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FORMATION OF HOLLOW CONCRETIONS IN NORTHEASTERN THAILAND

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The mysterious rocks "Naka's eggs" commonly found in Northeastern Thailand are hollow concretions derived from clastic rocks of the Khorat Group. The concretions appear in different shapes, such as spheroidal, ellipsoidal, and irregular with sizes varying from a few cm up to 60 cm. Their dark brown outer shells are much harder than the hosted rocks, and the inner surfaces of the hollows are rugged and occasionally contain remnants of pyrite (FeS_2) minerals indicating incomplete oxidation processes. The result of extensive examinations of these hollow concretions suggests that their formation involves subsurface water that penetrates through fractures of rocks and the boundaries of sand grains forming several species of iron solutions. Due to their exothermic nature, these solutions sieve outward to the region with lower temperature and pressure where chemical reactions can continue. When equilibrium is reached, reddish brown iron oxide sediments remained as hard shells of the concretions. The hollow is then created *in situ* as a result of these chemical processes. The size and shape of these hollow concretions clearly depend on the quantity of pyrite crystals and the morphology of the pyrite nodules. As an external erosion process subsequently takes place, the outer shells which are more resistant and have a smaller porosity due to the secondary cemented iron oxides survive with shapes of sphere, ellipsoid and others, whereas other sandy parts of the host were eroded away. Because it is evidently clear that the reddish-brown color of the clastic rocks in our study areas is secondary in origin, parts of chemical reactions discussed here are promising candidates for actual chemical alterations responsible for the reddish color of the Khorat Group red beds in Thailand.

1. Introduction

The continental Mesozoic rocks of the Khorat Group in northeastern Thailand have been intensively studied by many researchers.[1–5] These rock

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sequences vary in age from Upper Triassic to Cretaceous-Tertiary.[6–9] The rocks of the Khorat Group are subdivided into nine formations listed from the oldest to the youngest as follows: Huai Hin Lat, Nam Phong, Phu Kradung, Phra Wihan, Sao Khua, Phu Phan, Khok Kruat, Maha Sarakham, and Phu Thok Formations.[10,11] In this study, we present evidences of the formation of mysterious rocks, "Naka's eggs" or hollow concretions which are found in the low hills with gentle slopes and flat land within the terrain covered by the clastic rocks of the Phra Wihan and Sua Khua Formations (Study Area 1) and of the Phu Kradung Formation

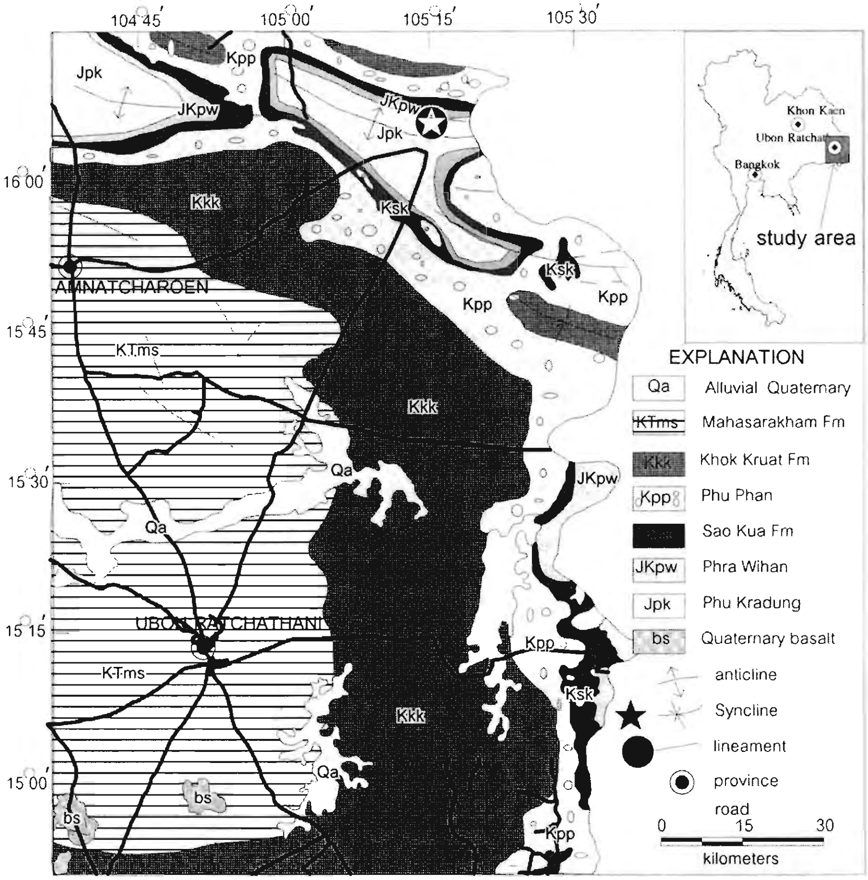

Fig. 1. Geologic map of Southeastern Khorat Plateau showing locations of the hollowed concretions Study Area 1 (filled circle) Phu Phrao near the Ban Chong Meg border town, Sirinthorn District, and Study Area 2 (open star in a filled circle) Ban Palai, Amphoe Po Sai, Ubon Ratchathani Province (filled star) Pak Moon Dam Site (modified after Sattayarak and Suteethorn, 1983).

(Study Area 2), shown in Fig. 1. Consequently, we propose, for the first time, the mechanisms responsible for the creation of the hollow concretions.

2. General Geology of the Study Areas

The Khorat Group clastic rocks in the southeastern corner of the northeastern plateau are generally flat lying beds, and slightly dip west toward the center of the Khorat basin (Fig. 1). The study areas predominantly contain three major rock formations. The first formation is classified as the Middle to Upper Jurassic Phu Kradung Formation normally distinguished by brown to grayish siltstones and fine-grained sandstones. This rock formation is mainly observed in the Study Area 2. Two additional formations observed in the Study Area 1 are Upper Jurassic to Lower Cretaceous Phra Wihan Formation containing mostly quartzitic sandstones and siltstones and the Lower Cretaceous Sua Khua Formation. This last formation is recognized as the rock unit where most vertebrate fossils were excavated in Thailand. Typical rocks in the Sao Khua ranging from most to least abundant are reddish brown sandstones, siltstones, conglomeratic sandstones, conglomerates, and intercalated shale, respectively.

3. Physical Descriptions of the Hollow Concretions

Most spaces of hollow concretions' cores are empty with minute amounts of loose sand, silt, or clay particles or detached hard lumps of clay materials resembling nuts. These concretions appear in various sizes and shapes. Their average sizes vary from a few cm up to 60 cm in lengths and greatly depend on the grain sizes of the pre-existing clastic rocks of the formation (Fig. 2).

The typical shapes of these concretions are spheroidal, ellipsoidal, distorted cylindrical, and irregular (Fig. 3). While embedded in the strata, these hollow rocks do not show any uniform patterns of distribution. The outer shells are significantly harder than the surrounding rocks in which they are buried. When viewing the cross section, the inner part near the hollow has a reddish brown color, and such color fades outward making the outermost crust relatively pale. The inner surface of the hollows is usually rugged showing distinct corroded features. In some cases, there are remnants of pyrite crystals (FeS_2) observed at the inner surfaces. We will explain in the next section that several species of iron solutions react as additional cementing media which hold the mantle of hollow concretions tighter than the sand grains farther away in the rock formations.

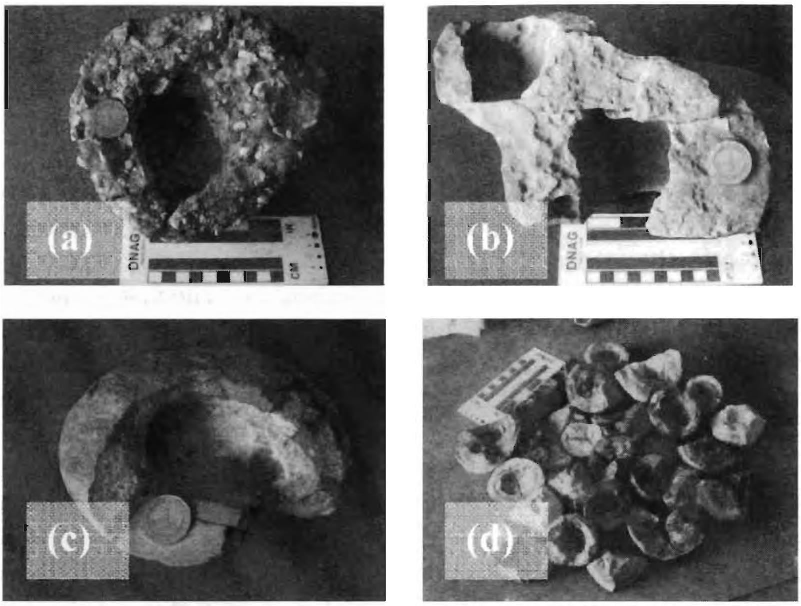

Fig. 2. The sizes of the hollow concretions are larger in the coarser-grained clastic rocks comparing to those of the finer-grained one, (a), (b), and (c) show the concretions from the Study Area 1 and (d) shows the concretions from the Study Area 2.

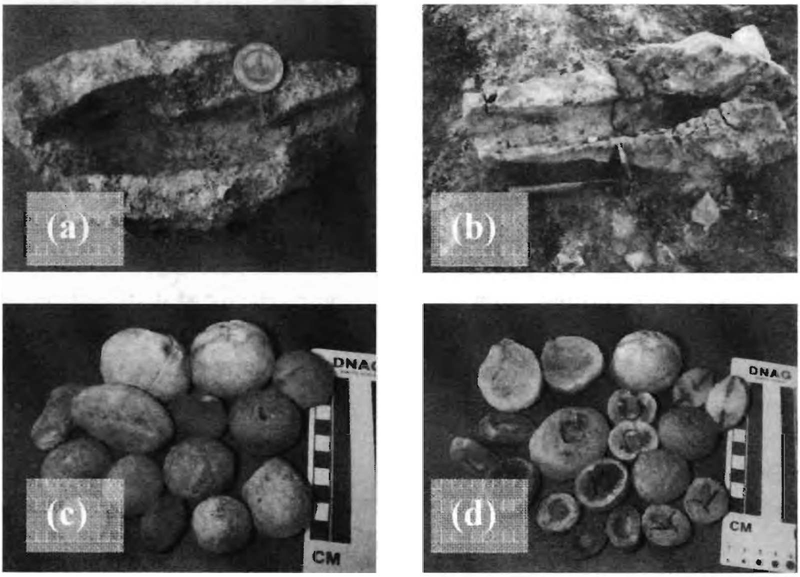

Fig. 3. The adopted shapes of the hollow concretions showing their dependence on the pre-existing pyrite nodules. (a) and (b) are from the Study Area 1, and (c) and (d) are from the Study Area 2.

4. Formation Processes

Extensive examinations performed on hundreds of samples of the hollow concretions collected from and observed in the fields lead to the conclusion that the most suitable processes responsible for their formation are sedimentary depositions followed by a series of chemical reactions and ended with weathering and erosion processes. From our present information, the best formation scenario is chronologically described as follows.

4.1. *Lithified stage*

The first stage is the formation of clastic sedimentary rocks, siltstone, sandstone, shale, and conglomerate present in the Phu Kradung, Phra Wihan, and Sao Khua Formations by meandering and braided stream deposits. The existence of pyrite (FeS_2) occurring as individual crystals, clusters of combined crystals or pyrite nodules, the existence of coal jets and carbonaceous materials suggest that these rock formations were formed under significantly reducing conditions. These crystalline pyrites distribute unevenly throughout the rock formations. The gray to greenish gray color of the rock formations also indicates reducing environment of depositions. This color can only be observed when the rocks are not subjected to prior chemical weathering processes, fresh rocks.

4.2. *Subsurface chemical reaction stage*

The second stage involves activities of subsurface water which sieves through fractures and grain boundaries of these pyrite-bearing rocks upon being exposed above the water table. The effectiveness of this water transmission is mainly regulated by the porosity and permeability of the rocks; therefore, properties such as grain size, primary rock structures, and the complexity of fracture system are important. The presence of water and oxygen gradually converts the system into oxidizing environment. As a result, several chemical reactions are triggered and often release heat and pressure to the system where reactions occur. The following four chemical equations show the general accepted sequence of pyrite reactions[12,13]:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 + 12H^+ \tag{3}$$

$$FeS_2 + 14Fe^{3+} \rightarrow 15Fe^{2+} + 2SO_4^{2=} + 16H^+. \tag{4}$$

In Eq. (1), FeS_2 which is stable under the previous reducing condition starts to react with oxygen and water to form ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and acid (H^+). Later, Fe^{2+} is transformed to ferric iron (Fe^{3+}), as shown in Eq. (2). Fe^{3+} ions can undergo two different reactions, either hydrolyzed with water to form the solid ferric hydroxide (ferrihydrite) ($Fe(OH)_3$) shown in Eq. (3) or further consume more FeS_2 releasing additional Fe^{2+}, SO_4^{2-}, and H^+, as shown in Eq. (4). These subsequent oxidation reactions of the pyrite crystals cause the textural failure; consequently, the individual sand grains (mainly quartz) previously held in the sedimentary rock matrix fall off becoming loose sand and silt particles. The Fe^{2+}/Fe^{3+} solution percolates outward seeking appropriate environments with lower temperature and pressure for chemical reactions to continue. This radially-outward percolation ceases at the outer shell of the concretion after the system reaches equilibrium leaving behind the rusty color of iron oxide.

In the presence of alkaline minerals such as feldspars, the H^+ and water from the above equations will be naturally neutralized by presumably, the following chemical reactions:

$$4KAlSi_3O_8 + 4H^+ + 18H_2O \rightarrow 4K^+ + 2Al_2Si_2O_5(OH)_4 + 8Si(OH)_4 \quad (5)$$

$$2CaAl_2Si_2O_8 + 4H^+ + 2H_2O \rightarrow 2Ca^{2+} + Al_4Si_4O_{10}(OH)_8 \quad (6)$$

The end product of both Eqs. (5) and (6) is mainly a kaolinite clay. This clay mineral can further react with SiO_2 and water yielding the solution of silica and silicic acid (H_2SiO_4). These iron oxide and silicic solutions which disperse throughout the mantle additionally strengthen the crust of the hollow concretions.

If carbonate minerals such as calcite are present, the neutralized process can be described by the following equations, and the chemical weathering product will be the mineral gypsum:

$$CaCO_3 + 2H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O + H_2CO_3 \quad (7)$$

$$CaCO_3 + H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O + HCO_3^- \quad (8)$$

The embedded FeS_2 crystals and nodules in the rock formations are evidently the essential starting materials for these chemical reactions to persist. Final size and shape of the hollow concretions are directly derived from the quantity of FeS_2 and the orientation of the FeS_2 nodules (Fig. 4).

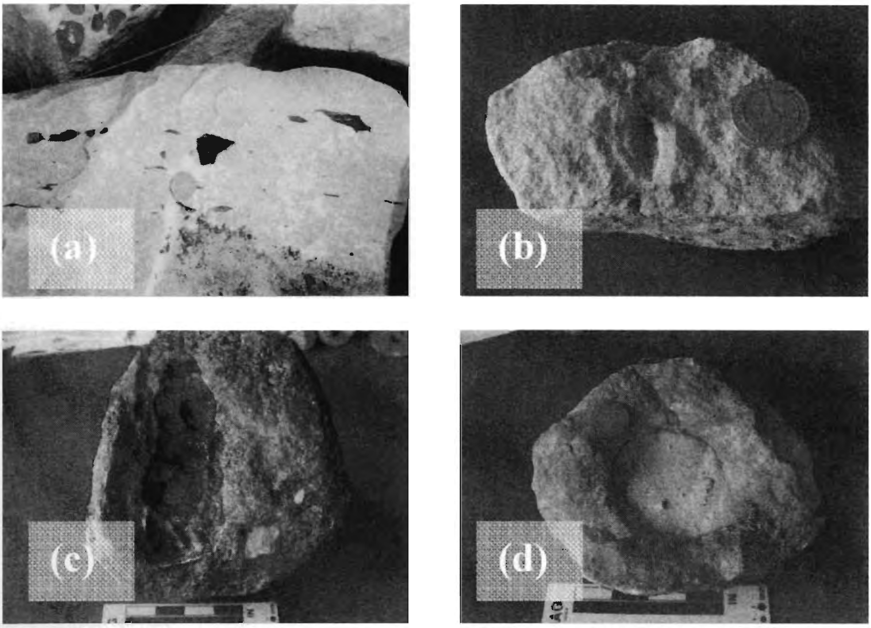

Fig. 4. Successive developments of the hollow concretions. (a) is gray to greenish gray, fresh sandstone with pyrite and carbonaceous materials of the Phra Wihan Formation excavating from the river bed near the Pak Moon Dam site; (b) shows the alteration of the similar rocks shown in (a) after being exposed to air for some years. Rusty spots and banded circles evidently ascertain the validity of chemical reactions caused by weathering; (c) shows the rugged inner surface of the hollow previously underwent severe chemical reactions; (d) shows trapped loose sand, silt, and clay particles which are always observed in the undisturbed hollows.

4.3. *Post-chemical erosion stage*

The last stage is the prolongation of weathering and erosion processes undertaking well after maturation of chemical reactions of the previous stage. The portions of the rock farther away from the crust of the concretion are subjected to erosion process much more severely and are easily removed. Without surrounding materials, some hollow concretions become free and can be transported to new depositional sites by various means. The remaining partially free hollow concretions are left embedded *in situ* within the outcrop exposures (Fig. 5).

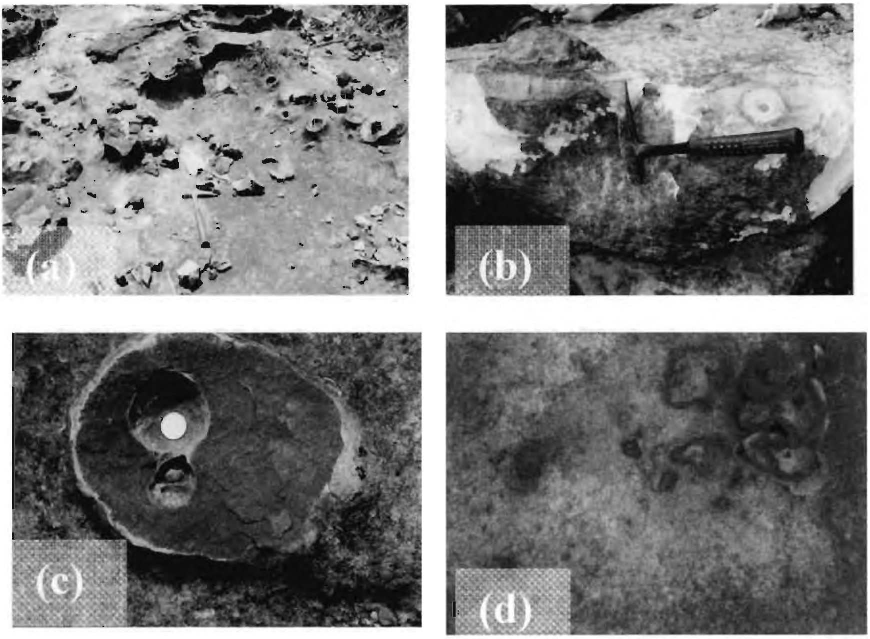

Fig. 5. The outcrops containing partially free hollow concretions embedded *in situ* at Phu Phrao, the Study Area 1.

5. Conclusion

The origin of hollow concretions can be summarized by the lithified stage, the subsurface chemical reaction stage, and the post-chemical erosion stage. The lithified process of the clastic rocks occurs under significantly reducing condition as indicated by the existence of pyrite nodules. Later on, the environment becomes more oxidized due to the presence of subsurface water and oxygen. Several chemical reactions take place forming hollows and strengthening outer shells of the concretions. The final post-chemical erosion stage explains the mobility and the distribution of the hollow concretions observed in the rock outcroups.

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