STUDY ON THE CONCRETIONS OF LAVA TUBES WHICH WERE FORMED BY THE 1991-93 ERUPTION ON MOUNT ETNA.

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Abstract

The 1991-93 lava flow on Mount Etna created many lava tubes all over its length. The spelaeologists of Centro Speleologico Etneo explored them as soon as the internal temperature let it. Cutrona Tube was the first one to be inspected. Concretions of different minerals were discovered in it. Among them there were some which had never been found in literature. The next step was a careful examination of two other tubes, which were born by the same eruption. The aim of our research was to collect a wide set of specimens of mineralogical species and to conjecture about the genetic processes, which originated them. Two different methods were used to conduct the analysis of concretions: traditional X-ray powder diffraction and IR spectroscopy. The purpose of this double analysis was to compare and evaluate the efficacy of the second method applied to this kind of research. According to previous studies the discovered concretions are mainly made up of Halite. The imposing concretions, which are present in the lava tubes formed by the 1991-93 eruption, are considered deeply connected to pneumatolytic phenomena acting inside lava itself, that is linked to the fumaroles without roots.

Introduction

Mount Etna is a volcano with a complex structure. It rises from Catania plain and its summit is at, about, 3300 metres.

On 14 December 1991 an eruption started. It lasted sixteen months and ended in March 1993. An eruptive fissure cracked on the west high wall of Valle del Bove, at an altitude of about 2400 metres. The lava flow, which came out of it, nearly reached Zafferana build-up area, a piedmont town located on the east face of the Etna. The lava flow reached a length of about 8.5-km. When the eruption ended, the members of Centro Speleologico Etneo carried on an intense exploration of lava tubes. They discovered many tubes, but only a few numbers of them could completely be explored because of their high temperature.

According to the physico-chemical features of lava and the topographical peculiarities of land, along the lava flow many lava tubes took form. All the lava tubes explored are the result of ‘a-‘a lava flow, the same kind as most other tubes present on Etna (Licitra, 1983).

Cutrona tube (MC1) was the first tube to be completely explored. An intensive phenomenon of concretions was discovered inside it (Forti et al., 1994). Later, after the good result of the first exploration, new inspections were conducted in other lava tubes originated from the same lava flow, among others: Grotta del Fumo (see Fig.1) and S.G.2 tube. They are respectively upstream Cutrona tube, near the eruptive fissure and downstream the same tube, scantily under Salto della Giumenta in Val Calanna. Because of the thermic conditions, the inspections of these tubes was impossible for a very long time.

Fig. 1 - Schematic map of Etna territory, location of the 1991-93 lava flow and of the analysed tubes.

More than a year after the end of the eruption rich amount of concretions were found in these tubes, although it was not comparable to that found in Cutrona tube.

The tubes, where the analysis were conducted, are located at different distance from the vents of the 1991-93 eruption: Grotta del Fumo partly coincides with the eruptive fissure (see Fig. 4), S.G.2 tube is located at 5.5 km from this eruptive fissure and Grotta Cutrona, whose presence had already been determined, is located between them. This is why the author decided to analyse the possibility of a mineralogical variation in the examined concretions according to the different distances from the eruptive fissure. The next step was the concrete analysis of the set of mineralogical specimens by means of X-ray powder diffraction and IR spectroscopy.

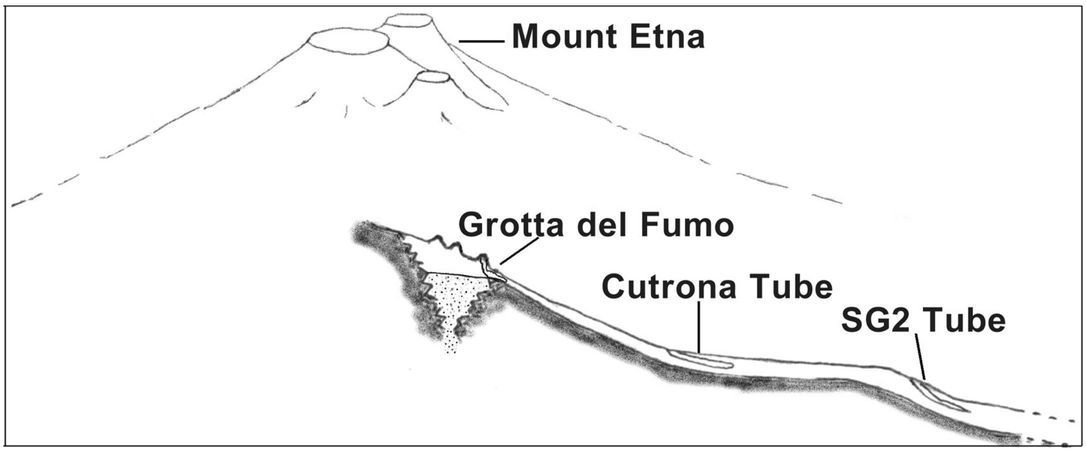
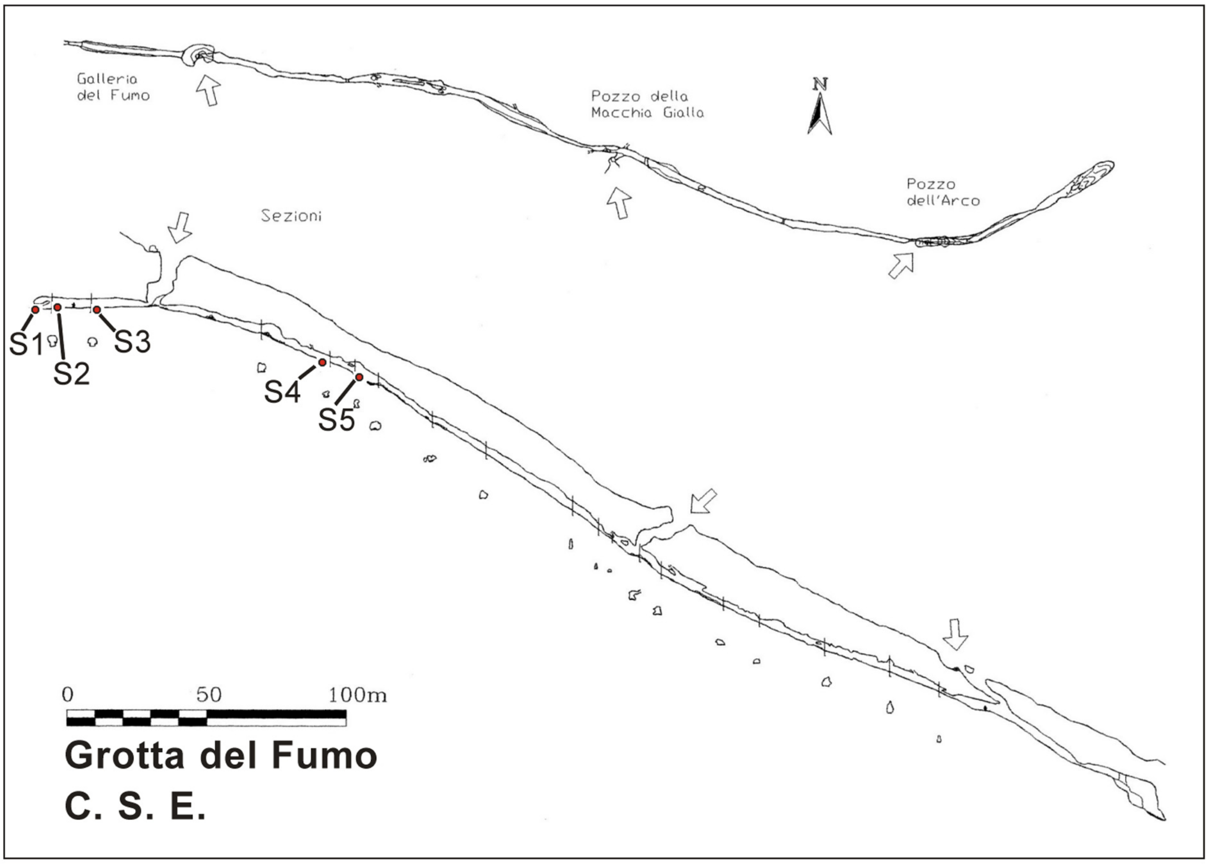


Fig. 2 - Schematic cutaway of the 1991-93 lava flow; it is important to highlight the partial overlap between Grotta del Fumo and the eruptive fracture.



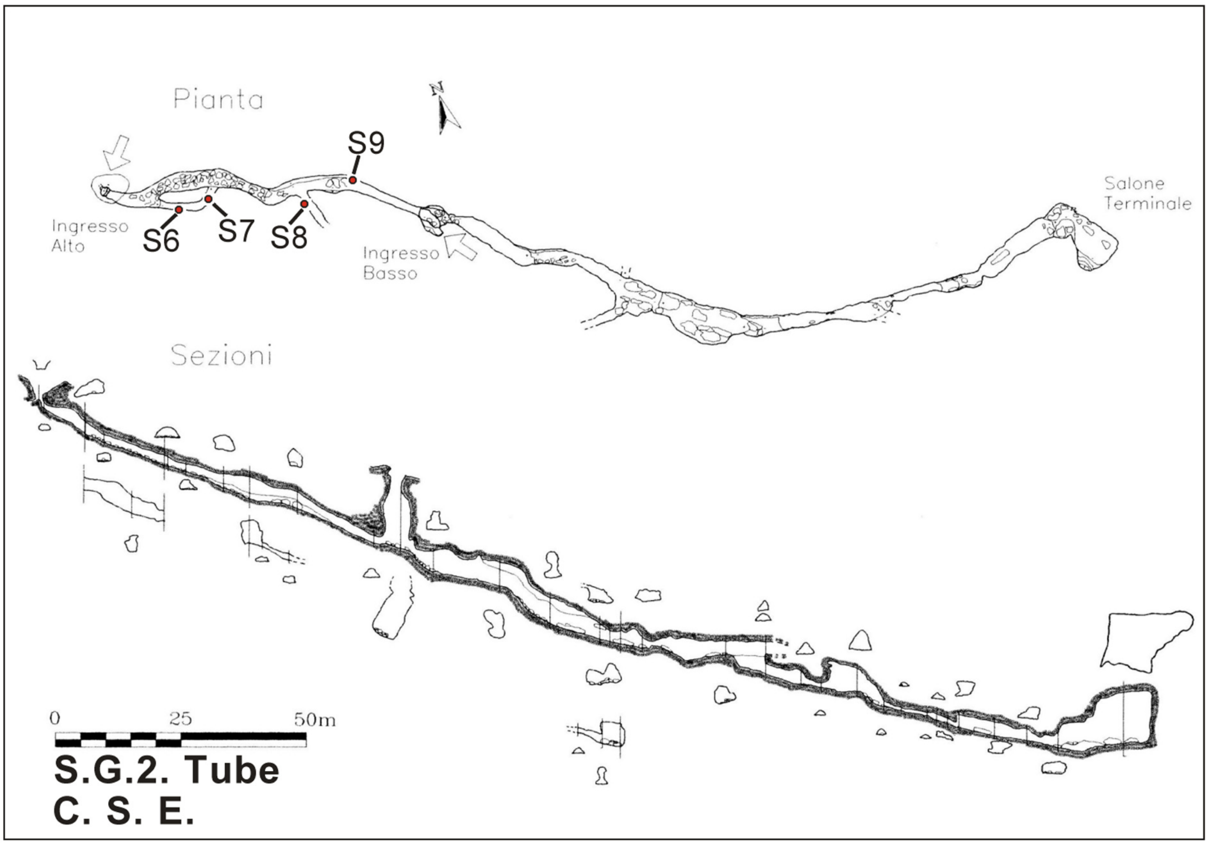


Fig. 3 - G. del Fumo and G.S.2 tube topography. The red marks indicate the places where the specimens were drawn. The abbreviations stand for the used specimens.

Specimen descriptions

The set of specimens was constituted according to the organoleptyc and morphochromatic features of concretions. The specimens were drawn from different places of each tube.
The descriptions of the specimens, which were picked up in the two described tubes, is as follows:

High Valle del Bove - Grotta del Fumo (see Fig. 3) - survey of 5 June 1995

Specimen 1: it is made up of clot-shaped aggregates which seem like the sea salt. It is wet at the touch and vitreous in its appearance. It does not taste too salty.

Specimen 2: it is made up of crusty concretion, which sometimes are coralloid. It is of milk-white colour and salty taste. It can easily be turned into dust (always white). It is anhydrous at the touch.

Specimen 3: it is made up of spheroidal aggregates of translucid orangey-red colour. It is salty and wet.

Specimen 4: it is a light brown crusty concretion. It is salty and dry.

Specimen 5: its colour is translucid milk-light. It is made up of spheroidal aggregates which are wet. They are covered of a patina, which is made up of spheroidal impurities (but milk-white inside). It is salty.

Salto della Giumenta - S.G.2 tube (see Fig. 3) - survey of 11 November 1995

Specimen 6: it is a milk-white concretion. This one is a stalactite rich in vesicles resulting from percolation. The stalactites are cannulae growing in length. They can have a smooth surface or they can be rich in globular protuberances, which are very often split.

Specimen 7: it is a coral-shaped milk-white concretion, vaguely resembling small ferns.

Specimen 8: pulverulent, white, white-grey concretion. It was found on the south branch where a strong hot current of air is present. The concretions seem to be made up of small globular flocks, which resemble the mould.

Specimen 9: it was found in the final part of the south branch where there was little or no air current (already at low temperature). The concretion is milk-white with vitreous brightness. Its innermost part is more similar to the transparent vitreous salt.

Analysis methods

The specimen analyses were carried out by means of infra-red spectroscopy (IR) and x-ray powder diffraction. The latter represents one of the most common and reliable methods of research in the field of mineralogical diagnostic. On the contrary, IR spectroscopy is commonly not used for this kind of analysis. However it was used in this specific case because it has a number of advantages, among which the fast performance and the need of small quantity of mineral: only 2 mg of concretion, for each specimen, were used.
The specimens were powdered and analysed by means of both research techniques.
A Philips diffractometer, which was equipped with a Bragg-Brentand geometry goniometer PW1130([1]), was used for the diffraction patterns. On the same specimens IR spectra were also obtained by means of Fourier transform infrared (FTIR) spectroscope, trademark Perkin-Elmer, mod.1710 (1) to survey the IR spectra in the interval of wave-length between 4400 and 400 cm^{-1} (2,27- 25 μm). The technique of KBr tablet was used to obtain the transmittance spectra. KBr tablets of 600 mg were prepared. They were pressed at 8 $tonn/cm^2$ per 1,5 min., so that the

[1] The diffractometer belongs to the Institute of Chemistry of the University of Catania. The spectroscope belongs to the Institute of Astronomy of the University of Catania.

background spectrum was surveyed and compared to the tablet holding the specimen to analyse. This tablet was obtained mixing little quantity of specimen (about 2 mg) with about 600 mg of KBr powder to obtain a tablet whose mass and thickness could be compared to those of only KBr.

According to the results of the applied analyses, the respective diagrams (Fig. 4), per each specimen, were drawn. The results are synthesised on Table 1.

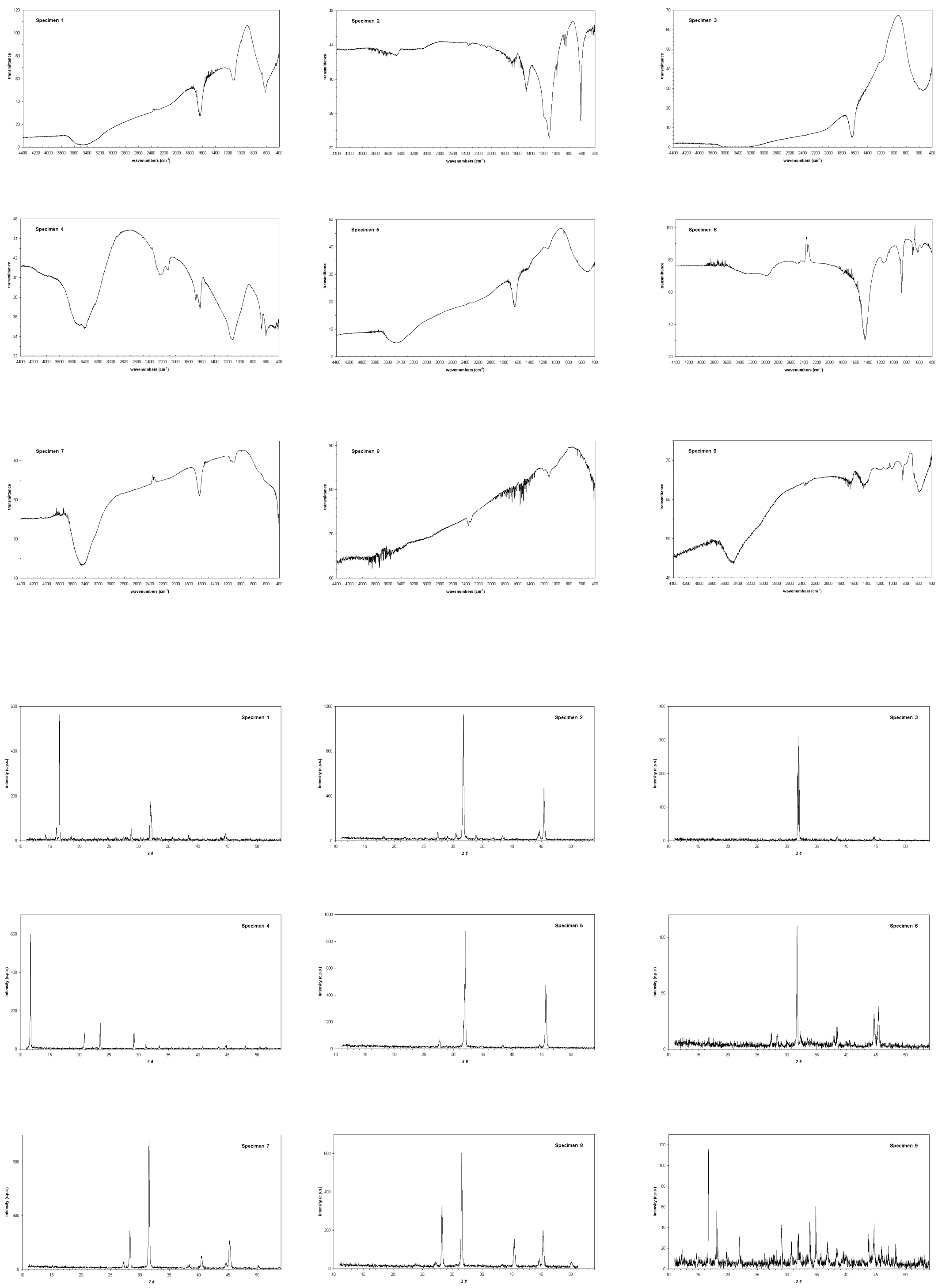


Fig. 4 - IR spectra and specimen diffraction patterns.

TABLE 1

	SPECIMENS	*IR METHOD*	*XRD METHOD*
Grotta del Fumo	Specimen 1	probably Epsomite ($MgSO_4.7H_2O$)	No recognisable bands.
	Specimen 2	Carbonate mineral (probably unstable $CaCO_3$) + $MgSO_4$.The specimen is anhydrous	Halite
	Specimen 3	Abundance of water and no recognisable bands.	No recognisable bands.
	Specimen 4	Gypsum	Gypsum
	Specimen 5	No visible bands	Halite
S.G.2 tube	Specimen 6	Carbonate mineral + Sulfate mineral (probably of Mg)	Halite + Thenardite
	Specimen 7	No visible bands	Halite + Sylvite
	Specimen 8	No visible bands	Halite + Sylvite
	Specimen 9	No visible bands	Trona

Table 1. Results of the specimen analyses and comparison of the two methods of research.

Analysis results

The results of the analyses have allowed to identify the most widespread kind of lava tube minerals described in literature. Among others, Halite (the most abundant), Gypsum, Sylvite (which is always joined with Halite), Thenardite and Trona (the last two minerals in smaller quantity) were found. There were not found new and rare species. This is probably connected to the late investigation of the above mentioned tubes. They were explored more than a year after the end of the eruption, that is after a rainy season which can have caused the washing away of those concretions (extremely soluble) which were present in the first phases of concretioning, but in small quantity. On the contrary, only the abundant species held out this process.

To confirm this theory, some specimens were drawn in dry areas and others where the percolation of meteoric water was very active. The latter were wet and deliquescent ([2]).

The specimen 3 resulted the richest in water. To identify its mineralogical species, by means of both RX and IR, was impossible. The IR technique was ineffective because the instrument could only survey the IR of wave-length between 4400 and 400 cm^{-1}. In this range the most abundant salts, which were found in the explored tubes, (Halite and Sylvite), were transparent, that is they have not characteristic absorption band. This technique, however, was useful to identify water in minerals and, summarily, to estimate its quantity. This allowed to compare specimen 3 with specimen 2, which, according to the result of RX exam, was made up of NaCI (Fig. 5).

The IR spectrum of specimen 2 (green, Fig. 5) showed the lack of water, which, on the contrary, was abundantly present in specimen 3 (red). In the latter the presence of a wide absorption band in the spectral range between 3700 and 3200 cm^{-1} and a pick at about 1640 cm^{-1} were observable. These bands characterise the water because they are respectively caused by stretching O-H and bending H-O-H.

Afterwards two other specimens were obtained by specimens two and three. One was specimen 3a (black in the figure) which was the result of specimen 3 dried in thermostatic

[2] It is important to consider that the tube located at the highest altitude (about 2150 metres above sea level) is inside an area where, according to the topographical features of land, the snow is present until July.

stove at 40 °C ([3]) for seven days and then dried again, at the same temperature, for one day after the pulverisation. The other was the specimen 2a (blue) which was the result of specimen 2 exposed to wet environment for about four hours. According to the comparison of the two spectra, the compositions of the two specimens seems to be comparable. The absorption of water in specimen 2 modifies the form of the spectrum mainly causing the mixing of the two picks between 900 and 800 cm^{-1} in one pick. At the same time the well-defined pick at 620 cm^{-1} of specimen 2 tend to lose its appearance. On the whole there is an overlap between the spectra of specimen 2a and 3.
Although the specimen 3a was dried, it still kept a large quantity of water. There is an interesting phenomenon to highlight, that is the appearance of a new pick at 1150 cm^{-1} (comparable with those of 2 and 2a). On the spectrum of specimen 3a an anomalous pick appeared at about 2350 cm^{-1}. However it is not relevant because it represents the atmospheric CO_2, which changes for each analysis. This means that the quantity of CO_2 present during the background-spectrum acquisition was different.
To sum up: because of the lack of information resulting from the RX analysis of specimen 3 and according to what is perceptible from the organoleptic characteristic of this specimen, the author supposes that the specimen 3 is mainly made up of water-imbibed Halite.
We should spend some more words about IR spectroscopy before ending the discussion. According to the results of the specimen analyses, IR spectroscopy has not always given definitive answers about the mineralogical species that constitute the concretions.
This is probably due to the kind of instrument which was used for the analysis: a better result is thinkable by means of such models which can operate a spectrum analysis that reaches 45 cm^{-1} (222,2 μm). The diffraction was not more effective to solve the mineralogical data. This is why the author considers IR spectroscopy applied to mineralogical analysis a helpful means when it is associated with the diffraction. This is also why it needs new examinations.

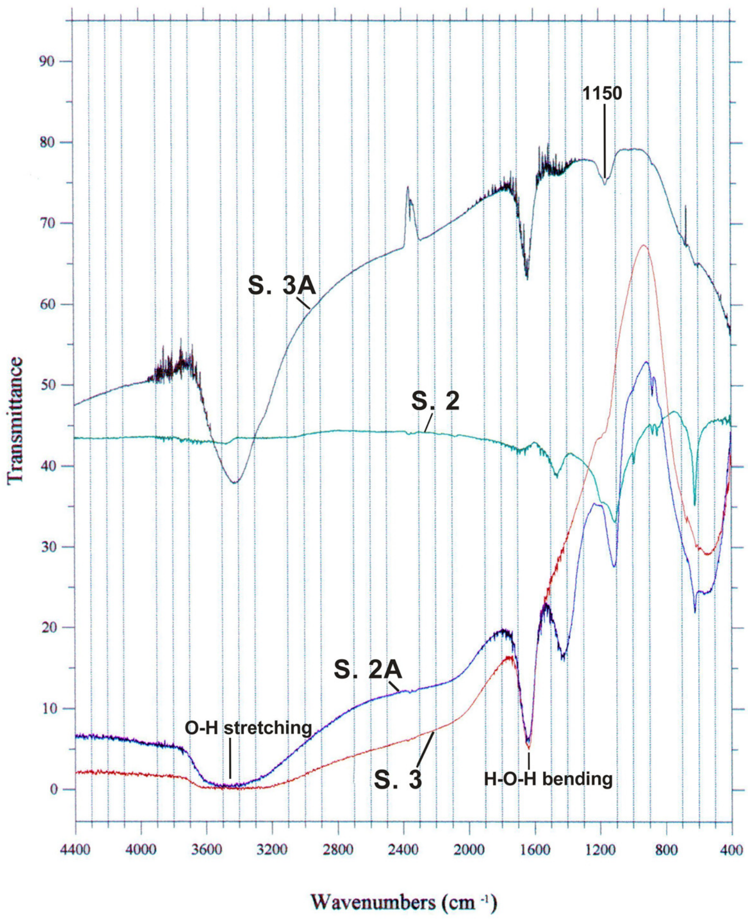


Fig. 5 - IR spectra for the comparison of specimens 2, 3 and of the modified specimens (see text) 2A and 3A.

[3] The temperature was chosen as the compromise between the need to "make " as much as possible water "evaporate" from the specimen and the necessity not to cause phase transition to the specimen whose composition was still unknown.

Genetic hypotheses

The considerable quantity of concretions is one of the main characteristics of just formed lava tubes.
Because of the relative abundance of chlorides, main features of these concretions, deep contributions of sea water to Etna volcanic structure were considered possible (Forti et al. 1994). The author thinks, on the contrary, that the presence of these salts is linked with the phenomenon of lava degassing, as well as of "pneumatolytic differentiation" processes (Rittman, 1976) or "gaseous transfer" (Fenner), which concerns the magma in volcanic environment and whose effect is the concentration of sublimates, particularly the haloid. In the magmatic system, pressure and temperature are the parameters governing the formation of sublimates. They allow a first separation of gas, as an independent phase of magma and then its transport to surface with precipitation in volcanic areas with fumarole activities.
In our case the process would be concerning with the lava which is coming out of eruptive vents and consequently it would be subject to P and T different from those of magmatic systems. It is possible to suppose that the mechanism of tube salt formation is connected to the degassing of those gases which are still in the lava, that is those gases which cause the formation of "fumarole without roots"([4]). The quantity of gas which is present in this lava is decreased by the large loss in vent areas (Swanson and Fabbi, 1973; Peterson and Swanson, 1974). Probably their composition is largely depleted of volatile elements. However, these are still able to aid the displacement of some solid phases, which, because of adhesion to gases, make a system less dense than the liquid in which they are dipped. This causes the coming out of gas bubbles from the vesicle formation phase to the last fumarole manifestations in the last phases of cooling. There is a P and T variation in gas bubbles when they reach the interface lava/air during their journey from inside lava to outside. Because of the fact that generally the reactions of formations of metal halogen compounds are endothermic, the elements moved by gas are handed over.
This process causes a lava "leaching" resulting in the concentration of minerals on the surface and, consequently, in their accumulation. This mechanism continuously acts inside lava tube aiding the deposition of minute minerals in the fissures, in the vesicles of the vault and of the tube walls. It also acts in the whole environment where gas interacts with the outside.
The hot gaseous mass, which takes with itself all the chemical components of the potential minerals, is defined "mineralising convoy" (Gottardi, 1978). In it (that is aerosol) the elements which later create the tube minerals either by direct precipitation or by alteration phenomena in water or air can be found. For example, the presence of S (surveyed inside Grotta Cutrona by Forti et al., 1994) is linked to air exposure of sulphydric acid in watery solution because the air oxygen oxidizes it at S.
Another example of metals kept in the gaseous phase as haloid (particularly as chlorides) is:

$$\underset{\text{(gas)}}{2FeCl_3} + H_2O \leftrightarrow \underset{\text{(hematite)}}{Fe_2O_3} + 6HCl$$

According to the common chemism of Etna lava, example of molecules that take part to the crystallization and of those that migrate to the gas coming out trough fumaroles are:

$$\underset{\text{Ab}}{2NaAlSi_3O_8} + \underset{\text{Di}}{CaMgSi_2O_6} + \underset{\text{Ol}}{5Mg_2SiO_4} + \underset{\text{gas}}{2HCl} \leftrightarrow \underset{\text{An}}{CaAl_2Si_2O_8} + \underset{\text{En}}{11MgSiO_3} + \underset{\text{gas}}{2NaCl} + H_2O$$

[4] They are generally polluted by the "resurgent gas". This is the name which characterises the gas resulting from organic substances and /or soil which are covered by lava flow. The case of 1991-93 eruption is different. In fact it is inside Valle del Bove where it covered the lava fields of previous eruptions; in the high Valle del Bove, particularly, there was not vegetation or thick soil.

or

$$\underset{Ab}{2NaAlSiO_8} + \underset{Di}{CaMgSi_2O_6} + \underset{Gas}{HCl} \leftrightarrow \underset{An}{CaAl_2Si_2O_8} + \underset{En}{MgSiO_3} + \underset{Qz}{5SiO_2} + 2NaCl + \underset{Gas}{H_2O}$$

the equilibrium of such reactions moves towards the right side when the pressure decreases with consequent escape of gas.
Now we can identify four phases, which turn the minerals that are produced by the pneumatolytic concentration into tube concretions:

1. the minerals, because of lava degassing during the cooling, are deposited on every side of lava. The salts resulting from this operation accumulate in minute crystals in the cavities, in the fissure and on the surface of the just formed lava. They could be modified by the exposure to air and humidity;
2. when the temperature decreases under 100°C, letting the circulation of water as liquid phase, the previously produced salts are mobilised by the meteoric water and moved to the internal part of the cavity trough many fissures which are present in the lava tunnel;
3. afterwards there is one more elaboration by pseudo-Karst processes, which start inside the cavity. They cause the precipitation with the same mechanism acting in the caves which are really Karst. They form different typologies of speleothems;
4. later the deposition can take place inside the tube by direct precipitation, that is by aerosol coming out from the fissures of the cavity and from those parts of lava flow which still have a high temperature. This does not imply the passage by the phase of solubilization in meteoric water. In this case, because of strong air current (aerosol current), the deposits can create some weak filiform concretions. They grow over old concretions, which were formed following the mechanism discussed at point 3.

Conclusion

Lava tube concretions, which are formed in the first phases of cavity cooling, hold out for little time after their formation. Because of their being soluble and metastable, they hardly leave traces of their past existence. They are immediately washed away by the meteoric water which acts in the tube. The result is, by contrast with the imposing phenomenon, a poor scientific production about the genesis of first-formation concretions.
Our research has allowed locating salts, whose presence inside Cutrona tube and other tubes had already been recorded. In fact no new mineralogical species was found. We can deduce that the chlorides are those minerals which are largely formed.
The relative poverty in mineral species, compared with the relative abundance of the phenomenon, is linked with the late exploration of new tubes, which had already been subject to the seasonal rains. The only preserved species were those which were present in larger quantity.
The possible genesis of the various mineralogical species is linked with the pneumatolytic differentiation which lead to the concentration and, consequently, to the accumulation of pneumatophil elements, particularly haloids.
A progressive impoverishment of the mineralising convoy when the distance from the vents increases could determine a variation in the chemism of the concretions which are located at different distances from the effusive vents. This is only a hypothesis, because according to our date it is impossible to get such kind of conclusions. Of course a future geochemical analysis of the gases coming out from the fissures of lava flows is necessary. The sampling should concern the whole length and should be periodic, so that the necessary comparisons can be made.
An analysis of lava flow chemism is also necessary to determine the schematic equations of the reaction taking place between lava and liberated gas. It is also useful to compare these results with those concerning other tubes.

Acknowledgements

I am very grateful to Prof. G. Strazzulla for the suggestions and the loan of the instruments, which are of the Institute of Astronomy, and to Dr. N. Gulino for the instruments of the Institute of Chemistry. My special thanks also to Dr. G.Cimino for having collaborated in the analysis, for the suggestions and for the critical reading of this paper.

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