# Holocene pisoliths and encrustations associated with spring-fed surface pools, Pastos Grandes, Bolivia

# FRANÇOIS RISACHER and HANS P. EUGSTER

UMSA-ORSTOM, Cajon Postal 8714 La Paz, Bolivia and Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218

# ABSTRACT

Calcite pisoliths, with diameters ranging from 1 to 200 mm, are forming now on the surface of a playa (salar) in the Andean Altiplano (4500 m above MSL) of Bolivia. They are associated with active or recently active hot springs (20-75°C) which flow onto the playa surface. Encrustations of pieces of an older caliche-type crust, of pisoliths, of indurated mud and of older concretions are also found as well as series of small (1-3 cm high) sinter terraces (rimstone dams). Arborescent concretions and overgrowths are common and they are reminiscent of drip-stone textures. Water analyses demonstrate that calcite supersaturation (about twenty times) occurs mainly through CO<sub>2</sub> loss, with photosynthesis by algae and degassing the main removal mechanisms. The two available analyses indicate slight evaporation and a calcium loss between spring and pool of 2.3 mmol per litre of water. It is thought that the hot springs pick up much of their solute load from the playa sediments. The closest analogues to these deposits have been reported from caves (cave pearls and concretions). Although the depositional processes may be similar, the environment on an evaporitic playa surface is quite different. The geological implications for this newly observed pisolith environment may be considerable.

## **INTRODUCTION**



Carbonate pisoliths are common in the geological record and they can form by a variety of processes in a range of environments. Scholle & Kinsman (1974) list the four major settings, caliche, caves, hypersaline lagoons and normal marine, and summarize the relevant literature. Processes range from purely inorganic precipitation, as in cave pearls, to the algal oncolites from modern marine and non-marine settings (see for instance Bathurst, 1971; Monty, 1972; Schöttle & Müller, 1969). Accurate definition of processes and environments in Holocene occurrences is crucial for our understanding of ancient examples. For instance, the pisoliths of the Permian Capitan reef complex of New Mexico and Texas have been interpreted variously as algal pisoliths (Ruedemann, 1929; Kendall, 1969), vadose pisoliths associated with caliche crusts (Thomas, 1968; Dunham, 1969) and as pisoliths formed in ponded lagoons (Esteban, 1976; Esteban & Pray, 1977).

Fonds Documentaire ORSTOM

 $\mathbb{M}$ 

Щ

80

Cote: 6× 55

0037-0746/79/0400-0253\$02.00 ©1979 International Association of Sedimentologists

This paper describes the occurrence of Holocene pisoliths, rimstone dams and arborescent encrustations (drip-stones) which form in shallow, spring-fed pools on the playa surface of the Pastos Grandes Salar in the Bolivian Andes. The pisoliths and associated encrustations are directly analogous to cave deposits, except that they form on the surface in an evaporitic setting. We believe this to be the first report of pisoliths from this kind of environment and the geological implications of these observations are obvious.

# CAVE PEARLS AND CONCRETIONS

Perhaps the most intensively studied Holocene pisoliths are those forming in caves. The literature on cave pearls is extensive, with some of the more notable contributions made by Kumm (1926), Hess (1930), Davidson & McKinstry (1931), Stone (1932), Royer (1939), Casteret (1939), Mackin & Coombs (1945), Pond (1945), Baker & Frostick (1947, 1951), Black (1952), Murray (1954), Kirchmayer (1962, 1964), Hahne, Kirchmayer & Ottemann (1968), Donahue (1965, 1969) and Dunham (1972). Cave pearls are normally calcite and they are dense, concentrically laminated spheroids which can reach a diameter of up to 4 cm ('pigeon eggs'). Non-spherical shapes are also common and some pisoliths are elliptical, oblong, irregular or even polyhedral (see for instance Hess, 1930, plate 7 and Baker & Frostick, 1947, p. 51). Larger pisoliths grade into concretions, which can reach sizes of up to 30 cm and are found in deeper pools (Donahue, 1969).

Splash cups and rimstone dam pools are favoured locations for loose pisoliths. Excellent photographs have been published by Hess (1930, plate 1), Pond (1945), Black (1952, p. 207), Kirchmayer (1964, fig. 2), and Dunham (1972, fig. II-98). The number of pisoliths per pool and their size seem to vary inversely. Reverse grading in single pools has been reported repeatedly (see for instance Mackin & Coombs, 1945, Baker & Frostick, 1947, and Dunham, 1972).

All cave pisoliths and concretions are concentrically laminated with the laminations usually in the form of light-dark couplets. Kirchmayer (1962, 1964) interprets such couplets as summer-winter layers. Thicknesses range from 0.003 mm to more than 0.1 mm and growth rates are quoted from 1 cm in 3 months to 1 cm in over 100 years (Hahne *et al.*, 1968). Laminations may have even thicknesses or they may be affected by contact with neighbouring grains. Black (1952, p. 209) has pictured excellent examples of grain interference in the form of an indentation in the bottom pisolith acting as the seat for the pearl lying on top. Donahue (1969) has noted thickness variations between top and bottom laminations of larger concretions. Small pearls (<1 cm) have smooth, polished surfaces, while the larger pisoliths commonly have a rugose, pustular appearance (see for instance Baker & Frostick, 1947, p. 51; Donahue, 1969, fig. 9).

There is still considerable argument with respect to rotation or oscillation as a prerequisite for spherical growth. Smaller pearls (<1 cm) have been observed to rotate freely because of their buoyancy and the agitation caused by dripping water, while the larger ones are thought to rock back and forth. Baker & Frostick (1951) and Donahue 1969) have correlated degree of agitation with lamination character. Rotation in high-energy environments not only insures even growth, but can also lead to surface polish and abrasion.

On the other hand, the larger concretions clearly do not move. Also, Davidson & McKinstry (1931) have shown that rolling is not necessary for concentric growth. Accretion on the underside occurs through the porous substrate and the pisoliths and concretions thus literally lift themselves off the floor (see also Moore & Nicholas, 1964; Thrailkill, 1976).

There seems to be general agreement that cementation of pisoliths to the floor or sides of the pools does not depend on their lack of ability to rotate. Rather, it is an indication of lowered water levels. Black (1952) has concluded from his observations in the Carlsbad Caverns that 'Inability to rotate is no criterion as to when an accretion will become attached or fixed in place; . . . practically all accretions will become attached when the zone of evaporation and mineral deposition is lowered to the point of contact between the accretion and the floor' (p. 210). Baker and Frostick (1947, 1951) made similar observations in Australian caves.

There are few quantitative studies of the mechanisms of cave pearl formation, but the mineralogy and geochemistry of cave deposits in general have been studied by Moore (1962), Roques (1963), Holland *et al.* (1964) and Thrailkill (1971). Waters which enter the caves are usually supersaturated with respect to the CO<sub>2</sub> atmosphere of the cave and hence CO<sub>2</sub> loss leads to supersaturation with respect to the carbonate minerals such as calcite and aragonite. CO<sub>2</sub> loss may be accomplished either by inorganic degassing or by bacterial CO<sub>2</sub> consumption. Details of the efficacy of these processes in caves are not yet available.

Although not related directly to carbonate cave pearls, it is interesting to note that Walter (1976, figs 15 and 16) has pictured silica pisoliths from splash pools associated with geysers.

# PASTOS GRANDES; LOCATION, GEOLOGY, HYDROLOGY

The salar of Pastos Grandes is located in the southern part of the Bolivian Altiplano (Lipez). The Altiplano is a Plio-Pleistocene continental basin bounded by the eastern and western Cordillera (Fig. 1). The immense salars of Uyuni and Coipasa, remnants of larger Pleistocene lakes, occupy the central and lower part of the Altiplano (3650 m altitude), while a number of small evaporitic basins occur at the high elevations (4000–4500 m) of the southern Altiplano. Pastos Grandes, with an area of 100 km<sup>2</sup>, is one of the largest of the southern basins. Salts found in the salars range from sodium chloride, sodium carbonates, sodium sulphates to borates and calcium sulphates. These sediments were described briefly by Ahlfeld (1956) and by Ahlfeld & Branisa (1960).

Cenozoic volcanism is extensive in the southern part of the Altiplano. Fernandez *et al.* (1973) characterized the ignimbrites and stratovolcanoes as dacites to rhyodacites, while in the neighbouring Chilean sector andesites to dacites predominate (Thorpe, Potts & Francis, 1976). Native sulphur deposits, some of which are mined, occur on many of the volcanoes. Thermal springs are numerous.

The climate is characterized by a wet and rather warm season from December to March (summer), and by a dry and cold season from April to November (winter). We have no accurate precipitation data for the South Altiplano. However we can estimate the annual precipitation at 20 cm, the annual evaporation at 1.5 m and the lowest winter temperatures (June-August) to  $-25^{\circ}$ C.

F. Risacher and H. P. Eugster



Fig. 1. Location map and cross-section through the Altiplano of Bolivia.

A generalized map of the surface formations at Pastos Grandes and of the general hydrologic relationships is given in Fig. 2. Carbonate crusts and concretions occur mainly in the western part of the salar, an area with many active hot springs, and many which have recently been active. The lowest formation studied is a beige carbonate mud which is thixotropic during the warm season and frozen to at least 1 m depth in the winter. Polygonal frost-action cells (cryoturbation) are about 1 m in diameter. This mud is believed to represent an earlier lacustrine period. It is overlain by a caliche-type calcium carbonate-rich duricrust, up to 30 cm thick. This crust is polygonally broken by frost action and many fragments are pushed on edge. It consists of carbonate-cemented fragments of old soils, gravel, carbonate concretions and pisoliths, one of which has been dated at  $620\pm220$  year B.P. (Fontes & Servant, 1976).



Fig. 2. Surface formations of the Pastos Grandes Salar. Contours in m above MSL. The heavy, dashed line represents the hydrological boundary of the basin and the dotted line the boundary of the salar. The fine, dashed lines are intermittent water courses. Location numbers are for water samples listed in Table 1.

This crust seems to have formed by capillary evaporation of ground water during an earlier dry period. A subsequent cold period, the small glacial age of 500 years B.P., presumably is responsible for the cryoturbation. A few outcrops exist where this crust is covered by 50–100 cm thick sands and clays.

An intricate system of ponds exists on the surface of the salar and on its shores (Fig. 2). They are fed by two types of springs. Cold, dilute (50–200 ppm dissolved solids) springs issue near the NE, E and SE shores and feed the respective ponds. More saline hot springs are encountered in the western part of the salar, a playa surface of some 40 km<sup>2</sup>. Fifteen high discharge springs were counted with temperatures between  $20^{\circ}$  and  $75^{\circ}$ C. Those near the shore are less concentrated (2000–3000 p.p.m. TDS) than those of the salar itself (10,000–30,000 p.p.m. TDS). Numerous algae, together with diatoms, thrive in the shallow surface pools and ponds fed by the thermal springs. The orifices of the hot springs seem to change with time, and hillocks of black sandy ferriferous material mark the locations of extinct springs.

The groundwaters of the central portion of the lake are NaCl-rich brines rich in boron and lithium. The main saline minerals found in this area are gypsum, ulexite (NaCaB<sub>5</sub>O<sub>9</sub>.8H<sub>2</sub>O) and halite.

Water compositions are given in Table 1. Brine 1 (Fig. 2 for locations) is a hot spring which emerges on the playa surface and feeds a pond 200 m further down (brine 2). Water 3 is a rather dilute hot spring from the shore area and water 4 a dilute cold spring from the S. The composition of the central subsurface brine of the salar is given by analysis 5. Water circulation and brine evolution can be evaluated only when more chemical data become available.

# HOLOCENE CALCIUM CARBONATE DEPOSITS OF PASTOS GRANDES

Holocene calcite pisoliths and crusts are found abundantly in the western area (Fig. 2) and they are invariably associated with the outflow and ponding of hot springs, either active or recently abandoned. Quartz is a major impurity in the crusts, but aragonite has not been encountered. The carbonate deposits are found in a number of forms: pisoliths, encrustations, arborescent concretions, rimstone dams and complex structures.

#### **Pisoliths**

Figure 3 shows the general appearance of the pisoliths. They are dense, more or less spherical structures which occur in a wide variety of sizes, ranging from a few millimetres to 20 cm in diameter. Their surface may be smooth or it may be rugose and covered by hummocky or arborescent protrusions, the latter being true for the larger sizes.

The pisoliths are concentrated in shallow hollows several centimetres deep and some metres to ten metres in diameter, which are associated with active or dead hot spring ponds. The pisolith diameters increase from shore to centre. In very flat and wide areas (some hundred metres in diameter), under very shallow water, we find large amounts of small, at most centimetre-size pisoliths. In deeper hollows, pisoliths reach 20 cm in diameter, which corresponds roughly to the maximum water depth. They can be loose or cemented on a hard carbonate substrate. The biggest, when they are loose, are lying on a carbonate sand or gravel (ooliths and millimetre pisoliths). They grow equally in all directions, except when they are cemented to the bottom, in which case they become asymmetric. In some ponds, such as that of Fig. 3a, they may also have flattened tops. Smaller pisoliths may become cemented, forming cauliflower-type concretions or even a continuous thin pisolitic crust similar to caliche (Fig. 4a and b).

### Encrustations and concretions

When calcium carbonate precipitation occurs on a support, it produces an encrustation or concretion which moulds the shape of the support. There is a large variety of such shapes, the most frequent being an encrusted flat piece of the old carbonate crust. Gray indurated mud can also be used for a nucleus. An example is shown in Fig. 6a. The surfaces of the large concretions are usually rugose like those of the larger pisoliths. Similar concretions from caves have been pictured by Hess (1930), Baker & Frostick (1947, 1951), Black (1952), Hahne *et al.* (1968) and Donahue (1969).

The encrustations forming at the bottom of the ponds may give rise to a continuous thin crust (some millimetres to one centimetre thick) upon which other concretions can be cemented.



Fig. 3. General appearance of pisoliths. (a) Partially dried-up pond with large, loose pisoliths; (b) small, loose, smooth pisoliths ('cave pearls'). Pencil for scale; (c) ranges in size and surface textures of pisoliths. Pencil notches are spaced at 1 cm.; (d) large pisolith with rugose, pustular surface and a polished cross-section showing the concentric laminations. No top-bottom features.



Fig. 4. Pisoliths and rimstone dams (sinter terraces). Pencil and pocket knife for scale. (a) Cemented pisoliths, mostly under water. Where they emerge, arborescent overgrowths have formed ('cave popcorn' of Thrailkill, (1976)); (b) crust consisting of cemented pisoliths. Top view left and cross-section right. Note grading from centre to periphery; (c) small 'birds nest' of loose pisoliths (above water) lying on sub-merged cemented pisoliths surrounded by rimstone dam. Large, rugose, loose pisoliths in foreground, one on the lower left emerging above the water level; (d) complex sinter terrace with loose and cemented pisoliths.

# Sinter terraces and rimstone dams

Sinter terraces and rimstone dams probably form in a similar manner. They are most common near the orifice of inactive hot springs. They may be several centimetres to metres in diameter and they form systems with elevation differences of a few centimetres or less (Fig. 4c and d). Each terrace is bounded by a thin dam, 1–3 cm high, protecting and forming a small, slightly elevated pond. This pond in turn may be floored by a layer of loose pisoliths, similar to the cave pearls in 'birds nests' or splash pools (Fig. 4c).

#### Arborescent concretions

4

Arborescent concretions consist of thin dendritic ramifications of some millimetres to three centimetres high, which are attached to any kind of support located just above the water level. They are very similar to the drip-stone textures of the supratidal aragonitic crusts (caniatolites) described by Purser & Loreau (1973, see particularly their fig. 20) and the cave popcorn of Thrailkill (1971, 1976). The most frequent shapes are in the form of 'ash-trays' (Fig. 5), which are formed by an arborescent wreath around an encrusted fragment of old crust, protecting a smooth, central depression, which is thinly laminated in cross section (Fig. 5a, c and d). Some of the flatter areas around the ponds are covered with forests of inclined, large branches (2–3 cm long, Fig. 5b), which are oriented towards the prevailing wind direction, which is from W to E. We have also observed arborescences on pisoliths, which emerge out of the water (Fig. 4a), as well as on top of living algae slightly above the water level.

The arborescences are presumably formed by wind-driven splash and their location delineates a horizontal line around the fragments of the old crust, marking an old pond level, or the present water level. It is interesting to note that the popcorn of the Carlsbad Caverns is also thought to have deposited subaerially, from a thin film of water supplied by splash from an adjacent drip (Thrailkill, 1971, p. 689).

#### Complex structures

Complex structures are built from elements described above, and they presumably represent a complex hydrological history. An examples is shown in Fig. 6b. A hot spring may be responsible for the first concretionary event. When it dies and a new spring emerges nearby, the old concretions become supports for a new generation, thus producing a complex structure. Another scenario could be the variation in flow of a single spring. A decrease of the inflow produces a lowering of the water level; thus arborescences are forming upon the emerging pisoliths and encrustations; later on, if the level is going up again, the arborescences will themselves become encrusted.

# Dissolution of arborescent crusts

Arborescent crusts from ponds associated with inactive hot springs can easily be recognized by their rounded features. None of the sharp protuberances characteristic of actively forming crusts remain and dissolution phenomena predominate. The pools have dried up and dissolution must be due to dilute, undersaturated waters, either rain or melt waters associated with spring thaws.



Fig. 5. Arborescent concretions and growths. (a) Typical assortment of 'ash-trays' partly submerged. Hammer for scale; (b) arborescent growths (pencil for scale) similar to 'cave popcorn'; (c) single 'ash-tray', showing the flat centre rimmed by arborescent growth; (d) cross-section through 'ash-tray', same scale as 5c. Note the reverse graded pisoliths forming the base, the plane parallel lamination of the centre and the arborescent rim.



Fig. 6. Complex concretions and thin sections. (a) Polished section of a mud encrustation; (b) polished section of a complex structure including two earlier pisoliths; (c) thin section photograph ( $\times$  22) of a pisolith showing light-dark couplets and calcite fans in the clear bands; (d) thin section photograph ( $\times$  63) of a pisolith showing radial fibrous calcite fans. (Cone-in-cone structure).

# Relationship to the main carbonate crust

The main carbonate crust which forms the polygonal frost-action cells also contains many pisoliths, encrustations and arborescences similar to those of the Holocene deposits. We are tempted to connect their formation with earlier hot spring activity, although simple groundwater feed may also be possible.

## Thin section observations

Polished and thin section photographs of concretions are given in Fig. 6. Figure 7 is a sketch of a part of a pisolith. The concentric banding consists of alternating clear and dark bands, with the clear bands showing a radial structure. This is similar to the light-dark couplets of cave pearls, which have been interpreted as summer-winter deposits (Kirchmayer, 1962; Hahne *et al.*, 1968).



Fig. 7. Schematic drawing of light-dark couplets and calcite fans of pisoliths and concretions.

The clear bands vary in thickness from 50 to 1000  $\mu$ m. As Fig. 6d shows, they are composed of radial, fibrous calcite fans, or in three dimensions, calcite cones, and these cones, oriented perpendicular to the laminations, form the basic elements of all bands. Lateral growth interference produces nested or imbricate cones which give the bands an undulating aspect in cross section (Fig. 6c and d) and appear as polygonal domes on the curved bedding surfaces. In their bands, the density of cones is high and they are squeezed together, forming a continuous band.

The polygonal domes representing the calcite cones are responsible for the rugose surface of the larger pisoliths. We believe them to be a primary growth feature, similar in nature to the gypsum 'mammelone' of the Solfifera Series of Sicily (Hardie & Eugster, 1971). Similar nested cone structures have been pictured in cave pearls by Hahne *et al.* (1968, fig. 15) and Donahue (1969, fig. 2). They may also be related to the undulose fibre-bundles described by Folk & Assereto (1976) from a flowstone, which they termed 'coconut-meat' calcite.

The dark bands (micrite) probably result from the incorporation of mud, organic matter or fluid inclusions. There is no radial structure visible. A fine concentric lamination underlined by very thin clear calcite can sometimes be observed. Generally we get the impression of predominantly clear bands moulded by black bands, but the dark bands are usually very much thinner (Fig. 7).

# ORIGIN OF THE HOLOCENE CARBONATE PISOLITHS AND CRUSTS

The carbonate precipitation mechanisms can be elucidated best by comparing the chemical composition of the spring water as it emerges (Analysis 1, Table 1), with that

<b>Table 1.</b> Chemical composition of five waters. For localities see Fig. 3.
All concentrations in mmol/kg H <sub>2</sub> O except for alkalinity, which is given
in meq/kg

Property	Water				
	1	2	3	4	5
Density	1.013	1.017	1.001	1.000	1.194
Temperature (°C)	37	12	31	8.5	12
pH	6.30	8.25	6.55	8.00	7.14
Alkalinity (meq/kg)	8.83	7.30	1.73	0.61	9.97
SiO <sub>2</sub>	$1 \cdot 45$	0.96	$1 \cdot 52$	0.49	0.28
Na +	195	258	13.8	0.29	3360
K+	13.0	18.4	1.09	0.042	228
Li+	10.0	12.6	0.75	<u> </u>	259
Ca <sup>2+</sup>	10.6	11.5	0.51	0.17	71.7
Mg <sup>2+</sup>	5.48	7.14	0.37	0.12	143
Cl-	247	331	$15 \cdot 8$	0.11	4420
SO4 <sup>2-</sup>	2.87	3.76	0.76	0.12	19.4
В	2.4	4.9	0.18	0.029	34.8

of water from a carbonate-precipitating pond 200 m further down, which derives its waters direction from this spring and has no other inflow sources (Analysis 2, Table 1).

A comparison can be made most meaningful by calculating  $p_{CO_2}$  and degree of supersaturation with respect to calcite and other phases. We need the following activities:

$$a_{H_{2}CO_{3}} = K_{1} a_{H_{2}O} p_{CO_{2}}$$
 (1)

$$a_{HCO_3} a_{H^+} = K_2 a_{H_2CO_3}$$
 (2)

$$a_{CO_3^{2-}} a_{H^+} = K_3 a_{HCO_3^{-}}$$
 (3)

$$a_{Ca2+} a_{CO_3^2} = K_4 a_{CaCO_3}$$
 (4)

Next we obtain the ion activity product from equation (3)

IAP=
$$a_{CO_3^{2-}} a_{Ca^{2+}} = K_3 \frac{m_{HCO_3^{-}} m_{Ca^{2+}} \gamma_{HCO_3^{-}} \gamma_{Ca^{2+}}}{a_{H^+}}$$
 (5)

which is then compared with  $K_4$ , the solubility product for calcite.  $p_{CO_2}$  is calculated from Equations (1) and (2)

$$p_{\rm CO_2} = \frac{1}{K_1 - K_2} = \frac{a_{\rm HCO_3^-} - a_{\rm H^+}}{a_{\rm H_2O}}$$
 (6)

Calculations were carried out using the computer program WATEQ (Truesdell & Jones, 1974; Plummer, Jones & Truesdell, 1976), which employs an extended Debye-Hückel formulation for calculating activity coefficients. All known complexing reactions are included and the calculations are carried out at temperature T. Saturation is checked with respect to a wide variety of solids. Results are shown in Table 2.

Table 2. Computer calculations (WATEQF) of  $p_{CO2}$ , degree of saturation with respect to calcite and silica glass for waters of Table 1, at 25°C

Water	$\log p_{\rm CO2}$	$IAP/K_4$	$Silglas/K_5$
1	-0.65	0.69	1.22
2	-2.87	21.27	1.51
3	-1.52	0.026	1.37
4	-3.51	0.065	0.78
5	-2.27	7.24	1.59

Spring water 1, as it emerges, is near calcite saturation and has a very high  $p_{CO_2}$ , considering that at this altitude atmospheric  $p_{CO_2}$  is near  $10^{-4}$  atm. After it has cooled to ambient temperature (Water 2, Table 1), the pH has risen and the  $p_{CO_2}$  decreased, each by two orders of magnitude, creating a water supersaturated twenty times with respect to calcite. This dramatic loss of  $CO_2$  can be associated either with degassing or photosynthesis of the algae which thrive in the pond or both. Evaporation is slight, with Cl and Na indicating a concentration factor of 1.3. This allows us to calculate the amount of Ca lost from spring to pond water, which amounts to about 2.3 mmol calcite per litre of water. In the process, very little magnesium is lost. Meanwhile, half of the silica which should be in the pond water has been removed, presumably by diatoms or by precipitation as silica cements. Computer calculations (Table 2) show all water to be nearly saturated with respect to a silica glass with an SiO<sub>2</sub> solubility of 58 p.p.m. SiO<sub>2</sub> (Sil gl.). This suggests that silica levels may be controlled by the solubility of volcanic glass.

It is interesting to compare the calcium content of the hot spring with that of a thermal spring located on the western slope (Analysis No. 3, Table 1). That spring has a similar pH and temperature, but it is much more dilute. Its calcium content is twenty times lower than that of the spring which issues on the salar and feeds the pond. This dilute shore hot spring is fifty times undersaturated with respect to calcite, and it does not form pisoliths further down. A similar conclusion holds for Spring 4, which issues at the southern shore. The lake brine, on the other hand, (No. 5) is clearly supersaturated with respect to calcite, though no pisoliths are observed forming. It is tempting to speculate that the springs which issue on the salar itself, rather than the shore, have picked up most of their solutes while traversing the underlying sediments. In that case, the calcite of the pisoliths and encrustations would simply have been recycled locally. The impetus for the recycling would be provided by the high  $CO_2$  content of the emerging hot springs, but the ultimate source of the high  $pCO_2$  is not clear. It could be either of volcanogenic origin or connected with organic activity, though organic matter is not particularly abundant on the surface of the salar. On the other hand, decay of organic matter may be much faster at this altitude, assisted by u.v. light (B. F. Jones, personal communication).

ß

As with cave deposits (Thrailkill, 1971, 1976), it is difficult to assign the CO<sub>2</sub> loss responsible for the calcite precipitation at Pastos Grandes to a single, unequivocal cause. There is no indication that the algae are physically involved as they are in the formation of algal stromatolites, but their potential role in reducing  $pCO_2$  seems clear. Degassing is also an effective mechanism and may be responsible for the formation of pisoliths which are not associated with algae, as well as the arborescent drip stones and 'ash-tray' concretions thought to form from small wind-driven waves and spray.

Many pisoliths and encrustations seem to grow while submerged, with the size of the pisoliths perhaps indicating maximum water depth. There is no sign of rolling of pisoliths, because they are normally very closely packed, although some rocking motion is certainly possible. The largest ones at least, some of which weigh up to 10 kg. would be hard to move except perhaps by frost heave. This must mean that they raise themselves off the porous substrate as they grow. Many are now cemented to the the bottom, but this probably happened after they stopped growing due to a drop in water level.

A crucial point in the formation of the pisoliths at Pastos Grandes seems to be the presence of large shallow pools of stagnant saline water highly supersaturated with respect to calcite. Precipitation is rapid and any nucleus becomes the centre for spherical growth. The growth is clearly cyclical as indicated by the light–dark couplets and these cycles may be somewhat related to wet–dry seasons. These are exactly the conditions observed in cave deposits.

# IMPLICATIONS

Concentrically laminated carbonate pisoliths and concretions are common in the geological record and they are usually interpreted as of algal or caliche origin. Cave environments are often dismissed as of local importance. In speaking of the Persian Gulf pisoliths, for instance, Scholle & Kinsman (1974) state that '... one can quickly eliminate a cave origin—these deposits are clearly not associated with any caverns' (p. 913).

We now, however, have described a surface environment in which cave-like pisoliths and concretions form in great abundance. That environment is characterized by shallow, stagnant pools of water which becomes supersaturated with respect to calcite by  $CO_2$  loss. The environment is evaporitic, but evaporation does not seem to play a significant role in this process.

We can imagine many environments in the geological past, be they continental playa surfaces or marine lagoons, in which similar conditions could have been attained. Thus deposition from stagnant to near-stagnant surface pools becomes a real alternative for many pisoliths and concretions. In the record, it should not be hard to differentiate this environment from that of caves.

It is tempting to apply the Pastos Grandes environment to the model developed by Esteban (1976) and Esteban & Pray (1977) for the pisoliths of the Capitan Reef, even though one environment is clearly continental and the other marine. Esteban & Pray (1977) suggest that the Permian pisoliths formed in shallow, saucer-like surface ponds bounded by tepee structures: '... the inverse graded pisolite part is thickest, best developed, and involves largest pisoliths in the deeper areas of the intertepee depressions... this unit strongly suggest(s) deposition controls ... involving ponding that permitted deeper and more continuous submergence in the depressions' (p. G-134). The analogy with cave deposits is clearly stated: '... the inverse grading resemble(s) nests of cave pearls ... However, there was no roof here, it was formed at the open depositional interface' (p. G-136).

In this view, then, the Permian pisolite rudstone facies would be equivalent to the loose pisoliths of the Pastos Grandes ponds, while the botryoidal pisolite facies would correspond to the Pastos Grandes concretions and complex structures. The hydrological, geochemical and sedimentological processes would be equivalent, even though the water chemistry may be different.

Finally, in searching for recent analogues of ancient environments, we are reminded of the fragility of many of these environments. If Pastos Grandes were not located in a nearly inaccessible region, it is likely that man would long since have altered it irrevocably.

#### ACKNOWLEDGMENTS

This work was supported in part by Grant No. 7653-AC2 of the Petroleum Research Fund, American Chemical Society. We thank C. Gebelein, L. Hardie, D. Kinsman, M. Lafon, B. Simonson, J. Smoot and J. Thrailkill for valuable comments, and B. Jones for arranging the computer calculations and important suggestions. H. P. E. wishes to acknowledge the hospitality of the ORSTOM-UMSA group in La Paz and in the field.

#### REFERENCES

AHLFELD, F. (1956) Sodaseen in Lipez (Bolivien). Neues Jb. Miner. Mh. 6/7, 128-136.

AHLFELD, F. & BRANISA, L. (1960) Geologia de Bolivia. Instituto Boliviano Petrolero, La Paz.

- BAKER, G. & FROSTICK, A.C. (1947) Pisoliths and ooliths from some Australian caves and mines. J. sedim. Petrol. 17, 39-67.
- BAKER, G. & FROSTICK, A.C. (1951) Pisoliths, ooliths and calcareous growth in limestone caves at Port Campbell, Victoria, Australia. J. sedim. Petrol. 21, 85-104.
- BATHURST, R.G.C. (1971) Carbonate Sediments and Their Diagenesis. Developments in Sedimentology, 12. Elsevier Publishing Co., New York.

BLACK, D.M. (1952) Cave pearls in Carlsbad Caverns. Sci. Monthly, 74, 206-210.

CASTERET, N. (1939) Dix Ans Sous Terre. Perrin, Paris.

- DAVIDSON, S.C. & MCKINSTRY, H.E. (1931) 'Cave pearls' oolites and isolated inclusions in veins. Econ. Geol. 26, 289-294.
- DONAHUE, J. (1965) Laboratory growth of pisolite grains. J. sedim. Petrol. 35, 251-256.
- DONAHUE, J. (1969) Genesis of oolite and pisolite grains: an energy index. J. Sedim. Petrol. 39, 1399-1411.
- DUNHAM, R.J. (1969) Vadose pisolite in the Capitan Reef (Permian), New Mexico and Texas. In: Depositional Environments in Carbonate Rocks: A Symposium (Ed. by G. M. Friedman). Spec. Publs. Soc. econ. Paleont. Miner., Tulsa, 14, 182–191.
- DUNHAM, R.J. (1972) Capitan Reef, New Mexico and Texas: facts and questions to aid interpretation and group discussion: *Permian Basin Section. Spec. Publs. Soc. econ. Paleont. Miner.*, *Tulsa*, 72-14.

ESTEBAN, M. (1976) Vadose pisolite and caliche. Bull. Am. Ass. Petrol. Geol. 60, 2048-2057.

- ESTEBAN, M. & PRAY, L. (1977) Locality guides stops 1 through 4. In: Upper Guadalupian Facies, Permian Reef Complex, Guadalupe Mountains, New Mexico and Texas (Ed. by L. C. Pray and M. Esteban). Permian Basin Section, Spec. Publs Soc. econ. Paleont. Miner., Tulsa, 77-16.
- FERNANDEZ, A., HORMANN, P.K., KUSSMAUL, S., MEAVE, J., PICHLER, H. & SUBIETA, T. (1973) First petrologic data on young volcanic rocks of S.W. Bolivia. *Tschermaks Mineral. Petrogr. Mitt.* 19, 149–172.
- FOLK, R.L. & ASSERETO, R. (1976) Comparative fabrics of length-slow and length-fast calcite and calcitized aragonite in a Holocene speleothem, Carlsbad Caverns, New Mexico. J. sedim. Petrol. 46, 486-496.
- FONTES, J.CH. & SERVANT, M. (1976) Dataciones radiometricas sobre el Cuaternario Reciente del Altiplano de Bolivia. Primer Congreso Geologico de Boliva-Potosi, 1976.
- HAHNE, C., KIRCHMAYER, M. & OTTEMANN, J. (1968) 'Höhlenperlen' (Cave Pearls), besonders aus Bergwerken des Ruhrgebietes. *Neues Jb. Geol. Paläont. Abh.* 130, 1–46.
- HARDIE, L.A. & EUGSTER, H.P. (1971) The depositional environment of marine evaporites: a case for shallow, clastic accumulation. *Sedimentology*, **16**, 187–220.

HESS, F.L. (1930) Oölithes or cave pearls in the Carlsbad Caverns. Proc. U.S. Nat. Mus. 76, 2813, 1-5.

- HOLLAND, H.D., KIRSIPU, T.V., HUEBNER, J.S. & OXBURGH, U.M. (1964) On some aspects of the chemical evolution of cave waters. J. Geol. 72, 36-67.
- KENDALL, C.G.ST.C. (1969) An environmental reinterpretation of the Permian evaporite/carbonate shelf sediments of the Guadalupe Mountains. *Bull. Geol. Soc. Am.* **80**, 2503–2526.
- KIRCHMAYER, M. (1962) Zur Untersuchung rezenter Ooide. Neues Jb. Geol. Paläont. Abh. 114, 245–272.
- KIRCHMAYER, M. (1964) Höhlenperlen (cave pearls, perles des cavernes) Vorkommen, Definition sowie strukturelle Bexiehung zu ähnlichen Sedimentsphäriten Öster. Akad. Wiss., Math. Nat. Kl. Anz. 10, 223–229.

KUMM, A. (1926) Zur Klassifikation und Terminologie der Sphärite. Z. Dt. geol. Ges. 78, 1-34.

MACKIN, J.H. & COOMBS, H.A. (1945) An occurrence of 'Cave Pearls' in a mine in Idaho. J. Geol. 54, 58-65.

MONTY, C.L. (1972) Recent algal stromatolitic deposits. Andros Islands, Bahamas. Preliminary report. Geol. Rundschau. 61, 742-783.

MOORE, G.W. (1962) The growth of stalactites. Bull. Nat. Speleol. Soc. 24, 95-106.

MOORE, G.W. & NICHOLAS, G. (1964) Speleology, the Study of Caves. Heath and Co., Boston.

MURRAY, J.W. (1954) The deposition of calcite and aragonite in caves. J. Geol. 62, 481-492.

PLUMMER, L.N., JONES, B.F. & TRUESDELL, A.H. (1976) WATEQF: a Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *Wat. Res. Invest.* U.S. geol. Surv. 76-13.

POND, A.W. (1945) Calcite oölites or 'Cave Pearls' formed in a 'Cave of the Mounds'. J. sedim. Petrol. 15, 55–58.

PURSER, B.H. & LOREAU, J.-P. (1973) Aragonitic, supratidal encrustations on the Trucial Coast, Persian Gulf. In: *The Persian Gulf* (Ed. by B. H. Purser), pp. 343–376. Springer-Verlag, New York. Roques, H. (1963) Observations physico-chimiques sur les eaux d'alimentation de quelques concretions. Ann. Spéléol. 18, 377-404.

ROYER, M. (1939) Sur la nature minéralogique de quelques substances minérales nord-africaines; étude aux rayon X. C.r. hebd. Séanc. Acad. Sci. Paris, 208, 1591–1593.

RUEDEMANN, R. (1929) Coralline algae, Guadalupe Mountains. Bull. Am. Ass. Petrol. Geol. 13, 1079–1080.

SCHOLLE, P.A. & KINSMAN, D.J.J. (1974) Aragonitic and high-Mg calcite caliche from the Persian Gulf: a modern analog for the Permian of Texas and New Mexico. J. sedim. Petrol. 44, 904–916.

SCHÖTTLE, M. & MÜLLER, G. (1969) Recent carbonate sedimentation in the Gnadensee (Lake Constance), Germany. In: *Recent Developments in Carbonate Petrology in Central Europe* (Ed. by G. Müller and G. M. Friedman), pp. 148–156. Springer-Verlag, New York.

STONE, R.W. (1932) Cave concretions. Proc. Penn. Acad. Sci. 6, 106-109.

THOMAS, C. (1968) Vadose pisolites in the Guadalupe and Apache Mountains, West Texas. Permian Basin Section, Spec. Publs Soc. econ. Paleont. Miner., Tulsa, 68-11, 32-35.

THORPE, R.S., POTTS, P.J. & FRANCIS, P.W. (1976) Rare earth data and petrogenesis of andesite from the North Chilean Andes. *Contrib. Mineral. Petrol.* 54, 65-78.

THRAILKILL, J. (1971) Carbonate deposition in Carlsbad Caverns. J. Geol. 79, 683-695.

THRAILKILL, J. (1976) Speleothems. In: *Stromatolites* (Ed. by M. R. Walter), pp. 73-86. Elsevier Publishing Co., Amsterdam.

TRUESDELL, A.H. & JONES, B.F. (1974) WATEQ, a computer program for calculating chemical equilibria on natural waters. J. Res. U.S. geol. Surv. 2, 233–248.

WALTER, M.R. (1976) Geyserites of Yellowstone National Park: an example of abiogenic 'stromatolites'. In: Stromatolites (Ed. by M. R. Walter), pp. 87–112. Elsevier Publishing Co., Amsterdam.

(Manuscript received 17 March 1978; revision received 26 June 1978)