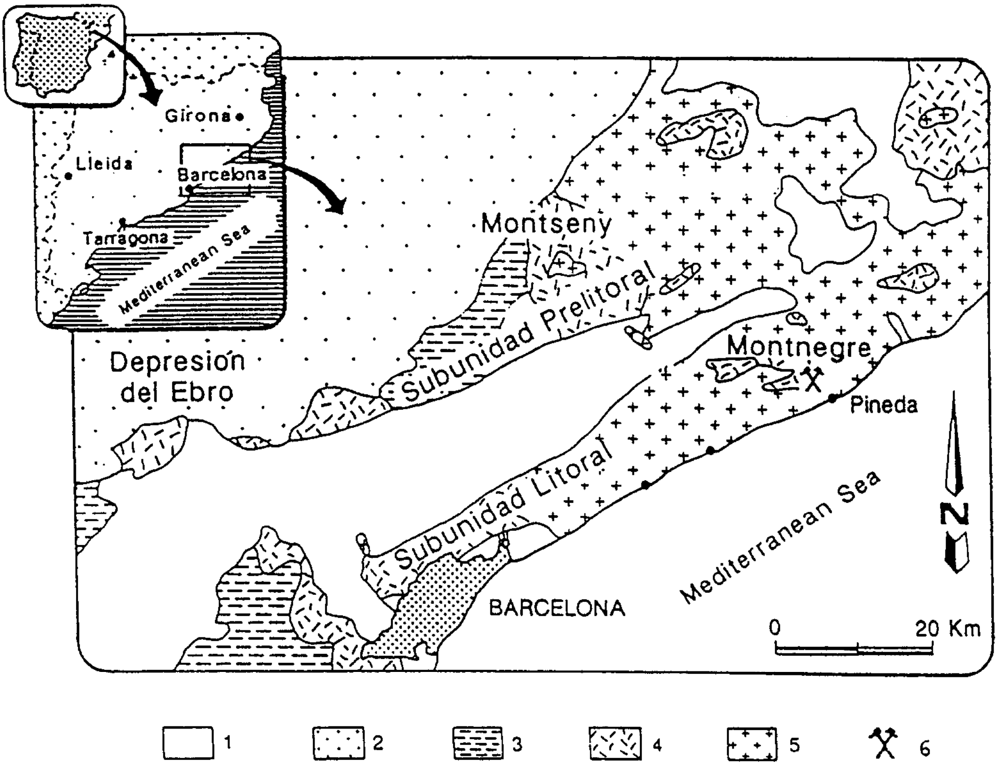

FIG. 1
Simplified geological map of study area (4): 1) Quaternary and Miocene, 2) Oligocene and Eocene, 3) Mesozoic, 4) Paleozoic, 5) Granites, 6) Location of Mont Palau quarry.

The materials consist of limestones ("Serie Carbonatada") and a minor proportion of black shales ("Serie Negra") attributed to an Upper Silurian age (4).

Limestones constitute approximately 70% of the mined rock volume. They consist of recrystallized calcite and dolomite with a calcite:dolomite proportion of 92:8. The limestones occasionally contain calsilicate masses of centimetre size, made up of grossular and wollastonite formed by circulation of hydrotermal solutions close to the granite.

Black shales constitute approximately 25% of the mined rock volume and consist of quartz, feldspar, muscovite and organic matter. In a 300 m aureole around the granite, that surrounds the quarry, the black shales contain abundant graphite and chiastolitic andalusite formed by contact metamorphism induced by the intrusion.

Two major sulfides occur. Hexagonal pyrrhotite is the predominant sulfide. It forms layers of milimetre to centimetre-size thickness and disseminated aggregates in limestones and black shales. They were formed as sedimentary mineralisations in a reducing environment contemporaneus to the limestones and black shales.

Pyrite is the next important sulfide. It formed from sulfurization of pyrrhotite in "bird eyes" textures that affect all the pyrrhotite (Fig. 2) and occurs in fracture areas of centimetre-sized range. The amount of Zn (70 ppm in limestones and 62 ppm in black shales), Cu (48 ppm in limestones and 32 ppm in black shales), Pb (37 ppm in limestones and 45 ppm in black shales) and As (<5 ppm for both rock types) implies very low amounts of other sulfides.

FIG. 2
Pyrrhotite (po) partially transformed into Pyrite (py) through veins and "bird eyes" textures. Reflected light micrograph.

Other minerals which occur include zeolites and clays. Laumontite ($CaAl_2Si_4O_{12}.4H_2O$) is observed forming powder-like aggregates filling fractures and coating surfaces of the black shales (Fig. 3). Laumontite, when exposed to the air, loses water molecules to form leonhardite (5); the reaction is reversible and quick (between 1 and 2 hours) and the phase change results in swelling of the material.

Kaolinite, vermiculite (retain a d(001) of 14.2 Å after glycerol solvation and collapse to 9.98 Å heating to 300 °C for an hour) and illite species have been identified by X-ray diffraction (XRD) in the clay fraction analysis of the aggregates. None of these clays is expansive or has an effect on concrete durability.

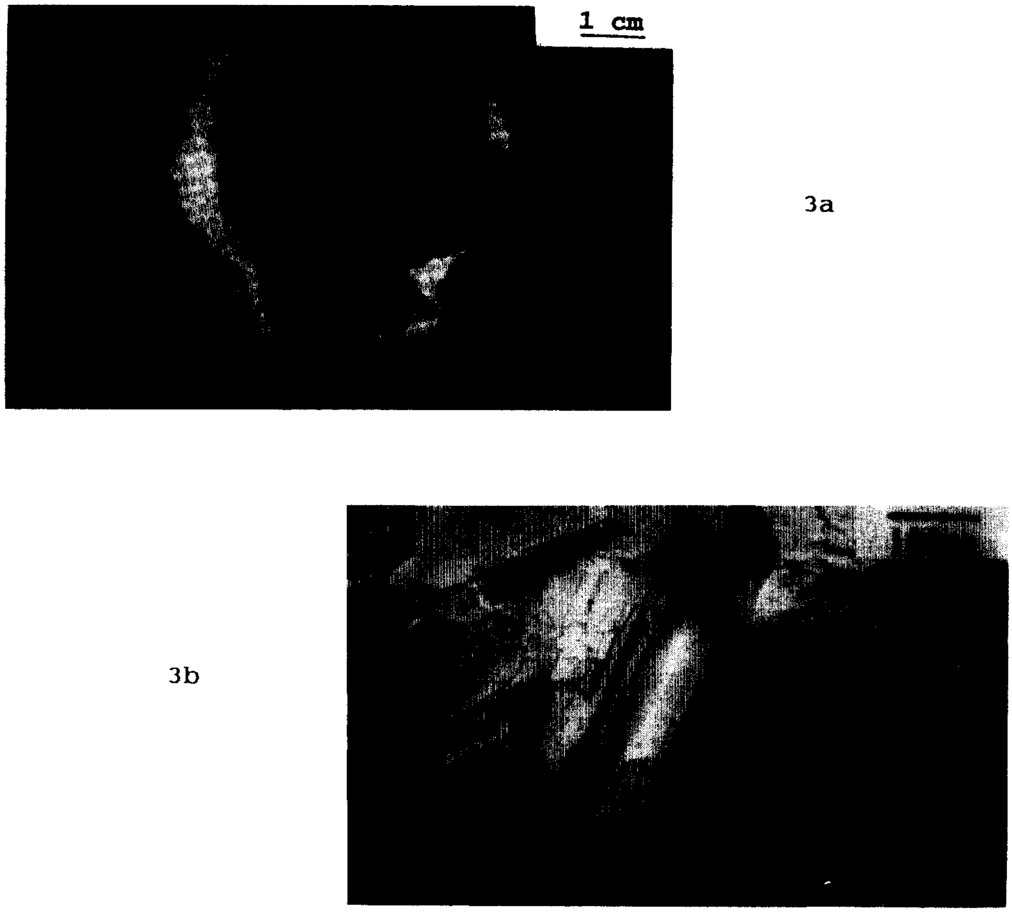

FIG. 3
3a: Black shale surface coated by laumontite, 3b: Scanning Electron micrograph of laumontite crystals.

Weathering Products

We describe here the weathering phases associated with both rock types.

Weathering compounds associated with the limestones:

Ferrihydrite, amorphous $Fe(OH)_3$.- Ferrihydrite forms powder-like masses on surfaces and in cracks. The later recrystallisation of ferrihydrite originates goethite. According to Steger (6), goethite (α -FeO(OH))is always present as a product of supergenic alteration of pyrrhotite and pyrite.

Weathering compounds associated with the black shales: Besides ferrihydrite, the following weathering compounds were found associated with the black shales:

Melanterite ($FeSO_4.7H_2O$) forms as powder-like masses on surfaces of the black shale. Melanterite was observed transformed to rozenite ($FeSO_4.4H_2O$) after several hours, which coincides with the melanterite dehydratation process (7). According to Ehlers and Stile (8), the melanterite conversion into rozenite is a quick and reversible process that depends on moisture variation. Wiese et al. (9) found that after long periods in the laboratory and therefore extensive dehydration, rozenite would finally convert into the more stable iron sulfate szomolnokite ($FeSO_4.H_2O$).

Halotrichite ($FeAl_2(SO_4)_4.22H_2O$) also forms on surfaces of the black shales. Wiese et al. (9) consider this sulfate together with szomolnokite as the most stable phase among the products of iron sulfide weathering.

Pickeringite($MgAl_2(SO_4)_4.22H_2O$). Because this phase is an isomorph of halotrichite, its identification was made by XRD using quartz as an internal standard. Likewise, the presence of Mg and the absence of Fe was determined by microanalisys using SEM-EDXA. Like halotrichite, pickeringite shows a needle-like morphology (Fig. 4a) very similar to that of secondary ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ (Fig. 4b) found in Maresme damaged concretes.

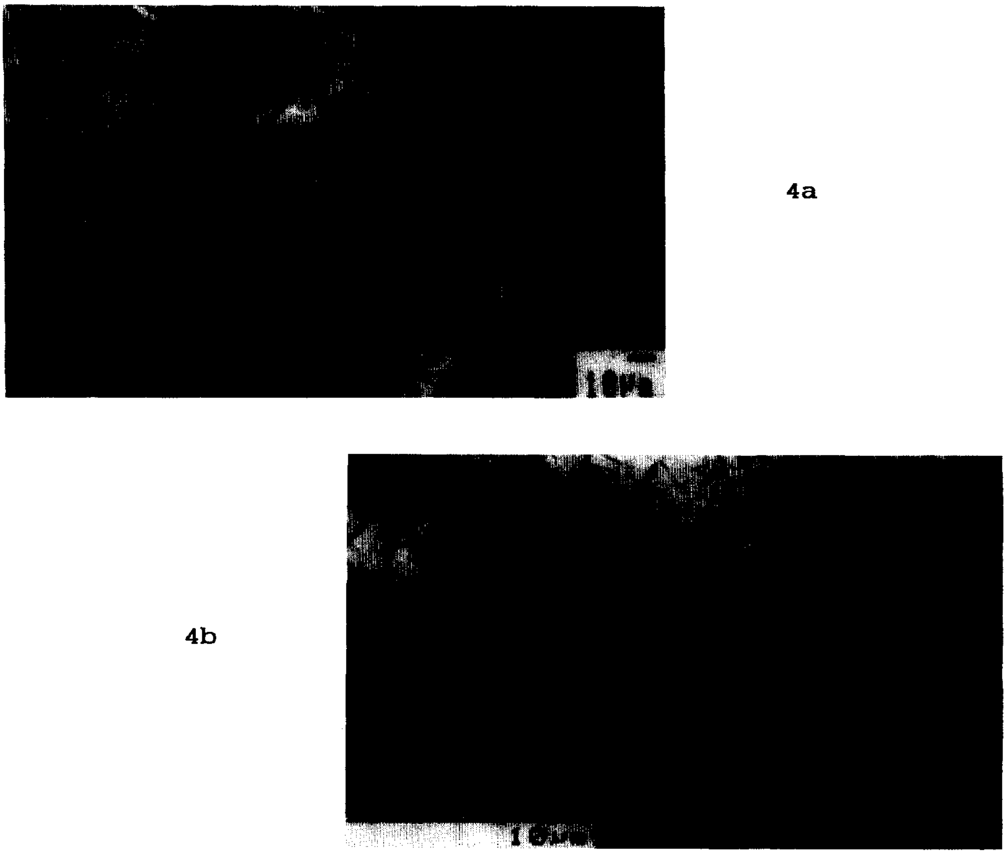

FIG.4
4a: Pickeringite SEM, 4b: Secondary Ettringite SEM

Gypsum ($CaSO_4.2H_2O$) comprises the rest of the sulfates, forming efflorescences either on surfaces or in the cracks of the black shales.

Discussion

The significance of the mineral associations found in Mont Palau quarry has been discussed from the point of view of their thermodynamic stability. The Fig. 5 shows the conditions under which the most relevant aqueous species and minerals involved in the system become stable. The stability limits are based on the assumption of chemical equilibrium of the reactions presented in the Table 1. The total solute concentrations assumed in water are within the limits of those found in surficial waters involved in sulfide weathering (12,13). The aqueous carbonate species have been assumed in equilibrium with atmospheric CO_2. Because of the log-scale of the diagram in Fig. 5, variations in these magnitudes may move slightly the boundary limits but do not alter significantly our discussion.

Surficial waters dissolving atmospheric oxygen plot in the higher pε region of the water stability field in Fig. 5. Under such oxidizing conditions neither pyrrhotite or pyrite are stable. As a consequence, the crystals of both sulfides dispersed in the black shales become oxidized giving rise to minerals and aqueous species stable in these conditions. The overall reaction for pyrite oxidation is commonly written as (13,14):

TABLE 1
Equilibrium constants of the reactions involved in Fig.5

	log $K_{25^\circ C}$	Ref.
Aqueous species		
1) $1/2O_2 + 2e^- + 2H^+ = H_2O$	41.56	(10)
2) $H^+ + e^- = 1/2H_2$	0.00	(10)
3) $Fe^{3+} + e^- = Fe^{2+}$	13.03	(10)
4) $Al(OH)_2^+ + 2H^+ = Al^{3+} + 2H_2O$	10.10	(10)
5) $HSO_4^- = SO_4^= + H^+$	-1.99	(10)
6) $S^= + 4H_2O = SO_4^= + 8H^+ + 8e^-$	-20.74	(10)
7) $HS^- + 4H_2O = SO_4^= + 9H^+ + 8e^-$	-33.65	(10)
8) $H_2S + 4H_2O = SO_4^= + 10H^+ + 8e^-$	-40.64	(10)
9) $CO_2(aq) + H_2O = HCO_3^- + H^+$	-6.36	(10)
Minerals		
10) $FeS_2 + 2H^+ + 2e^- = Fe^{2+} + 2HS^-$	-18.48	(10)
11) $FeS + H^+ = Fe^{2+} + HS^-$	-3.92	(10)
12) $S + H_2O = HS^- + 1/2O_2 + H^+$	-43.66	(11)
13) $Fe(OH)_3 + 3H^+ = 3H_2O + Fe^{3+}$	4.89	(10)
14) $FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$	-0.24	(10)
15) $CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.85	(10)
Gases		
16) $CO_2(g) = CO_2\ (aq)$	-1.47	(10)

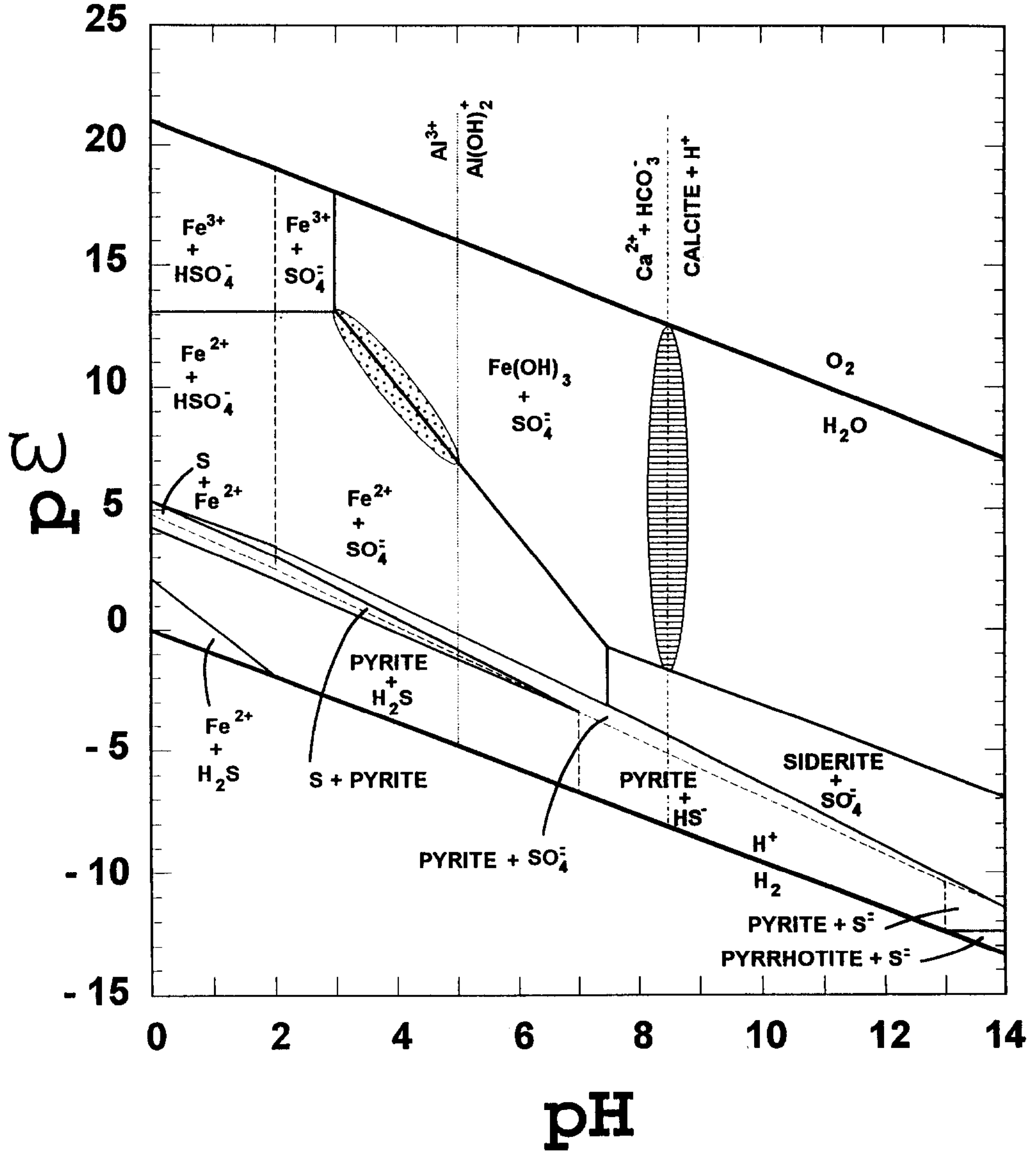

FIG. 5

pε -pH diagram of selected aqueous species and minerals in the presence of water at 25°C, $\Sigma S=10^{-2}$, $\Sigma Fe=10^{-4}$, $\Sigma Ca=10^{-4}$ mol/l, and $P_{CO2}=10^{3.5}$ bar. The lines limit areas of mineral stability and of predominance of aqueous species (Fe=plain, S=dashed, Al=dotted, Ca=dashed-dotted). The shaded areas indicate the more probable pε-pH values of weathering waters associated to black shales (dotted area) and limestones (striped area).

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{=} + 16H^+$$

where the Fe^{2+} is oxidized to Fe^{3+} by the action of bacteria.
A similar reaction could be written for pyrrhotite. The high amount of H^+ ions resulting from the reaction is responsible for the low pH commonly described (12,13). This high acidity of the solution accounts for the hydrolysis of silicates from the shales, giving also Ca^{2+}, Mg^{2+}, K^+, and Al^{3+} to the solution. The Fe^{3+} ions released from sulfide oxidation forms ferrihydrite (amorphous $Fe(OH)_3$), an insoluble phase commonly found in the quarry and aggregate piles. On the contrary, sulfate minerals are highly soluble and have not been included in Fig. 5. Evaporation of water, however, produces the precipitation of hydrated sulfates as characteristic crusts and efflorescences on surfaces. The formation of melanterite, halotrichite and pickeringite requires that, in addition to $SO_4^{=}$, the parental aqueous solution contained Fe^{2+} and Al^{3+} as predominant iron and aluminum species (15,16), respectively. As a conclusion, the weathering waters infiltrating the black shales have conditions close to the Fe^{2+}+Al^{3+}+$SO_4^{=}$ and $Fe(OH)_3$ limit (dotted area in Fig. 5).

In the case of limestones, however, the dissolution of calcite is able to consume most of the H^+ ions resulting from the oxidation of iron sulfides (reaction 15 in Table 1). The pH value of the water is maintained close to the calcite dissolution equilibrium (striped area in Fig. 5), and the iron and aluminum aqueous speciation described for the black shales environment are not possible. In agreement with prediction the only sulfide weathering product in limestone is ferrihydrite whereas iron and aluminum hydrated sulfates are not observed .

Jarosite, a common K-Al-bearing sulfate has not been found in the Mont Palau quarry. Nordstrom et al. (13) describe that, despite of the large supersaturation in jarosite of the acid mine stream waters from West Shasta District in California, this mineral is only found in particular places, probably related to bacterial activity.

The results presented here agree with those of other authors for the process of concrete degradation caused by iron sulfide weathering. Moum and Rosenquist (17) describe the same mineral associations in the degraded concrete formed in large areas of Norway when shales from the lower Cambrian-Ordovician with large amount of pyrrhotite are used as aggregates. Quigley and Vogan (18) refer to similar mineral phases in a study of the expansion generated in buildings of Otawa (Canada) constructed of iron sulfide bearing black shales from the Lorraine Formation of Ordovician age.

Conclusions

In Mont Palau quarry the following minerals of expansive character affecting the concrete durability have been identified: ferrihydrite, gypsum, halotrichite, pickeringite, melanterite and laumontite. These compounds were formed by a process in which the most important role is assigned to the pyrrhotite and pyrite weathering. However, the two lithologies, black shales and limestones, that compose the quarry aggregates show a very different geochemical behavior. Whereas the phases referred to above are always associated with the black shales, in the limestones the dissolution of calcite keeps the pH values high enough to avoid the formation of hydrated expansive sulfates.

Therefore, the aggregates extracted from Mont Palau quarry must be considered harmful to use in concrete manufacture. This is specially true if the geologic structure of the quarry precludes the selective industrial extraction of the limestones, which are also not advisable but much less harmful than black shales.

Acknowledgements

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