

GENETIC PROCESSES OF CAVE MINERALS IN VOLCANIC ENVIRONMENTS: AN OVERVIEW

PAOLO FORTI

Italian Institute of Speleology, University of Bologna, via Zamboni 67, 40126 Bologna, ITALY forti@geomin.unibo.it

Volcanic caves have been considered of little mineralogic interest until recent years. As a consequence, very few papers have been printed on this topic in the past. In reality volcanic cavities are a very favorable environment for the development of different minerogenetic processes. Cave minerals actually present in volcanic environments constitute up to 40% of secondary chemical deposits found in all the caves of the world, and 35 of them (corresponding to ~10% of the actually known cave minerals) are restricted to such an environment. In the present paper, the six minerogenetic mechanisms active in the volcanic caves (degassing, solubilization, alteration, karst process, biogenic activity, phase change) are described following the decrease of cave temperature. The genesis of some of the most important secondary chemical deposits is discussed and a tentative list of the most interesting volcanic caves for hosted speleothems is given.

Volcanic caves are widespread in the world and are actively explored by cavers so it is common to find descriptions of the exploration, speleogenesis and morphology of these caves in the literature. However, the accurate study of the speleothems hosted by these caves is rather new because, until recently, lava tubes and other volcanic cavities have been considered of little interest from the point of view of secondary minerals (Forti 1994). Most volcanic caves allow for the development of only a few small speleothems apart from lava stalactites and stalagmites, which normally cannot be considered as true cave formations (Hill & Forti 1997).

The first written report of minerals found in a volcanic cave appeared only at the end of the 18th century, some one hundred years later than the first descriptions of speleothems in limestone caves (Shaw 1997). Lazzaro Spallanzani in his renowned “*Viaggio alle Due Sicilie*” (1792-97) first wrote of minerals he found in Alum Cave in the Vulcano Island:

“...but the most interesting object is a natural cave...from which a column of smoke continuously exits...Sublimated sulphur gives rise to conical yellow to pink stalactites up to 3 feet long and two inch thick. ...Some water springs out from the cave wall giving rise to some deposits over the lava beds...consisting of stalactitic alum...sometimes with ammonium chloride...Deposits of iron sulphate are fairly common...”

After this first paper only a few others were printed up to the middle of the 20th century (Recupero 1815; Sava 1842; Scacchi 1850; Ulrich 1870; Mac Ivor 1887; Bellini 1901; Zambonini 1907).

However, within the last 10 years it has become increasingly clear that volcanic cavities are one of the most important cave environments in which minerogenetic reactions can take place (Forti 1994). The peculiar physicochemical conditions, which dramatically change from the early stages of lava tube formation to the maturity of the cavity, together with the high

number of different elements present inside the lava itself, allow for the development of a great variety of cave minerals (some tens of which are restricted to a volcanic environment). Even if only a few volcanic caves have been specifically studied from the mineralogical point of view, some of them are among the most interesting caves of the world for their hosted speleothems.

The present paper presents an update on the minerogenetic mechanisms active in a volcanic environment (Forti 2000) and it an overview of those minerals which are presently restricted to such an environment. Lastly, the most important volcanic caves in the world for the hosted speleothems are discussed.

MINEROGENETIC MECHANISMS IN THE VOLCANIC ENVIRONMENT

Despite the general scarcity of secondary chemical deposits, volcanic caves host up to six active minerogenetic mechanisms (Table 1; Fig. 1). The first two are absolutely peculiar to this environment; in fact, in the early stages of their development the extremely different environmental conditions that exist inside them allow for the activation of different processes which are practically controlled by the temperature of the cave atmosphere. In the time that passes as the lava walls cool, the active process changes, and therefore the chemical composition as well as the morphology of the resulting speleothems are quite different. The first place where such an evolution was experimentally demonstrated was the Cutrona lava tube on Mt. Etna (Forti *et al.* 1994). Here, the cave climate and the evolution of speleothems were monitored since the cave's discovery (some 8–10 months after the end of the eruption which generated the cave) until its internal temperature was no longer in equilibrium with the external environment. This study demonstrated that the evolution of secondary chemical deposits may start as soon as the lava stops flowing, and maybe even earlier, when the temperature inside the cave is still extremely high.

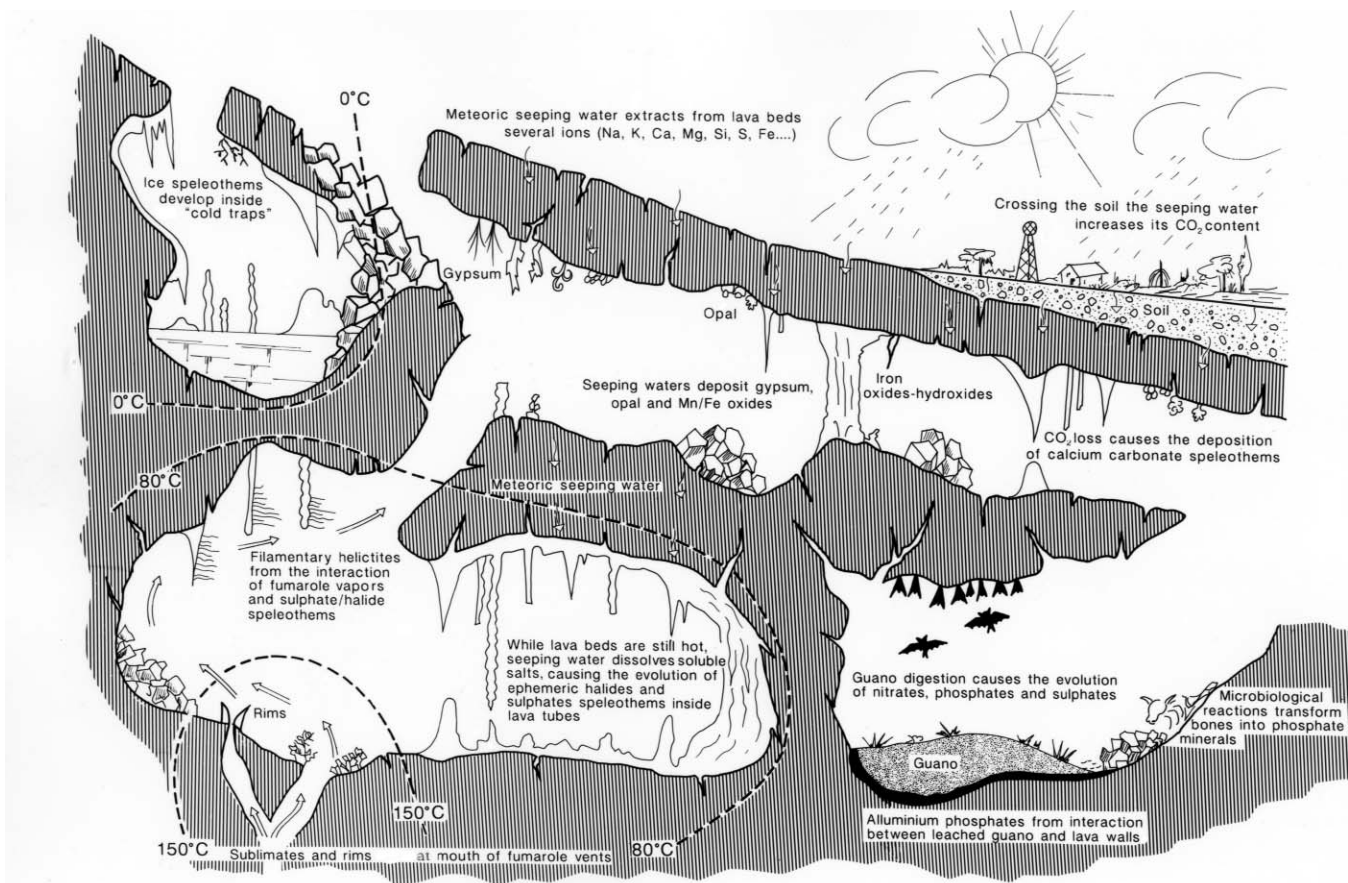


Figure 1. Minerogenetic sketch for cave minerals forming inside volcanic caves (after Forti, 2000).

Table 1. Temperature range, process, minerogenetic mechanisms and related chemical deposits in volcanic caves (after Forti, 2000, modied).

Process	Mechanism	T (°C)	Products
1 A- High temperature degassing	Sublimation	> 100	Elementary sulfur, oxides, hydroxides
B- Low temperature degassing	Deposition from aerosols and vapors	50–100	Sulfates, halides
2 Solubilization	Evaporation	10–100	Sulfates, halides
3 Alteration	Oxidation, hydration-dehydration, ionic exchange	0–100	Si-, Al-, Fe oxides-hydroxides, sulfates
4 Karst process	Diffusion	0–40	Carbonate
5 Biogenic activity	A- Digestion, dissolution-precipitation, double exchange	0–40	Phosphates, nitrates, sulfates, halides
	B- Guano combustion	200–400	Burned guano minerals
6 Phase change	Freezing	< 0	Ice

DEGASSING

When the lava walls solidify but the temperature is still very high the first minerogenetic mechanisms (1A of Table 1) become active, being related to the fluids seeping out from wall and/or floor fractures. The cooling down of fumarole gases, which is enhanced by their expansion in the cave atmosphere, allows for the deposition of sublimates of several different minerals, the most common being sulfur, but also some oxides, hydroxides and even sulfates (Figs. 2,3,4).

The fumarole activity, and therefore the process of sublimation, may last several months, but unavoidably when it does stop, the larger part if not all of the generated speleothems are

demolished in a very short span of time. This is partly due to their intrinsic metastability and partly to delicate structures formed through the sublimation processes. For this reason, such deposits in volcanic caves are rarely observed long after the end of fumarole exhalation.

SOLUBILIZATION

When the temperature of the volcanic rock goes below 100°C, the second mechanism (mechanism 2 of Table 1) is activated by rainfall. From this moment on, at least some of the meteoric water starts seeping into the cracks and along the porosity of the volcanic rock thus dissolving the soluble sub-



Figure 2. Cutrona lava tube, Mt. Etna, Italy: sublimates of polyhalite and tenorite at the mouth of a fumarole vent: the photo was taken when the temperature within the cave was still over 40°C (photo by Paolo Forti).

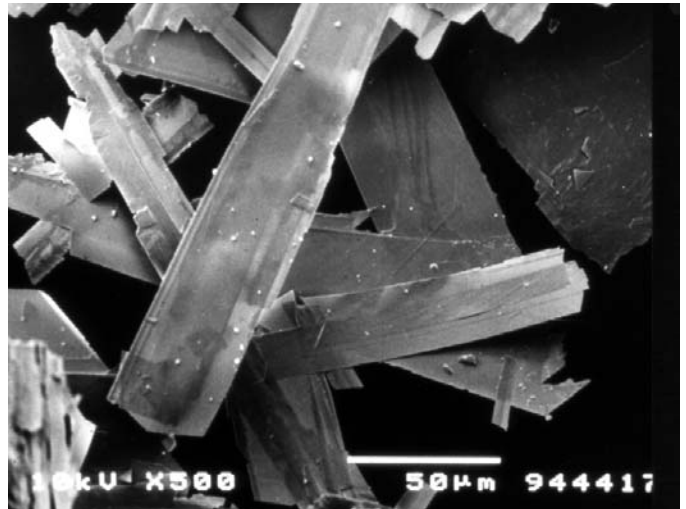


Figure 4. Cutrona lava tube: SEM image of thin blades of tenorite in the sublimate of Fig. 2.

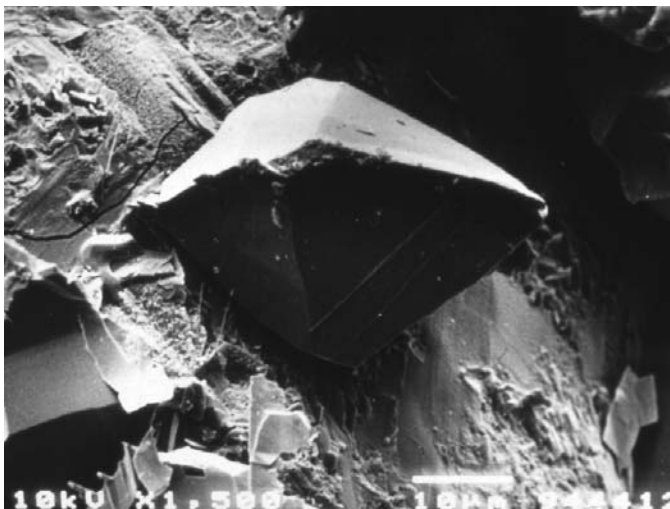


Figure 3. Cutrona lava tube: SEM image of pseudo–octahedral crystals of polyhalite in the sublimate of Fig. 2.



Figure 5. General view of the huge speleothems deposited in the Cutrona lava tube by a dissolution evaporation mechanism: presently all these speleothems are completely washed away (photo by Paolo Forti).

stances existing therein. Once this water comes in contact with the still-hot cave atmosphere, it rapidly evaporates, causing the deposition of even larger amounts of speleothems consisting of a series of sulfates and chlorides.

It is most certainly a “golden moment” for the decoration of volcanic caves, because not only the ceiling, but also the walls and the floor may become completely covered by an incredible variety of polychrome speleothems (stalactites, soda straws, stalagmites, flowstones, popcorn, coralloids, etc.). An

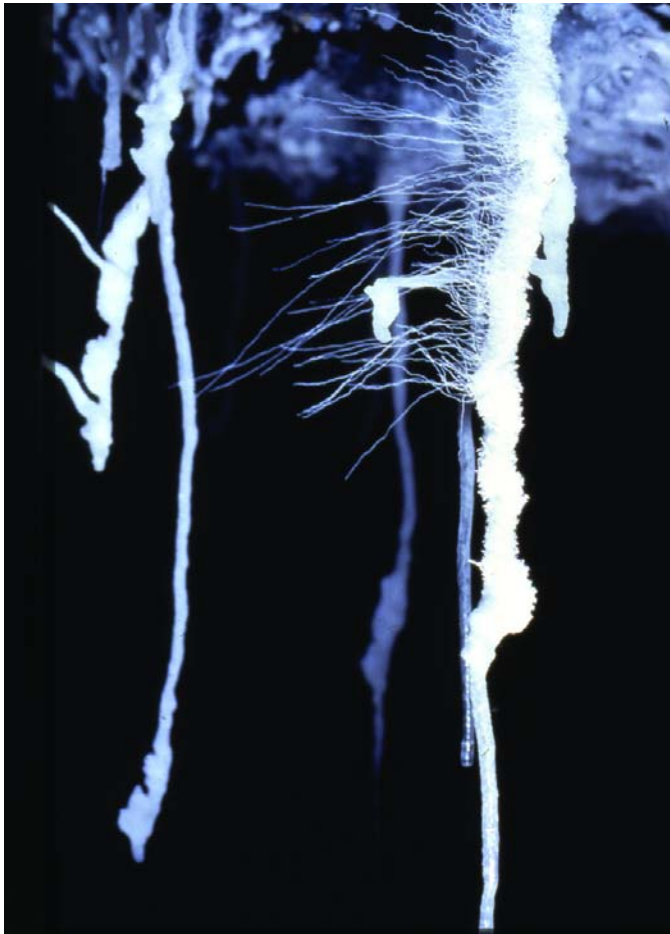


Figure 6. Cutrona lava tube: oriented anemolite helictites of thenardite developed over a stalactite of the same material. The anemolites develop along the interference between the fumarole “wind” and the speleothem forming by evaporation (photo by Paolo Forti).



Figure 8. Cutrona lava tube: thenardite rims at the mouth of a fumarole vent (photo by Paolo Forti).

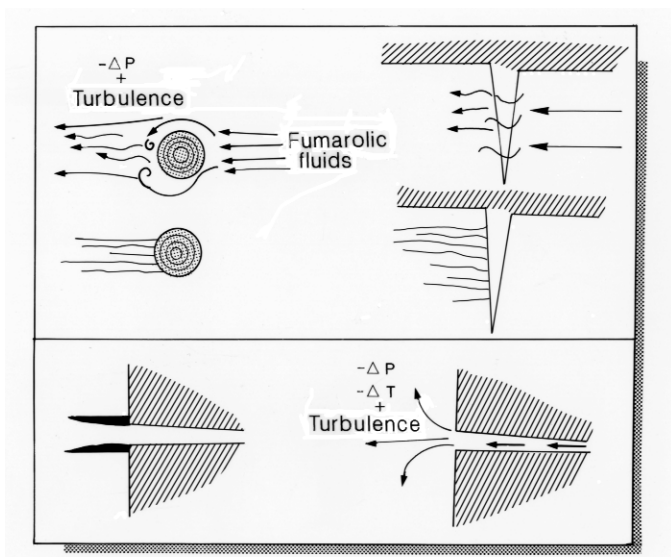


Figure 7. Genetic sketch for anemolite helictites and rims generated by fumarole vents (after Forti *et al.* 1994).

exceptional example of this kind of decoration was found in the Cutrona lava tube on Mt. Etna (Fig.5), but other caves are known in the world with similar formations (Jakobsson *et al.* 1992, Jónsson 1994, Davies 1998).

During this period, if the fumarole exhalations are still active, the interactions between these exhalations and the previous mineral deposits developing due to the evaporation can favour the evolution of peculiar speleothems which are deposited via aerosol and/or vapor condensation (mechanism 1B of Table 1). The most common deposits of this kind are extremely thin anemolite needles (hair-like with a diameter of 0.1–0.5 mm and over 10–15 cm long) which grow over the stalactite sides opposite to the fumarole exhalation, developing directly along the fumarole flow (Fig. 6). The anemolite genesis (Fig. 7) is related to the peculiar microclimatic conditions which develop immediately adjacent to the stalactites exposed to fumarole vapors. The enhanced gas turbulence in traversing the speleothem, and the lowered temperature due to the expansion of the vapors just after it, are responsible for the enhanced deposition of particles carried by the fluid itself. Other not-so-common speleothems originating by the same process are rims and bubbles, which develop along the border of the fractures from which the fumarole vapors escape (Fig. 8).



Figure 9. Gigantic opal flowstones in Algar do Carbalo magmatic chamber, Azores, Portugal (photo by Paolo Forti).



Figure 10. The wall of a lava tube in the Pico island (Azores, Portugal) covered by silica vermiculations (photo by Paolo Forti).

Unfortunately most, if not all, of the speleothems and cave minerals deposited by the second mechanism, similar to the first mechanism, are short-lived and are destined to disappear as soon as the cave temperature decreases. Basically, these deposits consist of highly soluble sodium, potassium and mag-

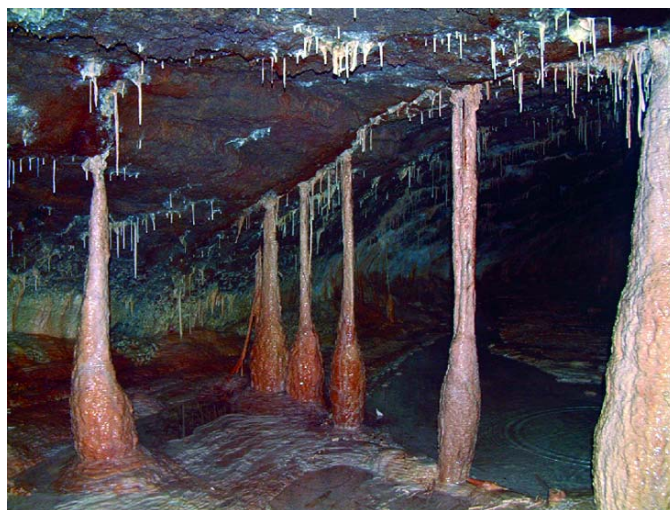


Figure 11. Calcite speleothems covering the ceiling and the wall of Dangecheomul lava tube, Jeju island (Korea) (photo by Kim Woo).

nesium sulfates and/or halides. Therefore, when the cave temperature becomes low enough to restore the normal hydrogeologic regimen, the mineral deposits are rapidly dissolved, leaving the walls and cavities completely bare. Of course, a higher degree of rainfall corresponds to a higher infiltration and therefore a faster redissolution. In the Cutrona lava tube on Mt. Etna, huge speleothems develop in a few months due to the second minerogenetic mechanism, but last for only a little more than one year even when snowfalls are normal during winter (Forti, 1994). Probably in drier areas, such as desert environments, the mineral deposits could develop over several decades and survive for hundreds of years.

ALTERATION

The removal of all the cave deposits formed during the second period does not signify that volcanic caves will no longer contain speleothems and cave minerals, however. In reality, quite the opposite occurs. In reality during the second period the third mechanism becomes activated consisting of an alteration of the minerals that make up the volcanic rock by seeping meteoric water. This alteration may result in the oxidation of sulfide minerals, the weathering of silicate minerals, or the simple dissolution of silica glass dispersed within the lava. In any case, these processes bring different ions and/or substances like silica, iron, aluminium, calcium, magnesium etc., into solution, which are deposited on the cave wall as opal, iron hydrated oxide-hydroxides, aluminium hydrated oxides and or silicates, gypsum and other sulfates (Marino, 1994).

At the beginning, the growth of such speleothems is very rapid as demonstrated by the evolution of a 3-cm-long opal soda straw in the Serracozzo lava tube (Mt. Etna) in less than four years (Del Monte *et al.* 1987), but this process normally slows down in a short span of time so it is very rare to see large cave deposits produced by this minerogenetic mechanism. Usually, they are only small earthy crusts (iron and aluminium



Figure 14. Kitum, erosional cave in volcanic ash, Kenya: a large void covered by tufts of natrolite, tetranatrolite and large crystals of apophyllite (photo by Paolo Forti).



Figure 15. Hibashi lava tube, Saudi Arabia: stalactites consisting of seven different cave minerals (archanite, biphosphammite, chlorapatite, niter, opal-C, quartz, whitlockite) (photo by John Pint).

oxides) or coralloids (opal). An exception, at times represented by gypsum for example, may also develop quite large crust and flowers. An absolutely unique display of gigantic opal speleothems (flowstones, stalactites, canopy bells, etc.) exists inside the Algar do Carbalo (Azores, Portugal) (Fig. 9), a very old magmatic chamber (Borges *et al.* 1991) where the mechanism of silica dissolution-redeposition is still active. This occurs not only because of the thickness of the lava field over the cavity, but also because some biogenic mechanisms have allowed for a rapid weathering of the volcanic rock to form highly soluble silica (Fig. 10) (Forti, 2001).

However, in general, only a few decades after the formation of the volcanic cave, even the third minerogenetic mechanism is practically extinguished, but with a significant difference from the first two mechanisms. The formations developed in this period will not be re-dissolved, allowing them to become permanent decorations in the caves.

The last three mechanisms begin to evolve when the cave temperature has been stabilized and suitable environmental conditions exist for their development. The karst process and the biogenic digestion need particular conditions to start and therefore these processes may become efficient only after a long period of time. Consequently their effect can only be observed in very old volcanic caves, which are in reality not so common because their degradation is much faster than that of karst cavities.

KARST PROCESSES

This mechanism responsible for the decoration of normal limestone caves (diffusion of the CO₂ into the cave atmosphere causing supersaturation with respect to calcium carbonate and deposition of normal speleothems) is exactly the same in volcanic caves which leads to calcite-aragonite speleothems within the volcanic environment. However, the amount of carbonate deposits inside volcanic caves is normally extremely sparse for two different reasons. First, in order to have a high concentration of carbon dioxide in seeping meteoric water, the volcanic rock must be covered by a relatively thick soil layer where the microbiological reactions can develop in order to raise the partial pressure of this gas significantly (Fig. 1). A great length of time must pass (several thousand years) before a layer of earth can evolve over a lava field, and therefore the karst process must wait this amount of time before it becomes active, but this is not enough. There must be a second condition; in order to produce carbonate speleothems it is also necessary to bring in relatively high amounts of calcium and/or magnesium into solution, but normally the concentration of such ions in seeping water is sparse even if calcium and magnesium are present in common basaltic minerals like olivine and plagioclase. This is because, as previously stated when describing alteration mechanisms, the weathering process slows down rapidly so that after hundreds of years it does not allow release of enough Ca⁺⁺ and Mg⁺⁺ to achieve supersaturation with respect to calcite and/or dolomite. Therefore, even if the seeping water contains high amounts of CO₂, few if any carbonate speleothems develop in volcanic caves.

The best display in the world of calcite speleothems in volcanic caves is in the Hyeobjae lava tube in Cheju island (Korea), where flowstones, stalactites, stalagmites, helictites, conulites, gours and even cave pearls cover almost all of the cave walls and floor (Kashima & Suh 1984; Kashima *et al.* 1989). It is the peculiar environment of this lava tube that has allowed this exceptional development of calcite speleothems. The lava is covered by a rather thick layer of microcoquina (a clastic limestone composed by cemented sand-sized grain particles of shell detritus) deposited by the surrounding sea. Therefore, the meteoric water, enriched with CO₂ from the soil humus before reaching the lava tube, slowly crosses the microcoquina via its porosity and thus becomes saturated with respect to CaCO₃ which is immediately deposited as soon as the excess carbon dioxide is released into the lava tube atmosphere (Fig. 11).

BIOGENIC ACTIVITY

The fifth minerogenetic mechanism is often very active within volcanic caves, with processes that sometimes are absolutely restricted to this environment and being related to the silicate composition of the cave walls. The presence of high silica content in the walls and/or sediments of volcanic caves may allow development of peculiar organisms which may in turn give rise to biogenic mineralizations. In some volcanic caves of Japan and Korea (Kashima *et al.* 1987, 1989) the development of several silica coralloids and helictites has been found to be strictly related to the presence of colonies of diatoms (genus *Melosira*) and these speleothems consist mainly of skeletons of such organisms that alternate with layers of clay and detrital material cemented by silica. The presence of diatom skeletons is strictly confined to those parts of the cave where some external light can reach the diatom colonies because the diatom colonies need light energy to survive. The light control is evident not only by the fact that these speleothems develop only in the threshold light zone, but also by their shape, which always point towards the cave entrance.

But microorganisms may also induce the evolution of silica-rich speleothems in areas with a total absence of light. For example, in many of the lava tubes of Pico Island (Azores), the weathering of the basalt leads to the evolution of a widespread amorphous silica moonmilk which often gives rise to vermiculations over the cave walls (Forti 2001). These speleothems are extremely rich in organic matter (over 20%, unpublished data by the author) suggesting that the unusually high weathering of the basaltic rock could be driven by microorganisms.

Apart from these biogenic processes, which are restricted to their environment, volcanic caves may host other minerogenetic processes driven by microorganisms active in the same manner as in all other types of natural cavities. In general, these reactions are a "digestion process," corresponding to all the different biochemical processes leading to the mineralization of organic matter. The digestion process needs the presence of rather large organic deposits inside the cave and requires substantial time to become activated.

The most common organic deposit in all types of caves is, by far, bat guano and rarely excrements from other animals. Mineralization of guano, like that of any other organic matter, is a complex mix of different reactions most of which are almost certainly biologically driven. The main reactions involved lead to the production of phosphoric, sulfuric and nitric acid (Forti 2001) which immediately react with different ions within the guano, allowing for the deposition of some secondary minerals (e.g., gypsum). Most of the guano-derived minerals (primarily phosphates and sulfates but also nitrates, halides, oxides, hydroxides) come from double exchange reactions between these strong acids and the different compounds present in the walls or on the floor of the volcanic cave. Generally speaking, even if the guano mineralization processes are identical in volcanic caves and other types of caves, the amount of resultant cave minerals is normally higher within the volcanic environment because the amount of different available ions is far higher than in limestone caves.

A peculiar minerogenetic mechanism strictly related to guano is the naturally induced combustion of guano deposits. The first, and up to now single, reference to such phenomena in a volcanic environment is that of Hibashi Lava Tube in Saudi Arabia (Forti *et al.* 2004). Guano fires may induce very high temperatures (up to several hundred °C) (Martini 1994a,b) and may cause the transformation of organic materials into extremely rare minerals (like arnhemite, pyrocoprite and pyrophospite).

PHASE CHANGE

The sixth and last minerogenetic mechanism consists simply of the solidification of seeping water, and obviously this process needs nothing other than a sufficiently low temperature for its activation. Ice speleothems inside most volcanic caves are only seasonal, but sometimes they may last perennially in areas where the annual average temperature is higher than 0°C. The lava, behaving as a very efficient thermal insulator, easily transforms caves with a single entrance and a general descending slope into "cold traps" where ice may accumulate in the wintertime without melting during the hot season. One very famous example of this is the Grotta del Gelo (Ice Cave) on Mt. Etna which has been renowned since antiquity because its ice deposits were exploited to supply Catania with ice cream even during summer months (Recupero 1815). Ironically, the Grotta del Gelo has become such a popular tourist attraction that the excessive amount of visitors, with consequent sharp alteration of the cave microclimate, may lead to the complete melting of its permanent ice formations in a few years (Centro Speleologico Etno 1999).

It must be stressed that some of the just-outlined six minerogenetic processes may be active simultaneously. Moreover, if the environmental conditions change (for instance if a new eruption supplies new lava) all of them may be reactivated.

CAVE MINERALS IN THE VOLCANIC ENVIRONMENT

Even though thousands of volcanic caves have already been explored, cave minerals have only been reported from a few tens of them. Presently, less than 20 cavities have been fully investigated from the mineralogical point of view and most of them just in the last few years. Specific studies on volcanic cave minerals have been performed on all five continents.

Despite the small number of studied caves, the observed minerals within the volcanic caves presently correspond to about 35–40% of the whole known secondary chemical deposits in the cavern environment (Hill & Forti 1997). Even if the great majority of these minerals consist of sulfates, most of the chemical classes are represented as a consequence of the great number of different elements normally present within the lava. Only sulfides, arsenates, borates, and vanadates are still missing, but the absence of minerals from the last three classes is not surprising because they are scarcely represented in the

Table 2. List of the cave minerals restricted to volcanic environment.

Mineral	Cave	Characteristics	Process	References
Aluminiocopiapite	Alum (Italy)	Tuffs of small translucent to transparent crystals	1B-2	Forti <i>et al.</i> 1996
Alumogen	Zolfo (Italy)	Small white to transparent crystals	1B	Bellini 1901
Apophyllite	Kitum (Kenya)	Prismatic white to transparent crystals	3-4	Udluft 1928
Aubertite	Alum (Italy)	Pale green to transparent small masses	1B-2	Forti <i>et al.</i> 1996
Epidote (Pistacite)	Santo (Italy)	Small yellow elongated crystals	3	Del Monte <i>et al.</i> 1987
Galearite	Grillid (Iceland)	Thin pale-yellow to transparent crusts	1B	Jakobsson <i>et al.</i> 1992
Glauberite	Grillid (Iceland)	White to transparent hard microcrystalline crusts	1B	Jakobsson <i>et al.</i> 1992
Hydrobasaluminite	Alum (Italy)	Small plastic clayey masses	1B-2	Forti <i>et al.</i> 1996
Hydroglauberite	Grillid (Iceland)	Minor component of the glauberite crusts	1B	Jakobsson <i>et al.</i> 1992
Hydroxylapophyllite	Kitum (Kenya)	Tetragonal prismatic crystals	3	Forti <i>et al.</i> , 2003
Kainite	Grillid (Iceland)	Colorless stalactites	1B	Jakobsson <i>et al.</i> 1992
Kalinite	Alum (Italy)	Small octahedral crystals	1B-2	Jervis 1881
Keramohalite	Alum (Italy)	Shining silver fibrous stalactites	1B-2	Panichi 1914
Kogarkoite	Suswa 13 (Kenya)	Aggregate of small bladed crystals	3-5	Forti <i>et al.</i> , 2003
Löweite	Grillid (Iceland)	Colorless stalactites with halite	1B	Jakobsson <i>et al.</i> 1992
Mendozite	(Kenya)	Blisters	3-5	Sutcliffe 1973
Metavoltine	Sulfur (Italy)	Thin yellow hexagonal blades	1B	Bellini 1901
Millosevichite	Alum (Italy)	Violet to green hygroscopic crusts	1B-2	Panichi 1913
Misenite	Sulfur (Italy)	Soft pale grey fibres	1B	Bellini 1901
Phillipsite	Kitum (Kenya)	Saccharoidal masses of twinned crystals	3-4	Forti <i>et al.</i> , 2003
Picromerite	Cutrona (Italy)	Sugar-like aggregates of pale-blue crystals	2	Forti <i>et al.</i> 1996
Polyhalite	Cutrona (Italy)	Minor component of shining yellow blades	1A	Forti <i>et al.</i> 1996
Portlandite	Eruption 1923 (Italy)	Spheroids of small crystals inside a calcite speleothem	1A	Forti & Marino 1995
Ralstonite	Surtsey 4 (Iceland)	Yellow brown crusts with opal and fluorite	1B	Jakobsson <i>et al.</i> 1992
Sal Ammoniac	Alum (Italy)	Minor component of alum stalactites	1B	Spallanzani 1792-7
Silhydrite	Post office (USA)	Small stalactites	2-3	Rogers & Rice 1992
Soda Alum	Alum (Italy)	Octahedral and cubic small transparent crystals	1B	Cossa 1878
Struvite	Skipton (Australia)	Present in the moist depth of guano	5	Ulrich 1870
Tamarugite	Sulfur (Italy)	Snow-white masses of elongated crystals	1B	Zambonini 1907
Tetranatrolite	Makingen (Kenya)	White acicular frostwork	3-5	Kashima & Ogawa 1998
Trona	Pisgah (USA)	Small white crystalline masses	3	Harter 1973
Voltaite	Sulfur (Italy)	Pale green crusts	1B	Bellini 1901
Zaherite	Alum (Italy)	Translucent to vitreous elongated crystals	1B-2	Forti <i>et al.</i> 1996

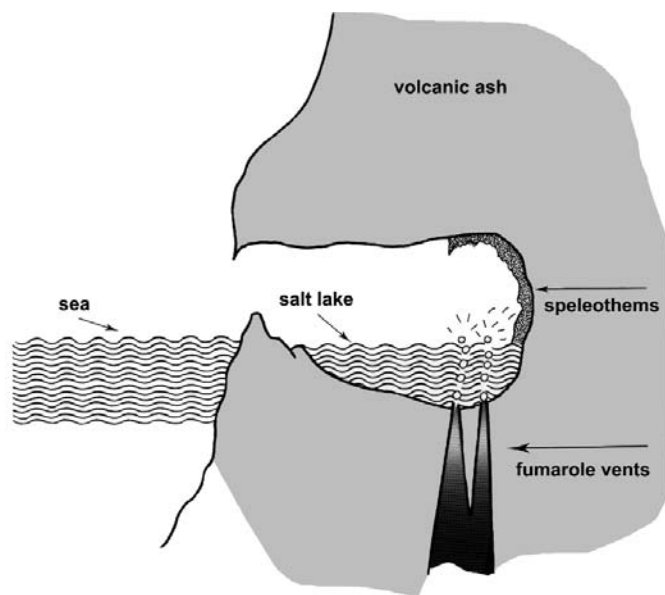
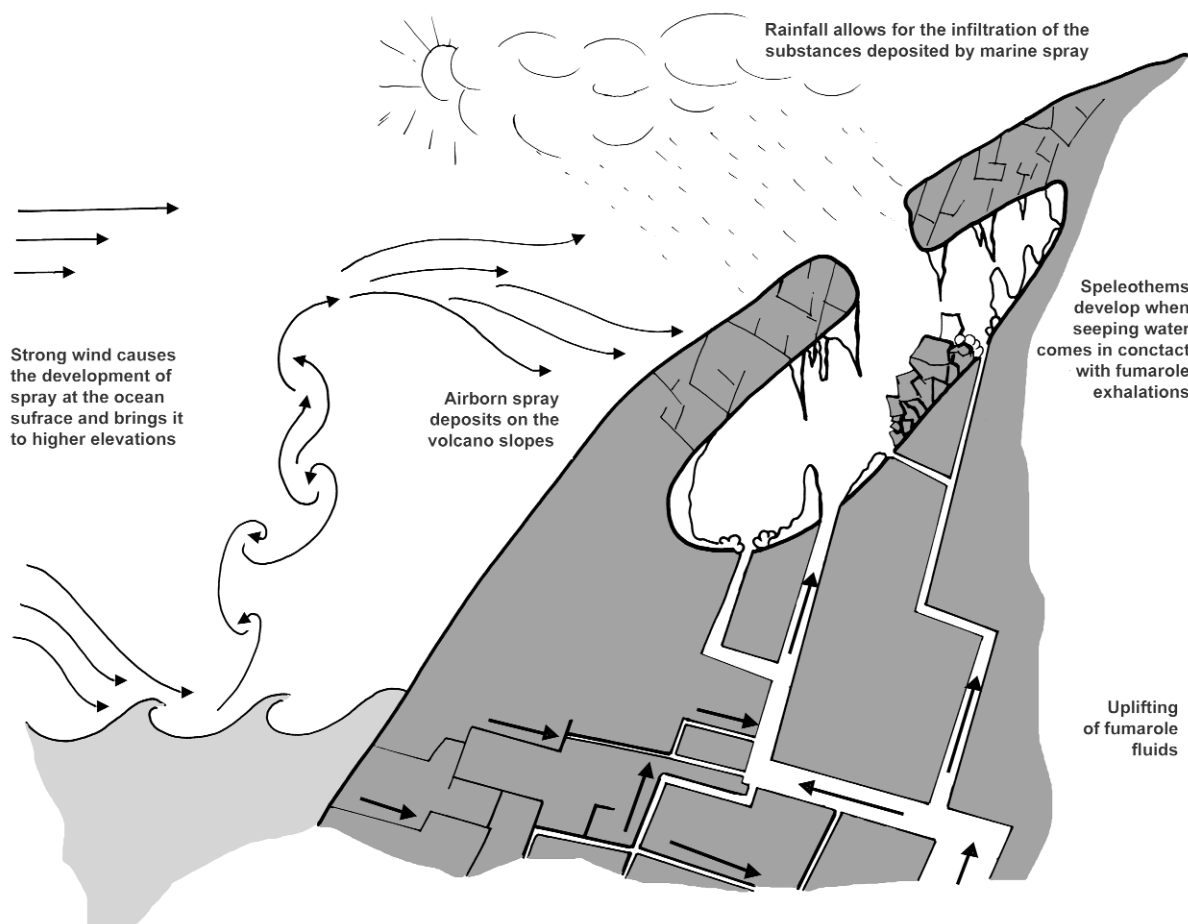


Figure 12. Minerogenetic mechanisms active in Sulfur Cave (sea cave in volcanic ash, Miseno Cap, Naples, Italy) (after Forti 2003).

whole cave environment, whereas the lack of sulfides is explained by the peculiar conditions in which all the chemical deposits form within volcanic caves. Deposition may begin only when the melted lava does not fill up the entire cave thus allowing for the presence of a gas phase. The gas inlet provides oxidizing conditions which are incompatible with the development of any sulfides, but are extremely favorable for the deposition of sulfate minerals which are relatively abundant in the volcanic caves. The mineralogical richness of the volcanic environment is also established by the very high number of cave minerals (33) which have been observed only inside volcanic caves (Table 2). These 33 minerals represent some 10% of the whole secondary chemical deposits known in the cavern environment, 18 of which have been discovered in the last 12 years.

In volcanic caves, the low-temperature degassing process (1B of Table 1), which has given rise to 20 new compounds, is by far the more important minerogenetic mechanism for new cave minerals followed by solubilization and alteration. Solubilization and alteration both give rise to nine new minerals, while biogenic activity produced just four new minerals and high temperature degassing and karst processes produced just two minerals each. If new minerals and the entire suite of

Figure 13.
Minerogenetic
mechanisms
active in the
Grillid Lava
Tube, Surtsey
Island, Iceland.



secondary chemical deposits developed within volcanic caves are considered collectively, the role of biogenic activity increases noticeably in importance similar to that of low-temperature degassing (fumarole activity) while that of the other processes remain relatively unchanged. This occurs because most of the reactions involving organic substances occur within the guano itself without contact with the host rock and therefore most of the products are the same in solutional and/or in volcanic environments. Except for some of the early research, the study of the guano deposits in volcanic environments has become reestablished only in the last decade and the actual knowledge of the related minerals is far from exhaustive. Therefore, it is reasonable to suppose that in the near future the importance of the biogenic digestion in the minerogenesis of volcanic minerals will become better recognized.

Finally, it is interesting to note that the three volcanic caves which actually host most of new cave minerals (Alum, nine new cave minerals; Grillid, five; and Sulfur, five) have the same environmental characteristics though not the same genesis. Alum and Sulfur are very small caves in volcanic ash while Grillid is a normal-size lava tube, yet all three host fumarole exhalations in direct contact with seawater which provides a large amount of different dissolved ions necessary for the development of the observed minerals. In Sulfur Cave the fumarole activity directly bubbles up into a small lake filled by seawater (Fig.12). In Alum Cave the contact between the hot

vapors and seawater occurs just a few meters below the cave floor, while in the Grillid lava tube the contact between seawater and hot fluids occur deeper (Fig. 13). These three caves are also exposed to marine spray, which has a different minerogenetic importance in the three caves. Minerogenetic importance is limited in Sulfur Cave, a bit more significant, but still of second order, in Alum Cave and very important in the Grillid lava tube, where the spray may be the prevailing agent. The importance of sea spray in the Grillid lava tube depends upon two factors; the elevation of the cave entrance with respect to the sea and the climate.

Sulfur and Alum caves are, respectively, at the sea level and only a few meters above it, their climate being Mediterranean dry with scarce rainfall and few storms. Therefore, marine spray is scarce and it percolates within the cave only rarely. The Grillid Lava Tube has an elevation of about 90–100 m above sea level and therefore the direct contribution of the seawater to the fumarole vapors is less than that for the other two caves, but the hard climate characterizing the northern Atlantic ocean (strong winds, frequent storms and rain) allows for the presence of a large quantity of sea spray even at its relatively high elevation. The abundant rain induces a constant infiltration of marine salts in the lava tube where the reaction between the cold and salt dripping with the hot fumarole exhalations is the most important process for the evolution of the observed speleothems.

Table 3. Volcanic caves noteworthy for their mineralogical development.

Cave	Location	Noteworthy features	Reference
Algar do Carbalo	Terceira Island (Portugal)	Best and largest display of opal speleothems	Hill & Forti 1997
Alum	Vulcano Island (Italy)	Largest number of secondary cave minerals in a volcanic cave	Forti <i>et al.</i> 1996
Cutrona	Mt. Etna (Italy)	Best display of anemolites, rims, and balloons related to low temperature degassing	Forti <i>et al.</i> 1994
Dangcheomul	Jeju island (Korea)	Best display of different calcite speleothems within a volcanic cave	Woo <i>et al.</i> 2000
Grillid	Surtsey (Iceland)	Single cave reference for five different new cave minerals	Jakobsson <i>et al.</i> 1992
Hibashi	(Saudi Arabia)	Noticeable variety of organic compounds, burned guano minerals	Forti <i>et al.</i> 2004
Kitum	Mt. Elgon (Kenya)	Silicate minerals related to meteoric water leaching	Forti <i>et al.</i> 2003
Skipton	Mt. Widderin (Australia)	Site for some new cave phosphates	Webb 1997
Togawa-Sakaidani-do	Kyushu (Japan)	Best display of coralloids made by diatoms	Kashima <i>et al.</i> 1987

THE MOST IMPORTANT VOLCANIC CAVES OF THE WORLD FOR HOSTED SPELEOTHEMS

Among the top ten caves of the world for hosted speleothems (Hill & Forti 1997), two were volcanic in origin; Alum Cave (Vulcano Island, Italy) and Skipton Cave (Australia), but other volcanic caves should be considered when the environment of interest is limited to a volcanic setting. Even though volcanic cavities in which a detailed mineralogical study has been made, it is not easy to choose those that might be considered the most valuable volcanic caves for hosted speleothems. The importance of a cave cannot be limited to the number of the minerals developed inside it. Many other factors should be considered such as the dimension and the beauty of these speleothems, the peculiarity of the minerogenetic mechanisms, and the different origin of the hosting caves.

On the basis of the outlined parameters Table 3 was constructed. The majority of these (six) are obviously lava tubes (Cutrona, Grillid, Skipton, Hibashi, Togawa-Sakaidani-do, Dangcheomul caves), but also a magmatic chamber (Algar do Carbalo), a sea cave in volcanic ash (Alum Cave), and a meteoric cave in volcanic ash (Kitum Cave) are represented. Four of these have been selected for the high number of hosted minerals, many of which are new to the cavern environment (Alum, Cutrona, Grillid and Skipton Caves) (Table 2). Three other cavities have been selected because of their speleothems. These are Algar do Carbalo for its gigantic opal speleothems (Fig. 9), Dangcheomul Cave for its calcite decorations which mask this lava tube as being a "normal" karst cave (Fig. 11), and Togawa-Sakaidani-do for being the first cave in which very small but completely new opal coralloids made by diatoms have been observed. Kitum Cave was chosen because of its peculiar genesis resulting from meteoric water seepage within thick ash deposits since their initial deposition, thus allowing for the evolution of peculiar silicates (Fig. 14, see page 8). Finally, Hibashi Cave (Fig. 15, see page 8) has been inserted because the still ongoing studies of its chemical deposits evidenced the presence of different guano-related minerals, some of which are still unknown. In particular, Hibashi Cave is extremely important because it hosts some of the best occurrences of burned guano minerals of the world.

It must be stressed that the criteria utilized to select the caves are subjective and therefore this list must be regarded as a first attempt to define the most important volcanic cavities for hosted speleothems. Moreover, in the near future it is reasonably sure that new studies will discover plenty of other volcanic caves extremely important from a minerogenetic point of view.

CONCLUSIONS

Although this overview on the actual knowledge on cave minerals in volcanic caves may be regarded as short and far from exhaustive, it is sufficient to point out the importance of this environment for the development of cave minerals. In the last ten years more specific mineralogical studies have been performed in different volcanic caves around the world than ever before, and it is now clear that the volcanic environment often results in ever more interesting mineralizations than all other types of natural cavities.

Although it must be admitted that only a part of the mineral deposits developing inside volcanic caves are actually known, it is enough to consider that the cavities which have been the object of mineralogical observations, though not systematic, are far less than 5% of those presently known in the world. Furthermore, some minerogenetic mechanisms, like those connected with guano digestion, are still scarcely understood, and some mineral classes, like that of oxides-hydroxides (mainly of iron and manganese), have been only slightly investigated.

In conclusion it can be affirmed that in the near future the systematic study of the secondary chemical deposits in volcanic caves will provide great satisfaction to investigators. The number of secondary cave minerals will be much increased and some new mineral(s) for the cave environment will be discovered.

ACKNOWLEDGEMENTS

The author thanks William Halliday, Sigurdur Sveinn Jónsson, John Pint and the President of the Vulcanospeleological Commission of the UIS Jan Paul Gustaaf Van der Pas for supplying useful information and/or materials. Research done within the MIUR 2002 Project “*Morphological and mineralogical study of speleothems to reconstruct peculiar karst environments*”

REFERENCES

- Bellini, R., 1901, La Grotta dello zolfo nei Campi Flegrei: Bollettino della Società Geologica Italiana, v. 20, p. 470–475.
- Borges, P.A.V., Silva, A., Pereira, F., 1991, Caves and pits from the Azores with some comments on their geological origin, distribution and fauna: 6th International Symposium on Vulcanospeleology, Hawaii, p. 121–151.
- Centro Speleologico Etneo, 1999, Dentro il vulcano: le grotte dell’Etna: Parco dell’Etna, 342 p.
- Cossa, A., 1878, Ricerche chimiche: Accademia dei Lincei, Roma, v. 3(2), p. 7.
- Davies, G.J., 1998, “Hades” – a remarkable cave on Oldoinyo Lengai in the East African Rift valley: International Journal of Speleology, v. 27B(1/4), p.57–67.
- Del Monte, M., Forti, P., Rabbi, E., 1987, A proposito di alcune concrezioni delle grotte di lava dell’Etna: 4th International Symposium on Vulcanospeleology, Catania 1983, p.31–39.
- Forti, P., 1994, Cave minerals in volcanic caves: Acta I^o Incontro Internacional de Vulcanoespeleologia das Ilhas Atlanticas, Pico, Acores, 1992, p.1–98.
- Forti P., 2000, Minerogenetic mechanisms and cave minerals in the volcanic caves of Mt. Etna (Sicily, Italy): Mitteilungen Verband Deutschen Höhlen-und-Karstforschung, v. 46(1/2), p. 37–41.
- Forti P., 2001, Biogenic speleothems: an overview: International Journal of Speleology, v. 30A (1/4), p. 39–56.
- Forti, P., 2003, Eccezionali ambienti minerogenetici: in Cicogna, F., Nike Bianchi, C., Ferrari, G., Forti, P., eds., Grotte Marine: cinquant’anni di ricerca in Italia: Ministero dell’Ambiente, p. 83–85.
- Forti, P., Marino, A., 1995, Nota preliminare sul ritrovamento di un nuovo minerale di grotta nei “Pozzi dell’Eruzione del 1923”: Atti Convegno Speleologico Regionale, Ragusa 1990, v.1, p.92–100.
- Forti, P., Giudice, G., Marino, A., Rossi, A., 1994, La Grotta Cutrona (MC1) sul Monte Etna e i suoi speleotemi metastabili: Atti Congresso Regionale di Speleologia, Catania, p.125–151.
- Forti, P., Panzica La Manna, M., Rossi, A., 1996, The peculiar mineralogical site of the Alum cave (Vulcano, Sicily): 7th International Symposium on Vulcanospeleology, Canarie 1994, p.35–44.
- Forti, P., Galli, E., Rossi, A., 2003, Minerogenesis in some volcanic caves of Kenya: International Journal of Speleology, v. 32(1/4), p.1–16.
- Forti, P., Galli, E., Rossi, A., Pint, J., Pint, S., 2004, The Hibashi lava tube: the best site of Saudi Arabia for cave minerals: Acta Carsologica, accepted for publication.
- Harter, R. 1973, Secondary chemical deposits in lava tubes. Speleograph, v 9(7), p. 114–116.
- Hill, C.A., Forti, P., 1997, Cave minerals of the World: National Speleological Society, Huntsville, 464 p.
- Jakobsson, S.B., Jónsson, S.S., Leonardsen, E., 1992, Encrustations from lava caves in Surtsey, Iceland. A preliminary report: Surtsey Research. Project Report, n. 10, p.73–78.
- Jervis, G., 1881, Tesori sotterranei d’Italia: Milano, v. 3, p. 197.
- Jónsson, S.S., 1994, Mineral encrustation in Icelandic lava caves: Acta I^o Incontro Internacional de Vulcanoespeleologia das Ilhas Atlanticas, Pico, Acores, 1992, p. 89–91.
- Kashima, N., Ogawa, T. 1998, Speleo-minerals in volcanic caves of Kenya, East African Rift Zone: Journal of Speleological Society of Japan, v. 23, p.46–52.
- Kashima, N., Suh, M.S., 1984, Hjeobaje cave system, a pseudo-calcareous cave in Jeju Island, South Korea: Journal of Speleological Society of Japan, v. 9, p.23–30.
- Kashima, N., Irie, T., Kinoshite, N., 1987, Diatoms, contributors of coralloid speleothems, from Togawa-Sakaidani-do cave in Miyazaki Prefecture, Central Kyushu, Japan: International Journal of Speleology, v. 16, p. 95–100.
- Kashima, N., Ogawa, T., Hong, S.H., 1989, Volcanogenic speleo-minerals in Cheju Island, Korea: Journal of Speleological Society of Japan, v. 14, p. 32–39.
- MacIvor, R.W.E., 1887, On Australia bat guano and some minerals occurring therein: Chemical News, v. 55 (1433), p. 215–216.
- Marino, A., 1994, La Buca della Martinite: Bollettino della Accademia Gioenia di Scienze Naturali v. 28 (348), p. 231–241.
- Martini, J.E.J., 1994a, Two new minerals originated from bat guano combustion in Arnhem Cave, Namibia: South African Speleological Association Bulletin, v. 33, p. 66–69.
- Martini, J.E.J., 1994b, The combustion of bat guano: A poorly known phenomenon: South African Speleological Association Bulletin, v. 33, p. 70–72.
- Panichi, U., 1913, Millosevichite nuovo minerale del Faraglione di Levante nell’isola di Vulcano: Rendiconti Accademia dei Lincei, p. 1–3.
- Panichi, U., 1914, Contributo allo studio dei minerali dell’isola di Vulcano: Memoria della Società Italiana di Scienze, s. 3, v. 19, p. 1–55.
- Recupero, G., 1815, Storia generale e naturale dell’Etna: Catania, 135 p.
- Rogers, B.W., Rice, P.H., 1992, Geology and mineralogy of lava tube caves of Medicine Lake Volcano: in Re, G.T., ed., Proceedings 6th International Symposium on Vulcanospeleology, Huntsville, p.45–49.
- Sava, R., 1842, Sopra alcuni prodotti naturali che si formano in una spelunca dell’Etna: Annali Civici del Regno Due Sicilie, v. 30 (60), p. 1–39.
- Scacchi, A., 1850, Memorie mineralogiche e geologiche della Campania: Rendiconti dell’Accademia di Scienze di Napoli, v. 3, p.317–335.
- Shaw, T.R., 1997, Historical introduction: in Hill, C.A., Forti, P., Cave minerals of the World: National Speleological Society, Huntsville, p. 27–43.
- Spallanzani, L., 1792–97, Viaggi alle Due Sicilie ed in alcune parti dell’Appennino: S.Tommaso D’Aquino, Bologna, v. 1, p. 353–356.
- Sutcliffe, A.J., 1973, Caves of East African Rift valley: Transaction of the Cave Research Group of Great Britain, v. 15(1), p. 41–65.
- Udluft, H., 1928, Zeolithe als Fossilizationsmaterial: Arkiv Kemischen Mineralogischen Geologischen, v. 9(33), p. 1–15.
- Ulrich, G.H.F., 1870, Contributions to the mineralogy of Victoria: Melbourne, p. 1–33.
- Webb, J.A. 1997 Skipton Lava Cave, Victoria, Australia: in Hill C.A., Forti P., Cave Minerals of the World: National Speleological Society, Huntsville, p. 331–335.
- Woo, K. S., Choi, D. W., Kim, R. and Kim, J. K., 2000, The origin of the speleothems in Dangcheomul Cave, Jeju Island, Korea: Journal of the Geological Society of Korea, v. 36 (4), p. 411–434.
- Zambonini, F., 1907, Su alcuni minerali della Grotta dello Zolfo a Misero: Rendiconti della Accademia di Scienze, s. 3, v. 13–14(12), p. 1–8.