THE PECULIAR MINERALOGIC SITE OF THE ALUM CAVE (VULCANO, SICILY)

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ABSTRACT

The Alum cave is a small tectonic cavity hosted in the volcanic tuff close to the pier of the Vulcano island: it has several entrances all a few meters above the sea level.

This cave was well known since the last century due to the abundance and variety of the minerals growing inside: for a period the cave was partially transformed into a quarry to exploit the alum.

Without any doubt the Alum cave is one of the most important sites for the cave mineralogy in the world, hosting more than 10 different and rare minerals, nevertheless up to present no topographic map of this cave was done and no photographic documentation was available. Moreover in the last eighty years nobody made a control on the minerals still present inside the cave.

This is the reason why we decided to explore this cavity, whose map is here presented. During the exploration we also did a detailed analysis of the hosted cave minerals, which still cover a large part of the cave walls: about the 40% of the minerals described in the past and many new ones have been observed still growing inside the cavity.

In the present paper all the observed cave minerals are shortly described and the genetic mechanisms discussed. Quite all the chemical deposits of the Alum Cave are generated by the reaction of the fumarolic fluids over the volcanic tuff in presence of sea sprays and aerosols.

RIASSUNTO

La Grotta dell'Allume é una piccola cavità di origine tettonica sviluppatasi nelle vulcaniti presso il porto dell'isola di Vulcano quasi a livello del mare. Questa cavità era già molto famosa nel secolo scorso per la grande abbondanza dei minerali che vi si trovavano: essa fu anche per un certo tempo utilizzata industrialmente per l'estrazione dell'allume.

Ciononostrante sino ad oggi di questa grotta non esisteva ancora un rilievo e una documentazione fotografica, inoltre da piu' di ottanta anni nessuno si era preoccupato di verificare quali minerali ancora esistessero al suo interno.

Considerato la grande importanza che questa grotta ha nel panorama mondiale dei minerali di grotta, a dispetto delle sue modeste dimensioni, si é deciso di procedere alla esplorazione della Grotta dell'Allume, di cui viene qui riportato il rilievo topografico. Durante l'esplorazione si é anche compiuta una dettagliata analisi delle mineralizzazioni presenti, che si sono dimostrate essere ancora molto varie ed interessanti.

Nel presente lavoro vengono quindi brevemente descritti i vari speleotemi osservati, la cui genesi può esser ricondotta innanzitutto all'attività fumarolica presente in prossimità della Grotta dell'Allume e poi alla presenza di abbondanti spray e aereosol marini.

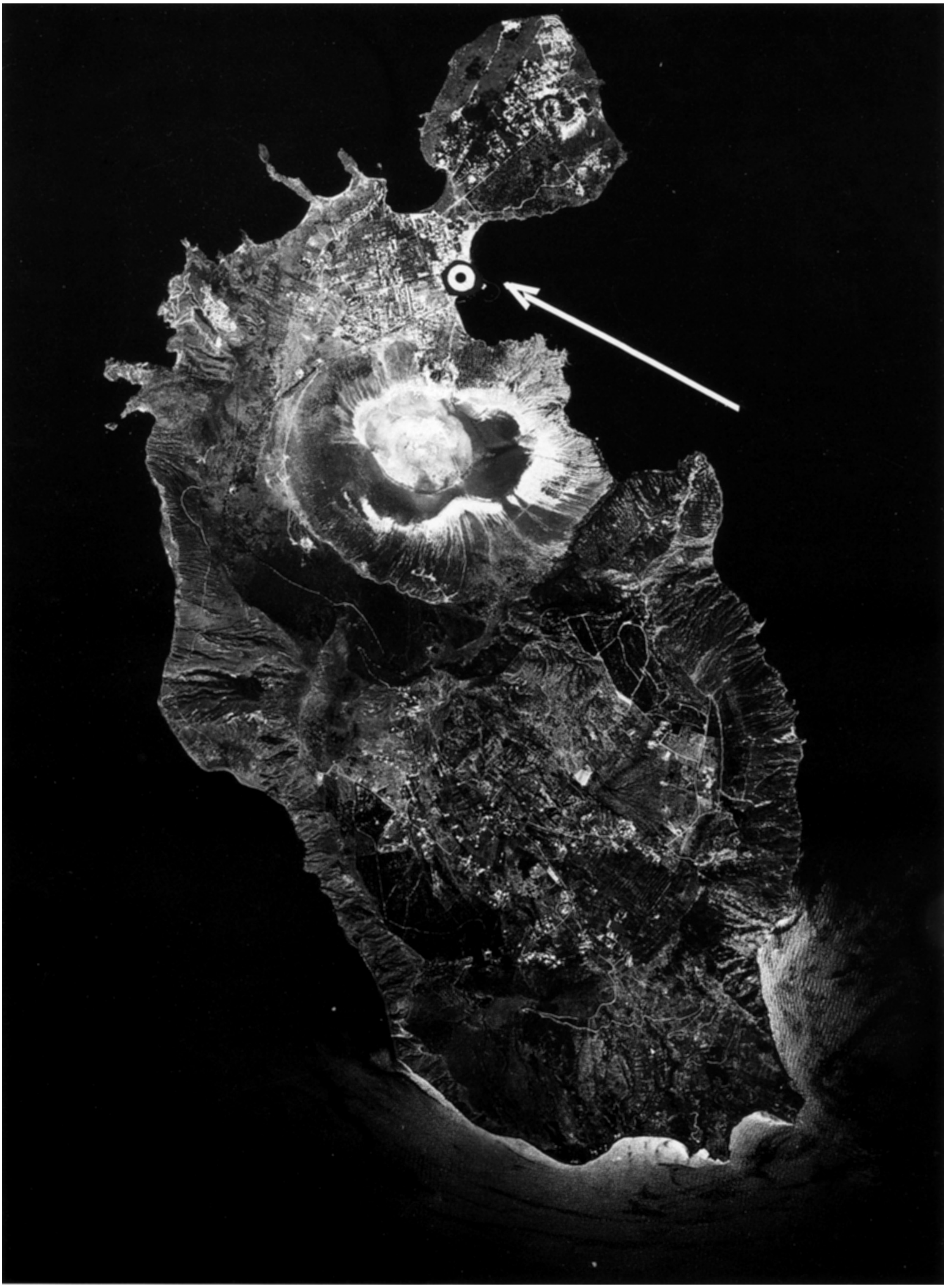

Fig. 1- Aerial photo of the Island of Volcano with location for the Alum Cave

INTRODUCTION

Over the past few years we have become aware that volcanic caves, on first sight seemingly scarce on speleothems are in reality perhaps the cave environment where it is possible to locate the greatest variety of secondary cave minerals (FORTI, 1992).

The motive for this variety depends essentially on the possibility that these caves have, contrarily to the normal karst ones, of developing peculiar speleogenetic mechanisms mostly based on the thermal fluid activity which can be present inside the cavity even a long time after its genesis .

The Island of Vulcano represents perhaps the best example in the world for the abundant variety of secondary cave minerals, due to its strong volcanic activity that has continued uninterrupted for some thousands of years.

In the XVIII Century SPALLANZANI (1792) cited an important cave on this island where abundant alumogen and ammonium chloride were found.

But the natural cavity of the Alum Cave near the Levante Port (see fig. 1) is by far and the most important natural cavity of the Vulcano Islans. This cave was already well known for the great abundance of secondary mineralization, essentially alum (LACROIX, 1907) and a quarry was settled thereinside to exploit alum during a good part of the XIX Cent. (PANICHI, 1914).

A very detailed study was effectuated at the beginning of the 1900's on the minerals of the Island of Vulcano and on that occasion 14 secondary minerals were cited deriving from the Alum Cave (PANICHI, 1914).

However, from then on this cave was lost to memory, so much so, that the cavity with its extremely important speleothems were in no way cited in the monography «Cave Minerals of the World» (HILL & FORTI, 1986).

The purpose of the present work taken on is to try to fill this lapse and principally to see how and up till what point the cave still hosts the minerals described in the past.

THE CAVITY AND THE HOSTED SPELEOTHEMS

The first work commenced with the cave survey, or rather what was left of it; infact the exploitation of alum in the previous century plus road construction had in part brought about the demolition of the Alum Cave.

All that remains of the cave, which practically opens at the foot of a small hill of markedly fractured and altered volcanic tuff, is presented as a great chamber with some lateral galleries connected externally by various, more or less large entrances (See Fig. 2,3).

Fig. 2.- General photo of the entrances to the Alum Cave

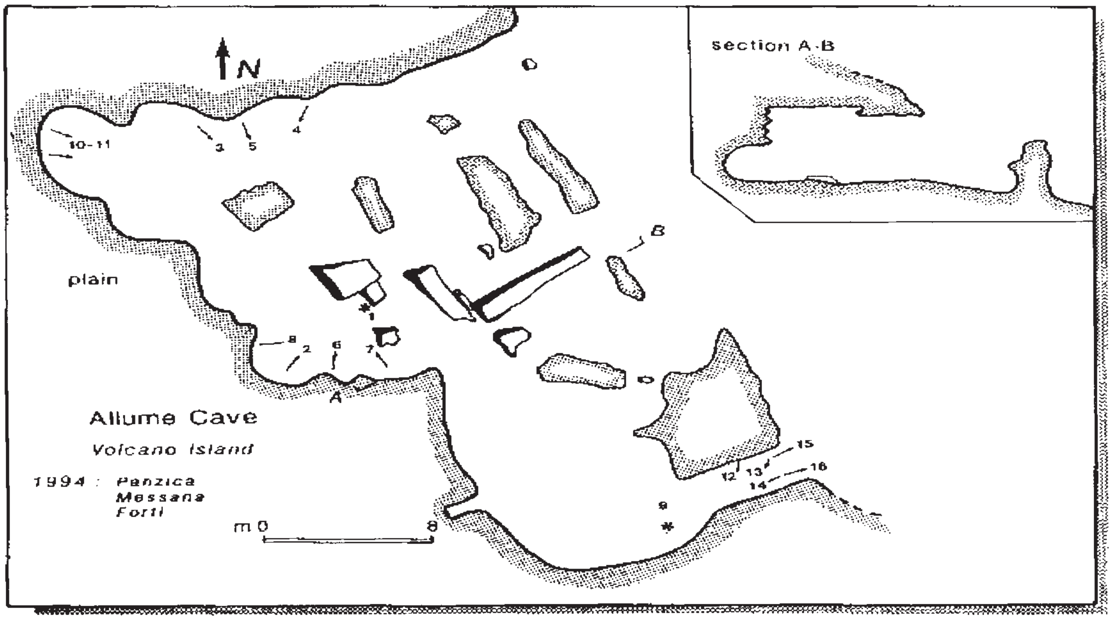

Fig. 3.- Map of the Alum Cave with sample locations

The cave walls are almost completely covered by a 1-3cm. layer of very thin acicular crystals of a translucid white or pearl grey colour while in more restricted areas we observed yellowish, bluish and greenish inflorescence and/or powdery masses.

The most different variety of deposits were located in the proximity of a floor crack which released hot vapours.

Selective samples were taken (16, see Fig. 3) based on chromatic and morphologic observations, organoleptic analysis and U.V florescence realized directly in the cave. Samples taken for further study were:

1 - Sample of the wall rock , made up of pumice englobed in micocrystalline cement. This sample has not been analysed for this work.

2 - Long white acicular crystals with a white U.V. fluorescent base. A microscopic view of the sample shows a construction of efflorescence aciculars positioned in a radial aggregation. The single filaments are transparent with a vitreous shine or iridescent and in some cases assume the typical aspect of hair (halotrichite). At the top of the fibre, individual crystals of an octahedral form are noted while in other portions the filaments are encrusted with a pulverulent material (soda or potash alum?).

3 - Coralloid. The microscope evidenced that each globule was constructed by the aggregation of microscopical individual elements, shining transparent with a tabular form (gypsum), while the surface showed even some elongated individual crystals (halotrichite ?).
4 - Microgours of an iron gray colour. The microscope showed that the sample was constructed by an aggregation of iso-oriented crystals, gray on the surface and snow white on the inside(gypsum).

5 - Vitreous crystals on the edge of a partially fractured speleothem. The microscope showed similar characteristics of sample 3. Very limpid crystals (gypsum) are present on the globule, while many of the fractures and micro cavities are filled with a pulverulent material (bassanite) which in some cases covers the limpid crystals.

6 - Dust that is acid to the taste. The microscope shows a desegregated mass of tabular or forming brief filaments, the individual crystals appear transparent with vitreous brightness. This would seem typical of tamarugite. There are also small masses of a shiny gray/brown colour with characteristic conchoid fracture (potash alum and/or soda alum?). Though rarely a whitish earth like dust is present (hydrobsaluminite ?)

7 - Plastic acicular crystals. The microscope shows a mass of woven filaments. The colour of the mass is white while the single filaments are transparent with vitreous brightness (halotrichite). Rare crusts are found in the mass, of a shiny gray/brown with evident conchoid fracture (potash alum) and shiny gray crystals of an octahedral form as in sample 2 (soda alum).

8 - A yellowish rim on fibrous materials. The microscope evidences the absolute dominance of needle like filaments component (halotrichite). The yellowish colour evidenced microscopically is apparently correlated to an earth like dust and tends to disappear with an increase of the enlargement. In some zones we noted transparent octahedral shaped aggregated crystals with glassy brightness and of grayish colour (soda or potash alum).

9 - Canary yellow dust. The microscope shows an aggregation of little individual pieces in a soft light mass of a yellow sulphur colour. It was possible to observe crystallines of a pinacoidal aspect inside a micro cavity. When the material was placed in water it melted giving origin to a yellow solution that became turbid if reheated (copiapite).

10 - Crust with a yellow U.V.fluorescence. Under the microscope the material looks like a snow white or slightly pink deposit; the little crystals which compose it present the usual pointed end and are perfectly transparent and shiny. They are of medium hardness and break-up very easily into many microscopic individual pieces. The most resistant aggregation could be of soda alum while the individual pieces that break-up (more rare) could be of potash alum or tamarugite (this in definitely minor quantitative).

11 - A rim with strong yellow violet U.V.fluorescence. It is impossible to distinguish it from sample 10 using the microscope.

12 - Brilliant yellow blades. The brilliant yellow colour tends to diminish under the microscope changing to a reddish brown-pinkish shade (metavoltine). The mass is constructed from piramidal elements. Some crystals show evident esfoliations and fractures perhaps through drying out (zaherite). The presence of needle like elements could be correlated to alum.

13 - Pale blue crusts near a crack with escaping hot vapour. It appears to be massive granular material under the microscope in a lovely shade of pale blue and transparent. The few crystalline elements recognisable have a pinacoidal abit (hematite). There is an extremely friable earth like material only slightly cemented (gypsum) in contact with this pale blue mass where small aggregations of transparent gray crystallines with a glassy aspect (soda alum?, taramugite?) can be observed. .

14 - Greeny/blue rim near a crack with escaping hot vapours. The sample seemed constructed with prevalently a greenish component and a minor whitish material seen under the microscope. The components are the same morphologically , transparent with a glassy shine and sometimes globular in shape. The sample would seem to be made of tamarugite partially discoloured green from copper impurity (suggested by the presence of copper sulphate in the nearby sample 13).

15 - Reddish coloured rim near a fracture with an active fumarole. Microscopic analysis shows that the rim is formed by various overlying blades from glassy brightness to resinous. A strong enlargement reveals the single blades are made of long individual crystallines which serve as a support for the smaller needles, though all of the same material (thenardite).

16 - A bluish/white rim near an active fumarole. The sample appears constructed by different mineralogical phases under the microscope. The most abundant are those made up of minute prismatic transparent needles (halotrichite). Its possible to recognise little groups of pyramid shaped individual pieces, perhaps octahedral with glassy brightness (soda alum? and/or potash alum? alumogen?). A thin layer of whitish pulverulent material is also present perhaps deriving from bumps or partial dehydration of the sample.

DETECTED MINERALS

As all the minerals were crystalline a X-ray diffraction analyses on the dust was utilised to identify the mineralogic species present in each sample. The results have since been confirmed by microscope analysis and by an electronic microscope study(see Fig. 4-14).

All the analised samples (15) have almost always resulted as mixture of more minerals, the most abundant is the halotrichite. The following reports the mineralogical composition in order of the relative quantity in each sample of speleothem.

2	halotrichite, soda alum, hydrobasaluminite (tr)
3- 4- 5	gypsum, bassanite (tr)
6	tamarugite, soda alum, potash alum, hydrobasaluminite (tr), gesso (tr)
7	halotrichite, soda alum, potash alum (tr)
8	halotrichite, soda alum, tamarugite, potash alum (tr), gesso (tr)
9-	copiapite, alumocopiapite (tr)
10-11	halotrichite, potash alum, soda alum, tamarugite (tr)
12	zaherite, metavoltina, alumogen
13	chalcantite, soda alum, tamarugite, gesso, aubertite
14	tamarugite
15	thenardite
16	halotrichite, soda alum, potash alum, alumogen

The studied samples revealed 15 different mineralogical species all referable to sulphate, more or less hydrated.

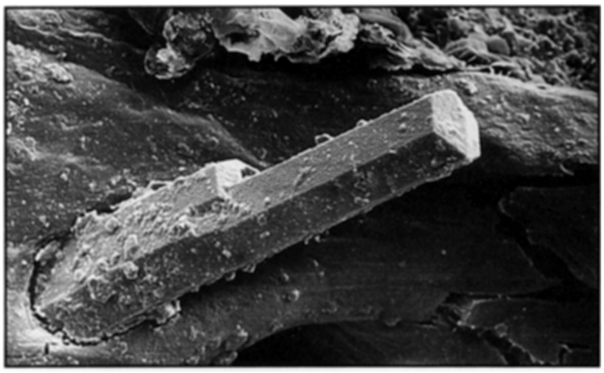

Fig. 4.- Calcantite crystal from sample 13 (photo SEM, Paolo Ferrieri)

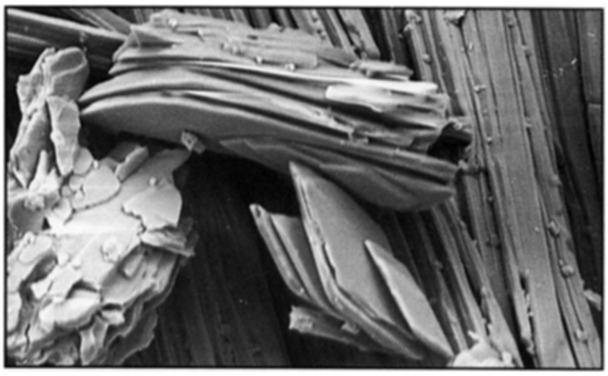

Fig. 5-Tabular crystals of copiapite from sample 9 (Photo SEM, Paolo Ferrieri)

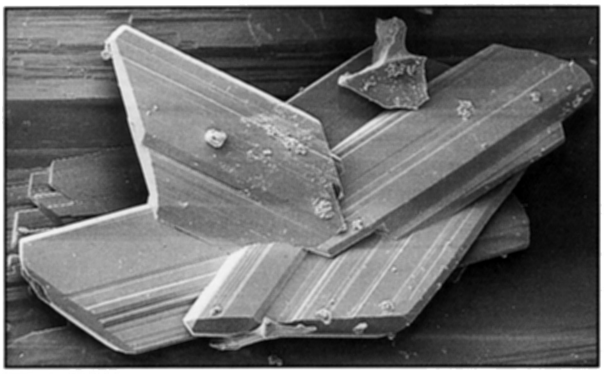

Fig. 6.- Gypsum rosette with bassanite granules from sample 5
(Photo SEM, Paolo Ferrieri)

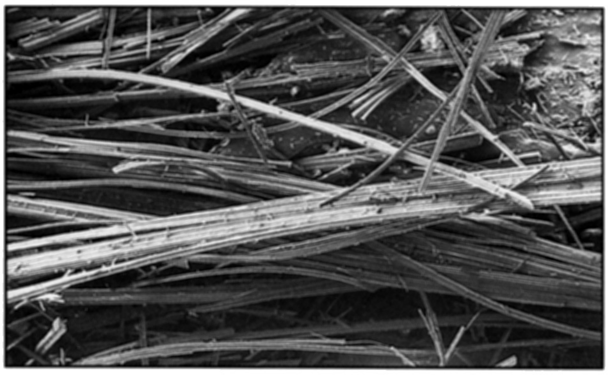

Fig. 7.- Bunches of halotrichite crystals from sample 2
(Photo SEM, Paolo Ferrieri)

Fig.8.-Tabular halotrichite crystals from sample 7 (Photo SEM, Paolo Ferrieri)

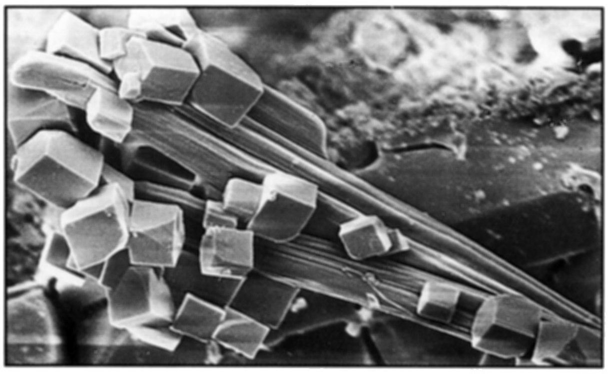

Fig.9.-Cubo-octahedral crystals of soda alum on the top of the halotrichite filaments from sample 8. (Photo SEM, Paolo Ferrieri)

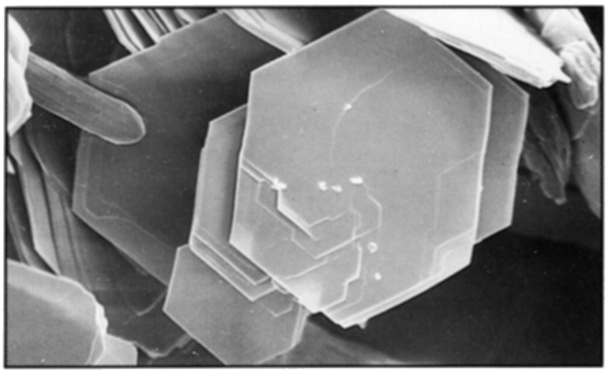

Fig. 5-Tabular crystals of copiapite from sample 9 (Photo SEM, Paolo Ferrieri)

Fig. 11-Tamarugite rosette from sample 14 (Photo SEM, Paolo Ferrieri)

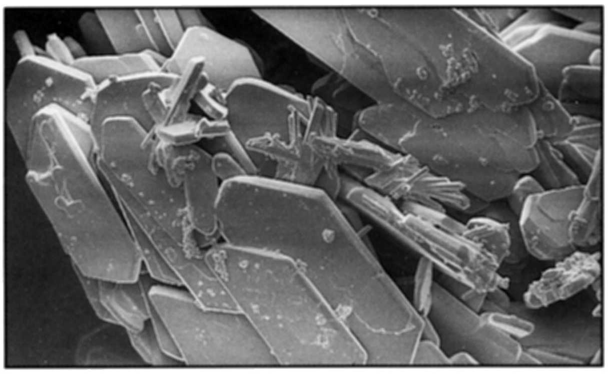

Fig. 12-Tamarugite crystals with small crystals of soda potash alum from sample 6 (Photo SEM, Paolo Ferrieri)

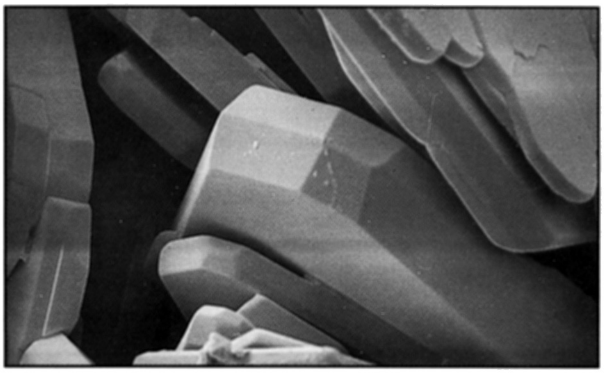

Fig. 13-Sound tamarugite crystal from sample 6 (Photo SEM, Paolo Ferrieri)

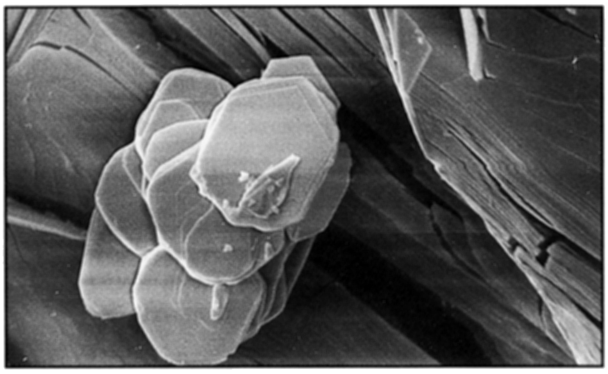

Fig. 14-Evident from of dehydration in the Zaherite mass surmounted by metavoltine from sample 12 (Photo SEM, Paolo Ferrieri)

The genesis of all these minerals is surely referable to the combined action on the volcanic tuff, which appears greatly altered by fumarolic vapours still escaping from some wall and floor fractures in the cave and by the abundant marine aerosols inside the cavity due to the vicinity of the sea.

The study proceeds with a correlation of what was observed at the beginning of the century by PANICHI on tab.1, where all minerals observed in the Alum Cave are reported in alphabetic order . It is interesting to observe that out of a total of 23 different minerals only 6 are noted in both studies. This would certainly depend partially on the speleothem samples analysed : in fact during this study all minerals were knowingly left out that didn't seem made from sulphate (as opal and aragonite speleothems) Some others could have gone unnoticed in the first or second study due to great dispersion and the modest amount of some of the mineralogic species observed.

The presence in the actual study of 9 minerals not reported at the beginning of the century, in our opinion would demonstrate that the conditions inside the Alum Cave (essentially fumarolic exaltation) have changed through time, with consequent possibility of speleothem deposition and with a different chemical composition.

What is exceptional is the fact that we found 5 absolutely new cave minerals in one time only during our study (aluminocopiapite, aubertite, copiapite , hydrobasaluminite and zaherite).

Table 1- Observed minerals (P: PANICHI; F: this study) in the Alum Cave and their principal morphological characteristics.

mineral	ref	formula	description
Aluminocopiapite	F	(Mg,Al)(Fe,Al)4(S04)6(0H)2·20H2O	tuffs of small transparent crystals
Alunogeno	P-F	Al2(SO4)3·17H2O	small white to transparent crystals
Aragonite	P	CaCO3	coralloids
Aubertite	F	CuAl(SO4)2Cl·14H2O	pale green to transparent small masses
Bassanite	F	CaSO4·1/2H2O	powder over gyspum crystals
Chalcantite	F	CuSO4·5H2O	pale blue bothrioidal masses
Copiapite	F	(Fe,Mg)Fe4(SO4)6(OH)2·20H2O	tuffs of small transparent to yellow crystals
Coquimbite	P	Fe2(SO4)3·9H2O	small violet to pink hexagonal tablets
Gypsum	P-F	CaSO4·2H2O	acycular crystals
Halotrichite	P-F	FeAl2(SO4)4·22H2O	white acicular fibers
Hydrobasaluminite	F	Al4(SO4)(OH)10·36H2O	small plastic clayly masses
Kalinite	P	KAl(SO4)2·11H2O	small octaedral crystals
Keramohalite	P	Al2(SO4)3·18H2O	shining silver fibrous stalactites
Metavoltina	P-F	(K,Na,Fe)5Fe3(SO4)6(OH)2·9H2O	thin yellow hexagonal blades
Millosevichite	P	Al2(SO4)3	violet to green hygroscopic crusts
Opal	P	SiO2·nH2O	white small stalactites
Pisanite	P	(Fe,Cu)SO4·7H2O	blue-green crusts
Potash Alum	P-F	KAl(SO4)2·12H2O	octaedral and cubic small crystals
Soda Alum	P-F	NaAl(SO4)2·12H2O	octaedral and cubic small crystals
Tamarugite	F	NaAl(SO4)2·6H2O	snow white masses of elongated crystals
Thenardite	F	NaSO4	translucent crusts
Voltaite	P	K2Fe5Fe4(SO4)12·18H2O	pale green crusts
Zaherite	F	Al12(SO4)5(OH)26·20H2O	translucent to vitreous elongated crystals

CONCLUSION

Study effectuated on chemical deposits from the Alum Cave of the Island of Volcano has confirmed the exceptional richness of secondary cave minerals, that they are still present and continue to develop inside this small but definitely interesting cavity.

A good 5 of them have only been observed in this cave , which considering its peculiarity would merit a great deal more attention on the part of territorial authority .

The number of hosted mineralogic species and that of the minerals up till now only observed inside this small and in some ways insignificant cave transform it perhaps into the most important in the world for the hosted secondary deposits.

Nevertheless, the Alum Cave is actually without any kind of protection and unfortunately in the last few years has been transformed into a rubbish tip.

All that remains is to hope for a possibility to save the cave in the near future, even through this study. We need to stop further degradement and transform it first of all into an «outdoor museum» dedicated to the cave minerals and then into an important laboratory where we can study the evolution in the time of the speleothems which form in function of the physico-chemical properties of the fumarolic gases rising inside it .

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