UNUSUAL PHOSPHATE CONCRETIONS RELATED TO GROUNDWATER FLOW IN A CONTINENTAL ENVIRONMENT

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ABSTRACT: Occurrence of phosphate cemented-sandstone concretions in alluvial sand containing archaeological layers implies that they have formed during the last 2000 years. Morphology and petrography of the concretions indicates a relationship with groundwater cementation. The phosphate cement of the concretions consists of concentric isopachous aureoles, about 10 μm thick, that wrap the detrital grains. Aureoles are formed of collophane, the cryptocrystalline or amorphous variety of hydroxyapatite.

Geochemical modeling indicates that the apatite cement likely results from the leaching of a preexisting phosphate deposit (bones?) in an acidic soil environment and the precipitation of dissolved phosphate under pH control at the mixing zone of down-moving soil–water with the calcite-saturated groundwater.

INTRODUCTION

Sedimentary phosphorites are predominantly marine sediments formed by upwelling of phosphate-rich waters into relatively shallow marine settings, where biological accumulation further concentrates the phosphate and eventually deposits it on the sea floor (Slansky 1980; Weaver and Beck 1977; Baturin 1981, 1988; Cullen 1986; Föllmi 1996). The role of rivers has been shown for some apatite deposits in deltaic and estuarine environments that were not fed by upwelling (Ruttenberg and Berner 1993; Lucotte et al. 1994). On the other hand, continental phosphate deposits are comparatively rare. Phosphate may accumulate in lacustrine deposits, where it results mostly from vivianite precipitation in highly reducing and organic-rich environments at the bottom of the lake (Stamatakis and Koukouzas 2001). Apatite occurrences in lacustrine deposits are generally thought to result from alteration of primary vivianite. Phosphorites are also common on coral islands. Their primary origin remains uncertain (bird guano, endo-upwelling, or volcanics), but they are always remobilized by fresh water in weathering or karst features with direct apatite precipitation or/and replacement of the calcareous bedrock (Bourrouilh–Le Jan 1989; Baker et al. 1998). The major continental phosphorite deposits are also related to karst features and have been recognized very early with regard to their high-grade ore (Dieulafait 1855). In karst deposits, phosphate occurs mostly as apatite by direct precipitation on the karst walls and replacement of the host-rock calcite. A whole series of phosphate minerals is found in karst deposits and especially alumina-phosphates within the clayey karst infillings. It is generally thought that phosphate originates from overlying formations (marine sediments or even bat guano), dissolved under acid conditions and precipitated under higher pH values in the karst environments (Altschuler 1973; Klaus et al. 1981; Billaud 1982; Cilek et al. 2001; Onac and Veres 2003).

Herein we describe another occurrence of phosphate concretions developed in alluvial sand deposits, for which we have not found any description in the literature. Moreover, development of these concretions within archaeological layers allows us to show their rapid development and discuss their mode of formation.

DESCRIPTION

Decimeter-size sandstone concretions occur in a fluvial terrace of historical age, at Roussigny, near Moret-sur-Loing (Seine-et-Marne, France). The concretions have been brought to light in several archaeological excavations. They occur at about 2.5 m depth, within fine-grained beige to yellow sand. The deposits are well dated by archaeological layers (Fig. 1). In the lower part of the excavation, about 20 to 30 cm below the concretions, a layer of ceramic pieces of the final Bronze Age (about 1200 B.C.) is found. The yellow sand that contains the sandstone concretions holds ceramic artifacts of the Gallic period (400–300 B.C.), and near the top of the section there are Gallo-Roman testimonies (about 100–400 A.D.). The lower artifacts of the Bronze Age are encrusted and wrapped in an ironpan (ferruginous crust formed in soil environment, also called "alios"). The sandstone concretions form highly contrasting cemented patterns within the loose sand. Their sizes average 5 cm in thickness and about 10 cm × 10 cm in the horizontal plane. Concretions are flat lying, elongated, and irregular shaped, often with several digitations (Fig. 2). All concretions have slightly tapered and rounded ends. The fingers and all the elongated shapes of the concretions have uniform orientation, towards the riverbank. Similarly elongated calcareous concretions developed in sandstones and alluvial aquifers have been interpreted as indicative of groundwater flow direction (Jacob 1973; Johnson 1989; McBride et al. 1994; Mozley and Davis 1996; McBride and
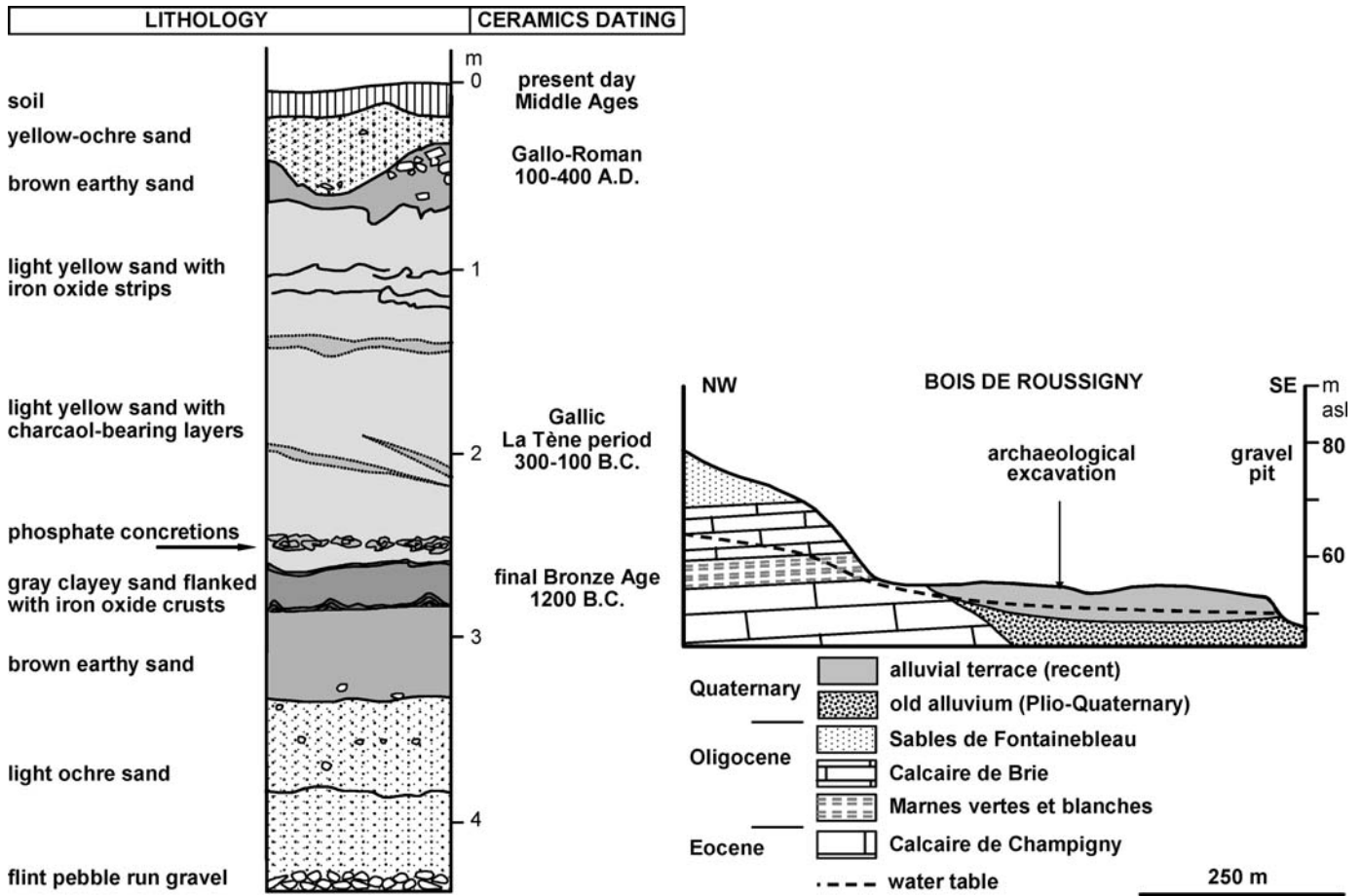
Fig. 1.—Section of the archaeological excavation showing the stratigraphy of the deposits and position of the sandstone concretions above the oldest dated layer. This means that the concretions are younger than the final Bronze Age (1200 B.C.).

Parea 2001). The well-oriented concretions described herein have to be related to cementation by paleohydrological flows.

METHODS

The cement of the concretions has been extracted by gentle grinding of the concretions, followed by ultrasonic treatment and then granulometric separation of the < 2 µm fraction. X-ray diffraction has been performed on a random powder sample run on a PHILIPS X'PERT diffractometer. Microprobe analyses have been performed on a CAMEBAX microprobe, with a 6 µm × 6 µm scanning area to avoid sample contamination as much as possible, and results have been corrected for ZAF effects.

MINERALOGY

Quartz is the main mineral of the concretions. Only a very weak and broad diffraction line is detected near 2.80 Å in addition to the quartz lines. X-ray diffraction performed on the < 2 µm fraction shows diffraction lines tallying with hydroxyapatite (Fig. 3). Diffraction lines are broad, relevant to the poor crystallization of the cement material.

PETROGRAPHY

Concretions show a very homogeneous and monotonous petrofabric. The sand grain size averages between 100 and 300 µm. The sand grains are composed only of subangular to blunt quartz fragments. Some grains show overgrowths with concentric rims; they are obviously inherited from the Fontainebleau sandstones nearby (Thiry and Maréchal 2001). Polycrystalline grains or rock fragments are exceptional. The detrital grains are clean, and intergranular spaces are empty, with only little iron oxides and clay minerals lining some pores. Concretions show homogeneous distribution of the cement, averaging about 10%, and a residual porosity varying from 20 to 25%. The cement consists of concentric isopachous aureoles, about 10 µm thick, that wrap the detrital grains (Fig. 4). Cracks crosscutting the cement aureoles are regularly spaced every 50 to 100 µm, and are most probably related to dehydration. The cement is isotropic, of higher refraction index than quartz, and dark under crossed polars. It appears amorphous under the microscope and must be considered to be collophane, the cryptocrystalline or amorphous variety of hydroxyapatite (Lacroix 1910).

CHEMICAL COMPOSITION

Chemical analyses of the concretion cement and of the ironpan have been performed by electron microprobe (Table 1). The analyses are typical of collophane, with a Ca/P atomic ratio of 1.75, which is slightly higher that the 10/6 theoretical ratio of hydroxyapatite. Moreover, the analyses also show a relatively high Ba content. Ba may substitute for Ca and thus further increase the total (Ca + Ba)/P ratio. The relative phosphate deficit is well know in collophane and is generally imputed to isomorphous substitution of PO_4^{3-} by CO_3^{2-} (Lacroix 1910; Nathan 1984). This leads to a structural formula for the collophane cement of:
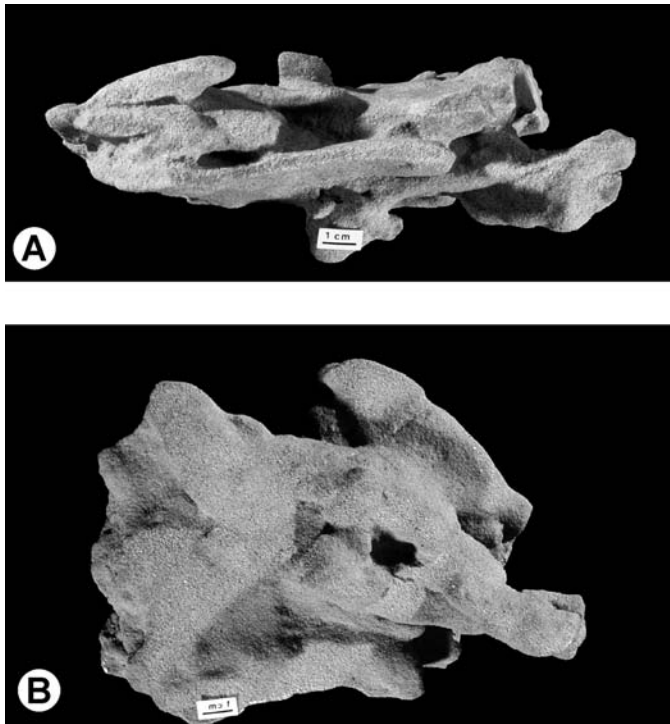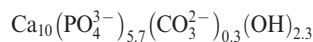
FIG. 2.— Digitate shapes of the sandstone concretions. Fingers and stretched shapes clearly point to water flows within the sand (towards the right of the pictures). **A)** Front view; **B)** top view.

$$Ca_{10}(PO_4^{3-})_{5.7}(CO_3^{2-})_{0.3}(OH)_{2.3}$$

The ironpan matrix is rather inhomogeneous, with a highly variable content of iron oxides and clay minerals. Rather high manganese contents are noticed, and the most ferruginous zones also have high phosphate contents. The high phosphate content of the ironpan matrix tallies with the well known iron oxide capacity to adsorb, and co-precipitate with, phosphate (Taylor and Schwertmann 1974; Deike et al. 1997; Torrent 1997).

ORIGIN OF THE PHOSPHATE

The primary source of phosphate has to be considered. Enriched solutions may result from the leaching of neighboring sedimentary phosphate deposits. There is no evidence of such deposits in the regional geology, nor in the marine deposits of the Cretaceous Chalk, nor in the Tertiary deposits, which are mainly of continental origin. Alternatively, phosphate may originate from human or animal bones in a neighboring necropolis or charnel. The existence of this latter source has yet to be confirmed, because existing archaeological excavations have not shown yet any indication of that sort.

GEOCHEMISTRY AND MODE OF FORMATION

The solubility of phosphate and a possible mechanism of precipitation of phosphate minerals in this environment has been examined using the quantitative geochemical modeling code CHESS (van der Lee 1998).

The solubility and general behavior of phosphorus species in soils and shallow aquifers is illustrated in the activity–pH diagram (Fig. 5). The diagram shows that phosphate solubility is dependent mainly on pH: (1) in acidic to neutral conditions phosphate remains largely soluble as
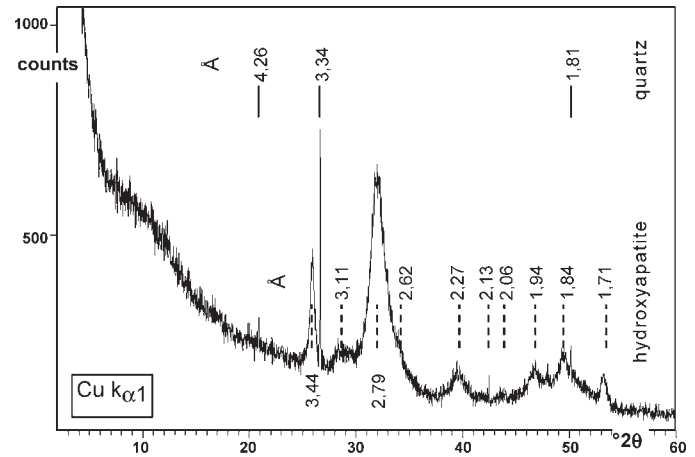

FIG. 3.— X-ray diffraction diagram of the concretion cement obtained by granulometric separation. The diffraction lines fit well with the hydroxyapatite pattern. The narrowness of the quartz impurities lines allows appreciation of the broadening of the hydroxyapatite lines, pointing to the cryptocrystalline nature of the mineral.

$H_2PO_4^-$, or the uncharged species $H_3PO_4(aq)$ and $CaHPO_4(aq)$; (2) in alkaline conditions phosphate precipitates as hydroxyapatite (or another mineral of the apatite family, such as fluorapatite, chlorapatite, or carbonate–apatite). Increased calcium concentration or the presence of fluoride lower the overall phosphate solubility but do not affect this
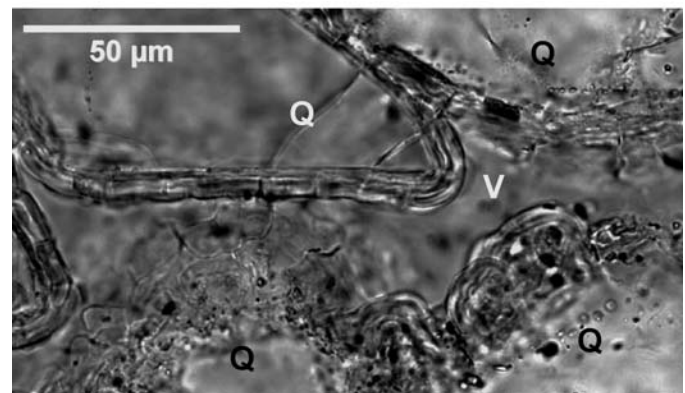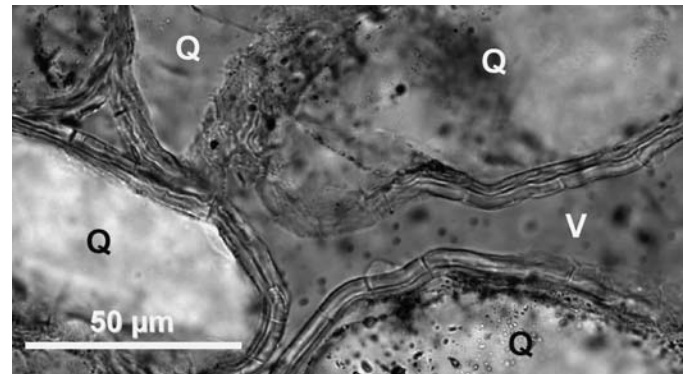

FIG. 4.—The sandstone concretions show isopachous cement aureoles that wrap around the quartz grains. Note the cracks that crosscut the aureoles; they may indicate that the primary deposit was hydrated. Botryoidal structures also develop in places. Q, quartz grain; V, void.

TABLE 1.—*Mean electron microprobe analyses of the sandstone hydroxyapatite cement of the concretion and of the ironpan matrix from the lower part of the section.*

	N	SiO_2	Al_2O_3	MgO	CaO	K_2O	Na_2O	Fe_2O_3	Mn_3O_5	TiO_2	BaO	P_2O_5	SO_4	F^-	Cl^-	Σ
sandstone cement	3	2.16	0.17	<0.10	43.56	<0.10	<0.10	<0.10	<0.10	<0.10	1.65	31.18	<0.10	—	<0.20	78.72
collophane	5	2.84	0.30	—	43.98	—	<0.10	<0.10	<0.10	—	—	31.50	0.13	< 0.20	<0.20	78.75
ironpan matrix yellow	3	50.91	15.83	1.11	0.87	1.95	0.11	9.15	<0.10	0.56	<0.10	0.45	<0.10	—	<0.20	80.94
dark	6	33.40	12.66	0.91	2.30	1.91	0.27	8.02	13.14	1.11	0.46	0.65	<0.10	—	<0.20	74.83
red	3	10.27	2.89	0.30	4.77	0.66	0.54	41.32	3.26	0.12	<0.10	7.72	<0.10	—	0.45	72.30

N = number of analyses.

scheme. Neither does moderate temperature variation have any sizeable effect on this diagram.

A pH-controlled mechanism of precipitation thus appears as the most effective process for the formation of this type of concretion. Given their mode of occurrence, the phosphate concretions here appear to fossilize a former water table where mixing of groundwater with down-moving soil–water has been taking place. Table 2 gives two typical analyses (A) and (B) of these waters for the Roussigny environment. Both are moderately mineralized, calcium bicarbonate waters. The groundwater (A), however, is slightly alkaline and calcite-saturated, whereas soil–water (B) is clearly more acidic, and undersaturated with respect to calcite.

Groundwater (A) would fall well within the stability field for hydroxyapatite in Figure 5, and its mixing with soil–water (B) could provide the required pH barrier to trigger phosphate precipitation. Neither of the two waters, however, currently have a sizeable phosphate content, and this points to the likely necessity for a local source of phosphorus. Because phosphorus is nearly insoluble in groundwater (A), this source must lie somewhere on the flow path of the down-moving soil–

water (B), either higher in the profile or slightly upslope or upflow from it.

Column (C) of Table II gives the computed composition of a soil–water enriched in phosphorus (and calcium) following the partial dissolution of (but well below the point of saturation with) a preexisting apatite source. The hypothesis of apatite precipitation from the mixing of the enriched soil–water (C) with groundwater (A) has been tested with the geochemical code CHESS in two ways:

- A simple mixing of the two waters has been simulated. It results in the precipitation of 20 to 30 mg of hydroxyapatite for each incoming liter of the enriched soil solution.
- A flushing of the aquifer with soil–water (C) has been simulated in order to model more realistically the evolution of the solid phase and interstitial water of the concretion-bearing horizon. The model aquifer has been defined assuming a porosity of 25%, with groundwater (A) as interstitial water and a solid phase containing quartz and a small amount of calcite. A typical result of this simulation is given in Figure 6. Soil–water percolation induces in the aquifer a steady precipitation of hydroxyapatite. Calcite, if present, is progressively dissolved; it helps buffer the pH and thus accelerates apatite formation. When calcite disappears the pH drops and apatite formation rate is markedly reduced. There is no significant leaching of quartz during the simulation or formation of other minerals.

Both simulations validate the hypothesis of this scheme of fluid mixing for apatite precipitation. They also allow a crude evaluation of the timescale required for the formation of the concretions: Assuming that the thickness of the phosphate-cemented horizon is close to 2 cm (averaged on the horizontal plane) and has an apatite content around 6%, the precipitated mass should represents some 12 cm^3, or 35 grams, for a 100 cm^2 area. The regional average infiltration rate being around 150 mm/year, the formation of the concretions would require 750 to 1000 years for the simple mixing model and around 400 years for the flush model (Fig. 6). The time is greatly reduced in the second case

FIG 5.— Activity–pH diagram of phosphate species for T = 15°C, and tot $(Ca^{2+}) = 10^{-2}$.

TABLE 2.—*Typical hydrochemistry of groundwater (A) and soil water (B) for the Roussigny area. Column C is the modified phosphate-enriched soil water used in the simulation (see text).*

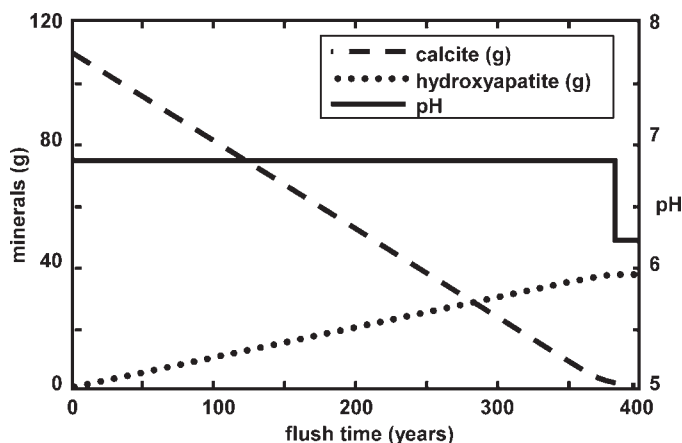|	A groundwater	B soil water	C modified soil water
pH	7.35	6.25	6.25
Eh mV	415	488	488
HCO_3^- mg/L	244.9	187.0	186.6
Cl^- mg/L	13.1	31.3	31.3
SO_4^{2-} mg/L	6.72	40.8	40.8
HPO_4^{2-} mg/L	nd	<0.1	25.9
SiO_2 (aq) mg/L	3.1	3.0	3.0
Na^+ mg/L	6.7	5.6	5.6
K^+ mg/L	2.3	0.9	0.9
Ca^{2+} mg/L	83.9	115	132.9
Mg^{2+} mg/L	2.9	2.1	2.1

FIG 6.—Simulated flushing of the aquifer by the phosphate-enriched soil–water. Note that hydroxyapatite precipitates while calcite is steadily dissolved. The horizontal axis is labelled in estimated flush time, on the basis of regional infiltration rate (see text).

because calcite buffers the pH. Traces of calcite are effectively still present in the profile but pH buffering is also probably assured by the continuous renewal of groundwater. The shorter evaluation thus appears more likely. Of course, the calculated duration should be augmented somewhat if the incoming soil solution is less enriched in dissolved phosphate, or possibly reduced if a wider catchment area is considered. In conclusion, geochemical modeling (1) validates a simple pH-controlled precipitation mechanism, (2) points to a necessary primary local source for dissolved phosphate, and (3) shows that a few hundred to one thousand years are required for the concretions to form, a duration that looks perfectly compatible with archaeological data.

CONCLUSIONS

The elongated phosphate concretions that developed within well-dated archaeological layers have formed from flowing groundwater, most probably near the water table. The archaeological dating constrains the precipitation of the concretions to less than 2,000 years, which appears as rather rapid. Geochemical modeling allows to specify that phosphate precipitation was most probably pH controlled, by mixing of slightly acidic phosphate-enriched soil–water with slightly alkaline and calcite-saturated groundwater. Mass-balance calculation shows that the formation of concretions would require 500 to 1,000 years, regarding the water flow and regional infiltration rate hypothesis. These times are fully in agreement with the stratigraphic dating.

To our knowledge, phosphate concretions of this particular type have not been described previously, but one should point out that they are very similar to more common calcitic concretions, and for this reason could have been overlooked easily unless properly analyzed.

ACKNOWLEDGMENTS

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