THE GUANO HOLES: A NEW CORROSION FORM FROM NATUTURINGAM CAVE (PALAWAN, PHILIPPINES)*

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Abstract. A totally new corrosion form has been recently observed inside the Natuturingam cave (better known as Puerto Princesa Underground River) in Palawan (Philippines): the guano holes. They consist of perfectly rounded holes, 4–5 cm wide and up to 10–15 cm deep, developing over a flat limestone surfaces covered by a thin layer of fresh guano. In the same cave larger guano-related corrosion forms have also been encountered, but are not presented in detail here (guano pots). A 3D photogrammetric survey has been carried out on a series of guano-holes to make some morphometric measurements. Their development is controlled by the peculiar Palawan climate, which is characterized by short but heavy rainfalls followed by rather long dry periods. During rainfalls each water drip drills a perfectly rounded hole into the fresh guano reaching the limestone surface which is then corroded by the acids produced by guano digestion. The corrosion process on the exposed limestone surface continues during the whole subsequent dry period and causes the deepening of the initial depression with respect to the surrounding area. At the end of the dry period the drilled holes are partially refilled by fresh guano, and the process restarts at the beginning of a new rainstorm. Subsequent cycles of wet and dry periods cause a progressive deepening of each hole. When two or more drops and their splashing areas interfere, their holes coalesce thus giving rise to relatively larger and complex forms. Finally, during the dry periods, capillary rise and evaporation of the solution trapped within the hole may cause the deposition of small aggregates of different minerals (mainly hydroxylapatite, with minor quantities of calcite). During the next rainstorm, sometimes dripping may not be able to wash away all these minerals, so that they progressively accumulate inside the hole developing a layered speleothem.

Key words: Corrosion form, climatic control, genetic mechanism, cave minerals.

1. INTRODUCTION

Guano is a very strong agent of limestone corrosion in caves. Its digestion processes produce large quantities of CO_2 and several strong acids (among which sulfuric and nitric acids are the most common, but also hydrochloric and

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phosphoric acids are often present). For this reason evident corrosion forms and plenty of cave minerals are often related to the presence of guano deposits in caves (ONAC & FORTI, 2011).

Recent investigations in the Natuturingam cave (Puerto Princesa Underground River, Palawan, Philippines) have allowed to discover a new limestone corrosion form (DE VIVO & FORTI, 2017), the guano holes (Fig. 1). These forms are rather common inside the cave, where they were observed in three different branches, far from each other (Fig. 2).

Morphologically the guano holes are very similar to the conulites developing over a soft (clay) substratum by dripping erosion, but obviously their evolution must be driven by different factors, being developed in hard limestone. Their development is related to the strong acids produced by the oxidation of guano deposits.

In the present paper, after a short description of the cave and its main peculiarities, the mechanisms allowing these forms to develop are discussed in detail.

Fig. 1. Navigator chamber: hundreds of empty guano holes on a flat limestone surface (Photo by Marco Vattano).

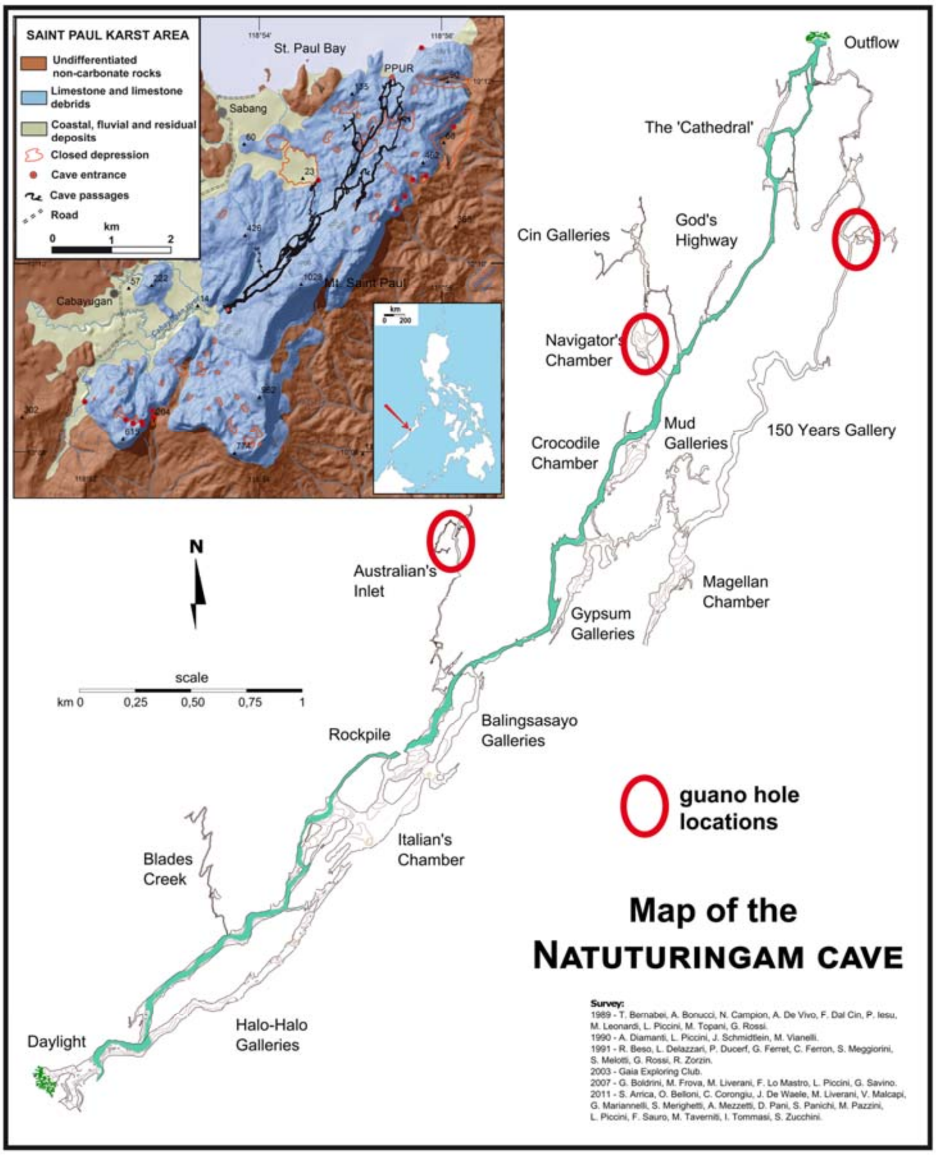

Fig. 2. Sketch of the Natuturingam cave with the location (red circles) of the guano holes.

2. THE NATUTURINGAM CAVE

The Natuturingam cave (better known as PPUR, acronym of Puerto Princesa Underground River) is one of the largest subterranean estuaries of the World (PICCINI & IANDELLI, 2011), where tides propagate over 6.5 km inside the mountain. Actually it consists of over 34 km of giant galleries (thus resulting one of the longest caves of the Philippines), but its exploration is still ongoing; it hosts an extremely complex ecosystem based on the large and widespread guano deposits formed by huge colonies (over hundred thousands) of bats and swiftlets living in the cave (AGNELLI *et al*., 2018). This site was recognized as World Heritage by UNESCO since 1999. In 2004 it was declared a National Geologic Monument by the Philippine Committee on Geological Sciences (RESTIFICAR *et al*., 2006), becoming one of the New Seven Wonders of Nature in 2011 and, finally, the fifth Wetland of International Importance (Ramsar Site) in the Philippines in 2012.

The first 2 km of its navigable branch were transformed into a show cave at the beginning of the 80s of the past century. Since the start of the third millennium it has become the most visited show cave of the Philippines and one of the most visited of the whole far East Asia, with more than 300,000 visitors/year. A unique characteristic of this show cave is that no fixed structures have been built (i.e. no pathways, no lights), and therefore it can still be considered as a pristine cave.

The cave system has been studied from a geomorphological point of view in the last ten years (PICCINI & IANDELLI, 2011; COOMBES *et al*., 2015). In the last two years, thanks to an international multidisciplinary research project (DE VIVO *et al*., 2017) it was possible to make a detailed analysis of the Natuturingam speleothems and morphologies. This study, still in progress, allowed to discover several uncommon forms, among which a few are absolutely novel for the cave environment (BADINO *et al*., 2017; CALAFORRA & FORTI, 2018). Moreover, it appears that the evolution of all these forms is mainly controlled by the Palawan climate.

3. THE CAVE CLIMATE

Palawan is located in the Intertropical Convergence Zone (ITCZ) and therefore its average temperature is relatively high (~27 °C) with daily, monthly and yearly excursion rarely exceeding ± 5 °C. The climate is "tropical wet and dry"; the average rainfall is relatively high (close to 2,000 mm/yr, 95% of which falls during the wet period from May to November) concentrated in few, short but heavy rainstorms (BADINO *et al*., 2017).

The cave is also unique for its underground climate: it is extremely stable, being controlled by the general climate of the island (BADINO, 2013) and by the tides, which, during the dry season, invade a large part of the cave with more than 100.000 m^3 of sea water twice a day (FORTI, 2014). Due to the tropical climate of the area the flow regime within the cave dramatically changes from less than 0.2 m^3/s to well above 10 m^3/s in only a few hours during and just after heavy rainstorms (CALLIGARIS *et al*., 2018).

As a consequence of this special climate dripping in most of the cave passages is scarce, or totally absent, for long periods of time. Speleothems are thus dry and inactive for most of the time, while during and immediately after the heavy rains intense and widespread dripping characterizes large areas of the cave, where most of the speleothems reactivate allowing the development of some peculiar forms (CALAFORRA & FORTI, 2018).

The very high external relative humidity, together with the extremely low daily in-cave temperature fluctuations and the presence within the cave of a wide free water surface, greatly inhibit the evaporation processes that are limited to branches at some distance from the underground river, or places where relatively strong air currents occur (up to 1.5 m/s displacing over 100 m^3/s of air). At some sites within the cave system, it is sometimes possible to see active condensation processes with the development of large cave clouds, the genesis of which is induced by cold air currents coming from the upper cave levels (BADINO, 2017) or when relatively cool percolation water coming from the top of the mountain rapidly reaches the main cave passages.

4. THE SHAPE OF THE "GUANO HOLES"

Guano holes have been found in three different locations in the cave system (see Fig. 2), but the characteristics of these sites are always the same. Guano holes are always grouped in clusters of tens or hundreds of elements, developed over rather flat, or only gently inclined, limestone surfaces, which are covered by a relatively thin guano deposit (just a couple of cm thick).

The guano holes are perfectly rounded vertical cylinders, or very elongated upside-down cones with a average diameter ranging between 3 and 6 cm (Fig. 3A), but a few of them (up to a maximum of 3–4 holes) may coalesce giving rise to a more complex plan shape (Fig. 3B). The depth of the holes ranges between 10 and 15 cm, although younger holes with a shallower depth have also been observed. Many of the holes are empty, showing a smooth inner surface, but sometimes a layered speleothem, partially detached from the limestone surface and mainly consisting of phosphates (hydroxylapatite and minor calcite) (Fig. 3C) is found.

Some guano hole fields have been mapped by means of 3D photogrammetry to carry out morphometric measurements (DE VIVO *et al*., 2017).

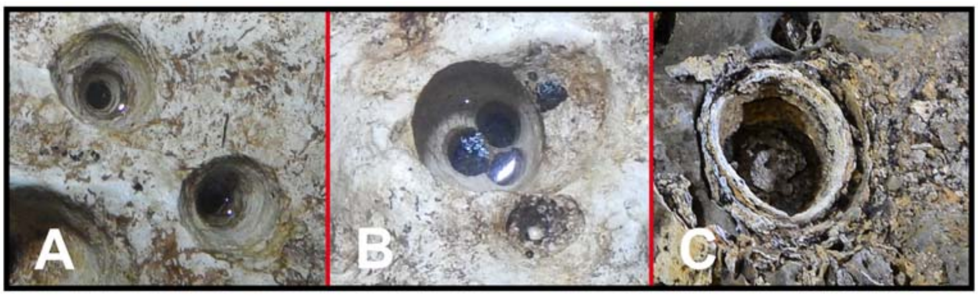

Fig. 3. Navigator's Chamber: A) two perfectly rounded guano holes; B) the coalescence of several guano holes; Australian Inlet: C) layered phosphate ring developed inside a guano hole (Photos Marco Vattano).

5. BOUNDARY CONDITIONS FOR THE DEVELOPMENT OF THE GUANO HOLES

In order to allow guano holes to develop, the area of the cave has to be characterized by three conditions, which prevent the development of a uniformly corroded limestone surface.

The surface of the limestone needs to be close-to-horizontal

This condition is necessary to allow the guano to accumulate, but also to prevent the percolation waters passing through the guano to drain downward. These percolates are enriched in strong acids, produced by the oxidation of the guano, and their reaction with the limestone has to occur always more or less in the same spots.

The thickness of the guano deposit should not exceed a couple of centimeters

The thickness of the guano deposit is a conditioning factor because of two main reasons:

A: in absence of dripping, if the guano layer is too thick the acid produced by the oxidation processes may not be able to reach the underlying carbonate surface, also because the evaporation at the surface favors capillary-driven upward movement of the fluids.

B: when dripping is active, the mechanical erosion of the drops has to be able to remove all the guano from the carbonate rock, exposing the underlying surface to the acid corrosion. With a thick guano deposit the mechanical action of the falling drops would not be able to reach the underlying rock surface before the deposition of new fresh guano. The guano would simply be soaked with water, and the corrosive action would occur on the entire underlying guano-rock surface.

The area has to be under intense dripping for short periods of time, interrupted by long periods of drought (no dripping)

The long periods of absence of dripping are required to allow the guano to accumulate over the entire close-to-horizontal surface, whereas the intense dripping allows the underlying carbonate rock to be cleaned under the dripping points. It is in these last places that corrosion will be greater because of the free rock surface, creating the depressions that will progressively evolve into the deeper guano holes. The monsoonal climate, and rainfall regime, of Palawan coupled with the large amounts of guano brought by both swiftlets and bats are thus the fundamental criteria to be fulfilled to have the formation of guano holes.

6. THE EVOLUTIONARY STEPS IN GUANO HOLE EVOLUTION

Guano holes can start developing if the above described boundary conditions are all fulfilled.

Normally a single dripping is responsible for the evolution of a guano hole, the diameter of which (corresponding to the impact area) is proportional to the dimension of the falling drop and its kinetic energy, which in turn depends on the height of the ceiling from which the droplets fall (Fig. 4).

When, and only when, two or more impact areas partially overlap a coalescence of holes occurs just along their interference areas, thus more complex guano hole planimetries can develop (Fig. 5).

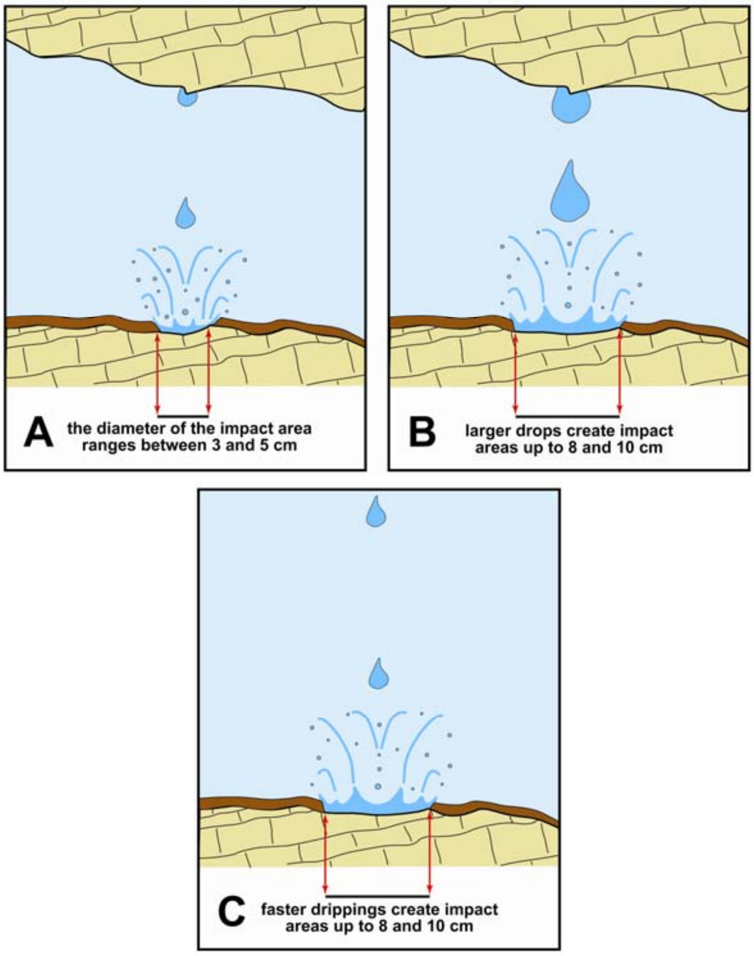

Fig. 4. The impact area normally ranges between 3 and 5 cm (A) but is directly proportional to the drop dimension (B) and falling velocity (C) therefore larger hole diameters are also possible.

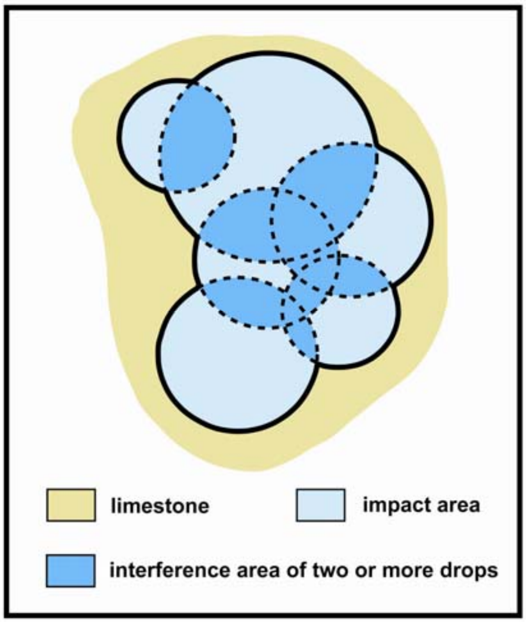

Fig. 5. A partially overlapped impact areas and the resulting complex guano hole planimetry.

In any case the stages in the development of complex or simple guano holes are always the same.

The first stage (Fig. 6A) consists in the formation of a thin layer of guano upon a close-to-horizontal surface of the carbonate rock (generally limestone). Guano deposition (without removal) normally occurs during a more or less long dry period. During this period the absence of dripping will allow the guano to be relatively dry, thus slowing down the corrosion of the lower guano-rock surface: in fact the organic decomposition of the guano is accelerated in the presence of water, which enhances the oxidation and the microbial growth. The small quantities of strong acids that are produced even under drier conditions will mostly be directed upward by capillary forces, driven by the evaporation occurring on top of the guano layer. In fact, the higher temperatures of the slowly decomposing guano induce evaporation to occur. At the guano-atmosphere boundary also secondary minerals are produced. It is therefore difficult to envisage these acids to descend and react with the underling guano-rock surface.

The evolution of the guano holes starts when dripping occurs on the guano, triggered by rain events (Fig. 6B). The impact of the droplets on the unconsolidated guano layer causes its removal where the drips hit the surface. This exposes more or less circular portions of the underlying carbonate rock with diameters ranging between 3 and 10 cm (depending on the height of the ceiling).

These small exposed rock surfaces will be subjected to both erosion and corrosion processes of the water droplets, which are undersaturated respect to calcite (or other carbonates) because of their fast percolation through the vadose zone. The exposed rock will thus undergo a surface lowering, small but sufficient enough to allow collection of the percolation water that seeps through and from the guano deposit once the dripping has come to an end (Fig. 6B.1).

In the meantime the water that has been absorbed by the guano has allowed decomposition processes to start with the production of carbon dioxide, together with small amounts of strong acids. These substances can percolate downward and reach the underlying guano-rock surface, flowing toward the more depressed areas (i.e. proto guano holes) causing corrosion and further carbon dioxide release. These corrosion processes are stronger in the lower lying proto guano holes, leading to a faster surface lowering in these spots respect to the rest of the surface. The water percolating through the guano is also enriched in organic material that accumulates in the depressions. These organics oxidize easily inside the guano holes, also because of the direct contact with the free atmosphere in these guano-free spots. Both processes will thus focus dissolution in the guano-free areas, in a self-sustaining manner. The *in situ* oxidation will cause the formation of new mineral substances (in general nitrates and sulfates) that will stay in solution initially.

Small amounts of secondary minerals, formed by the reaction within the guano itself or its reaction with the carbonate rock, will remain at the end of the evaporation processes at the surface of the guano deposit and on the borders and bottom of the proto guano holes (Fig. 6C.1). These minerals are generally ephemeral because of their high solubility and their small size, and they are often removed once intense dripping resumes. During the long periods in which dripping is absent the guano starts accumulating again in thin layers, covering both guano holes and earlier guano.

The alternation of dripping/drying and guano deposition cycles progressively leads to the development of mature guano holes (Fig. 6D). With the deepening of the guano holes the oxidation-corrosion processes, that are mainly active during the drier periods, become more and more efficient, since the growing depression can contain an increasing amount of liquid. This is a self-accelerating process. Despite the fact that the water contained in the guano holes will always be able to dissolve the carbonate rock, the lateral enlargement of the holes is much slower than their deepening. This lateral enlargement sometimes causes the coalescence of adjacent guano holes if their impact areas partially overlap. The difference in corrosion rate between walls and bottom is due to the fact that the oxidation of the organic material mostly occurs on the bottom of these forms, where guano is accumulated. In addition, the organic decay causes the production of carbon dioxide, which is released to the atmosphere at the water-air interface, decreasing the acidity in the upper layers of the liquid contained in the guano holes.

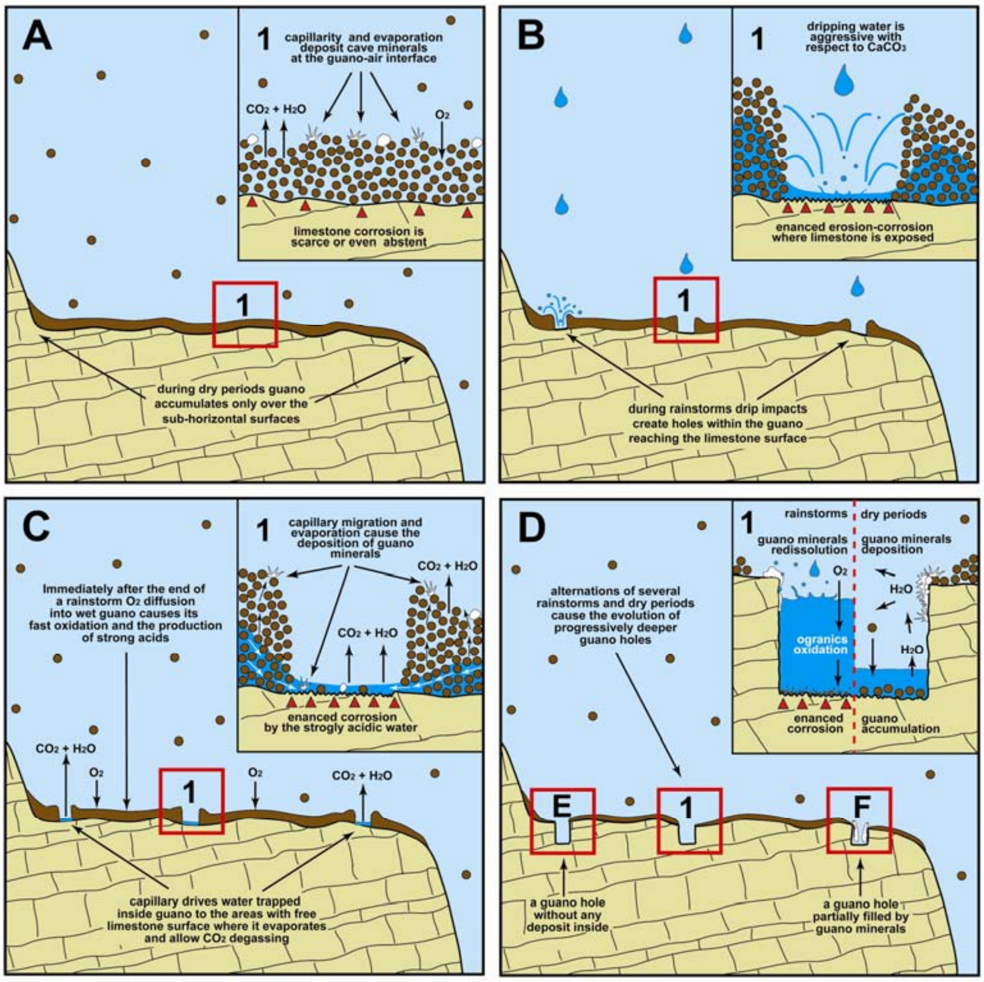

Fig. 6. Development stages of a guano hole. A) during the dry season a thin guano layer deposit is formed over a close-to-horizontal limestone surface: due to the relatively dry environment only small amounts of strong acids are produced and driven upward by capillary movements (1) thus leaving the limestone surface almost unaffected by corrosion processes. B) Immediately after strong rainstorms dripping washes away the guano and the exposed limestone surface is mechanically eroded and simultaneously corroded by the still aggressive meteoric water (1). C) After the end of dripping strongly acidic water flows toward the lower-lying free limestone surface, thus causing further corrosion. Later capillary uplift (1) and evaporation cause the deposition of different guano-minerals. D) Several A-B-C cycles (1) cause the progressive development of the guano holes, which are often completely empty (E) but sometimes contain some secondary minerals (F).

Some of the guano holes do not contain secondary minerals and are empty (Fig. 7A), and others are almost completely coated by secondary deposits, sometimes forming a sort of conulites protruding from the guano holes (Fig. 7B). The energy of the dripping water probably controls the presence of secondary deposits inside the guano holes. At the start of a new dripping period the minerals and organic debris that are trapped inside the holes are normally dissolved or removed by the intense dripping. Thus these deposits normally do not survive more than one cycle of dripping/drying and guano deposition. In some exceptional cases, however, the erosional force of the dripping is not strong enough to entirely remove these deposits, and is overruled by the inflowing percolation water coming from the nearby guano sheet. Every cycle these secondary deposits will tend to grow, sometimes totally filling the guano holes, and even leaving a raised rim around the holes. These secondary mineral deposits take the form of conulites, since erosion by the droplets will be stronger at the center of the holes, while deposition (mainly by evaporation) after dripping stops will be greater on its sides.

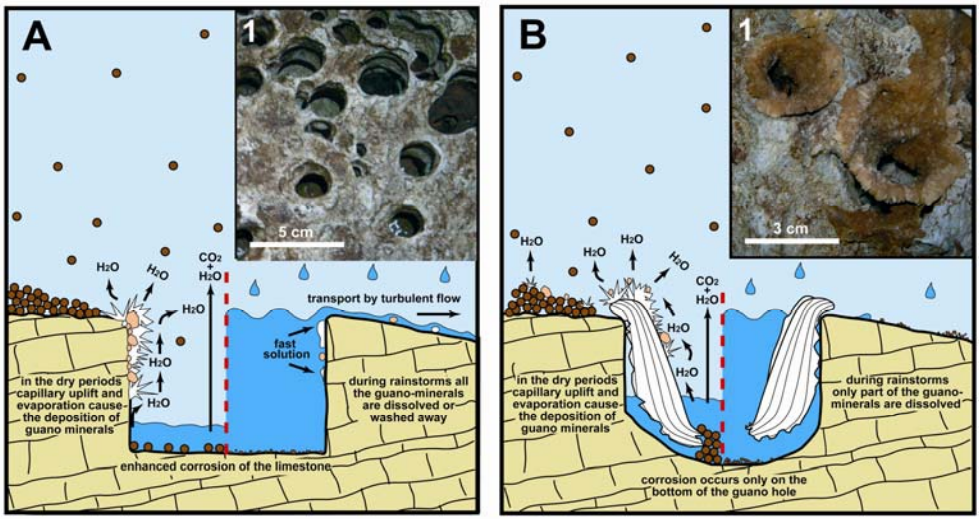

Fig. 7. A) The evolution of guano holes without cave minerals encrusting their walls (1, photo by José Maria Calaforra) is the direct consequence of the flow regimen during rainstorms, which allows the total dissolution/erosion of the deposits developed during the dry periods. B) The evolution of a "conulite-shaped" deposit of secondary minerals (1, photo by José Maria Calaforra) inside a guano hole occurs when the flow regimen during rainstorms is unable to destroy all the material deposited during the dry periods. Normally the mineral deposit covers the walls of the guano-hole while its bottom it is maintained free thus allowing its further corrosion.

This will create the typical upside-down cone shape of these coatings. In general the falling of the undersaturated droplets is big enough to inhibit the formation and deposition of minerals on the bottom, thus allowing the guano-hole to deepen by corrosion, but a mineral coating will protect, at least partially, its lateral sides. The bottom of mineral-free guano holes in general will almost be flat (similar to kamenitze), while those with secondary deposits inside will have a bottom with a more conical shape.

7. FINAL REMARKS

Inside the Natuturingam cave some totally new corrosion-depositional forms had the possibility to develop thanks to the peculiar Palawan climate and the presence of widespread guano deposits.

Among them the most characteristic ones are the "guano holes", the development of which is controlled by the flat morphology of the bedrock, the thickness of the guano deposits and the dripping regimen.

Beside guano holes, the Natuturingam cave hosts other different corrosion-depositional forms induced by dripping over guano deposits: the "guano pots" (similar to the guano holes, but one order of magnitude bigger) that were observed, for the first time, during the last expedition (Fig. 8). Their genetic mechanism is probably similar to that just described for guano holes, but the boundary conditions should be different (thicker guano deposits, higher amount of dripping water, etc).

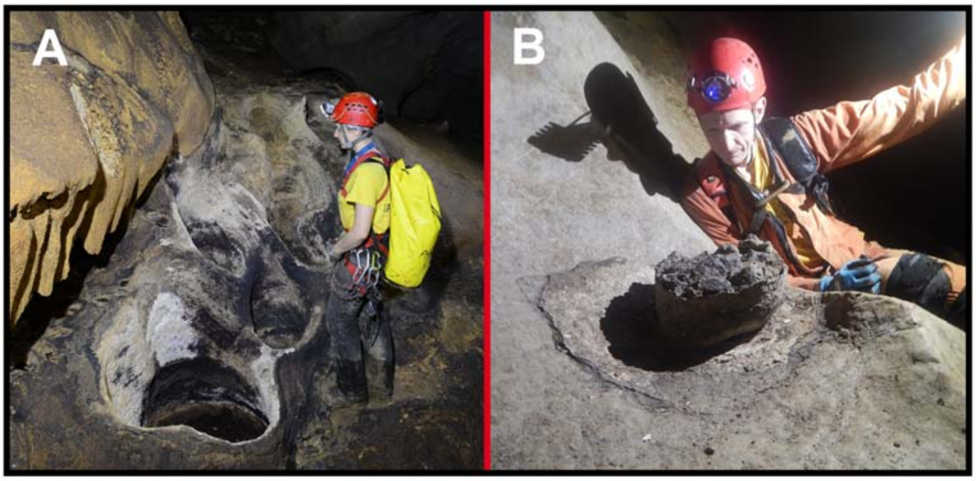

Fig. 8. Natuturingam cave, Gaia Branch: A) a series of guano pots; B): river conglomerate with phosphate (?) cement developed within a former pothole now completely destroyed by selective erosion-corrosion processes (Photos by Marco Vattano).

During the last expedition these new forms have only been documented, so they still need further experimental observations in order to define the mechanism controlling their evolution. Therefore the guano pots will be the object of a detailed study in the next expedition to Palawan.

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