Rediscovery of the Elements

Phosphoro di Bologna

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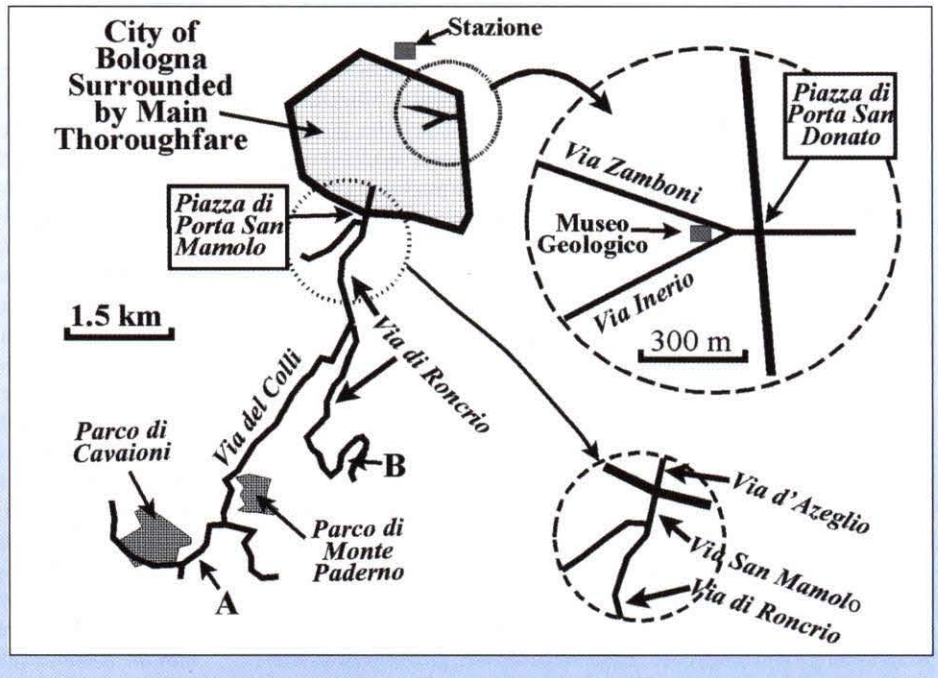
In Bologna, Italy during the first decade of the 1600s, a cobbler named Vincenzo Casciarolo discovered a stone in nearby hills which became phosphorescent when "calcined by art."[1,2] This material, which became known as the "glowing stone of Bologna" or "phosphoro di Bologna" was the subject of intensive study by many alchemists and chemists through the years. Many recipes were developed, most of which included secret ingredients, but a basic theme included such things as eggs or charcoal and a "firing to redness." Throughout chemical history, the study of various "phosphorus" materials has always been of keen interest and has led to the discovery of such materials as "Baldium's phosphorus" or "Hermetic phosphorus" (calcium nitrate),[2] "Canton's phosphorus" (calcium sulfide),[2] the element phosphorus, itself,[3] or the mineral fluorspar (calcium fluoride) from which the name "fluorescence" orginates.[4] Today we know "Bologna stone" is barite (barium sulfate). Actually, the active phosphorescent form is barium sulfide,[5] reduced from the original barium sulfate. Recent studies by Italian chemists have tried to duplicate the original recipe, and it appears that an admixed metal is necessary and probably was one of the secret ingredients.[6] This added metal probably served as a doping ingredient, which today forms the basis of certain luminous paints, such as "Balmains Luminous Paint" described by Oliver Sacks in his recent Uncle Tungsten.[5]

Our spoor to the discovery of "phosphoro di Bologna" originated from Lémery's account[7] which located the main site of Bologna stone as "Mt. Paternò about one French league" (three statute miles) from Bologna, Italy (Note: in the literature there are variants of the spelling of "Paderno" and "Roncrio"). By various queries we were able to make connection with Gian Luigi Felice, curator of the Geological Museum of the University of Bologna, who graciously accompanied us to a modern site where the Bologna stone could be found. A short drive from the medieval walls of Bologna (Figures 1 and 2) took us to the heavily eroded gray argillaceous (clay) hills (Figure 3) where pieces

LEFT: Figure 1. The backbone of Italy is the Apennines, the foothills of which have generated "Bologna stone" outside Bologna. Italy has been described as a "mound of breccia" generated when the African plate smashed into Europe millions of years ago.



BELOW: Figure 2. Details of Bologna (surrounded by an ancient wall) and its environs. The Museum Bombicci (geological museum) can be found at Piazza di Porta San Donato, 1 (N 44° 29.89, E 11° 21.35). From the south exit of the wall, Piazzi di Porta San Mamolo (N 44° 29.18, E 11° 20.37) one can drive southward up the hillside, taking the Via del Colli fork (intersecting with Via di Roncrio at 44° 28.46, E 20.23) upwards to an eroded field (very muddy when wet) at 44° 26.73, E 11° 18.81. Roncrio, another historic site of "Bologna stone," is located at N 44° 27.20, E 11° 20.00.

LEFT: Figure 3. View of clay badlands where "Bologna stone" is found, looking northeast with Bologna in the distance. This portion of the Apennines dates from the Miocene, about 15 million years ago. The "Bologna stone" crystallized out from the gray-colored clay.

BELOW: Figure 4. Discovery! Fragments of "Bologna stone" are found in the hillside of Monte Paderno by one of the authors.

of Bologna stone could be found (Figure 4). These pieces were originally part of a large concretion, a "boule tuberculeuse fribreuse et radiée" (swelling nodule of radiating threads)[8] (Figure 5) formed by a selective crystallization of alkaline earth sulfates in the clay hillsides.[9] Hence, as one dug through the muddy slopes of Mt. Paderno, the discovered shards of the original concretion would vary from light to heavy, (calcium or barium sulfates, respectively) (Figure 5). The best samples of complete nodules of Bologna stone are on exhibit at the Bombicci Museum at the University of Bologna (Figure 6).

In original accounts,[1] the "Bologna stone" could be observed in three sites: "Monte Padernò, Roncaria, and Pradalbino." Gian Luigi Felice and other geologists of Bologna University were well aware of the first two sites (Monte Paderno and Roncrio, see Figure 2) but had never heard of the third site, the exact location of which shall probably never be known. However, other locations where the barite concretions can be found are notably at Monte San Giovanni (N 44° 24.67, E 11°09.94, approximately 12 km WSW of Monte Paderno). Taking the train from Bologna to Rome, in the stretch a few kilometers south of Bologna, one can spot several locations of the typical clay badlands (Figure 3).

To continue the story from phosphoro di Bologna to modern times, we must travel to Sweden, France, and Great Britain. In the middle 1700s Gottlieb Gahn and Carl Wilhelm Scheele of Sweden recognized "Bologna's stone" as identical to "heavy spar" from Sweden and recognized "barium" as a separate earth. In 1789 France's Antoine-Laurent Lavoisier recognized barium as one of the elements ("baryte," or "terre pesante" = "ponderous earth").[10] In 1808 Sir Humphry Davy through his voltaic pile isolated metallic barium. However, each of these stories must wait for a future time.

Acknowledgments

We wish to thank Gian Luigi Felice, Dip. Scienze delle Terra e Geologico, Museum Bombicci, Piazza di Porta San Donato, 1, Bologna, Italy, who directed us to the Bologna stone sites and furnished historic and geological information.

Figure 6. The Bombicci Museum (geological museum) in the University of Bologna which is famous for the Bologna stone, amber, and other specimens. The University of Bologna has a long history dating back to the Middle Ages. Already by the 12th century the University was famous throughout Europe and attracted students in law, medicine, and other disciplines. Agricola studied medicine here in 1524 before his famous mineralogical researches in the Saxony-Bohemia region.

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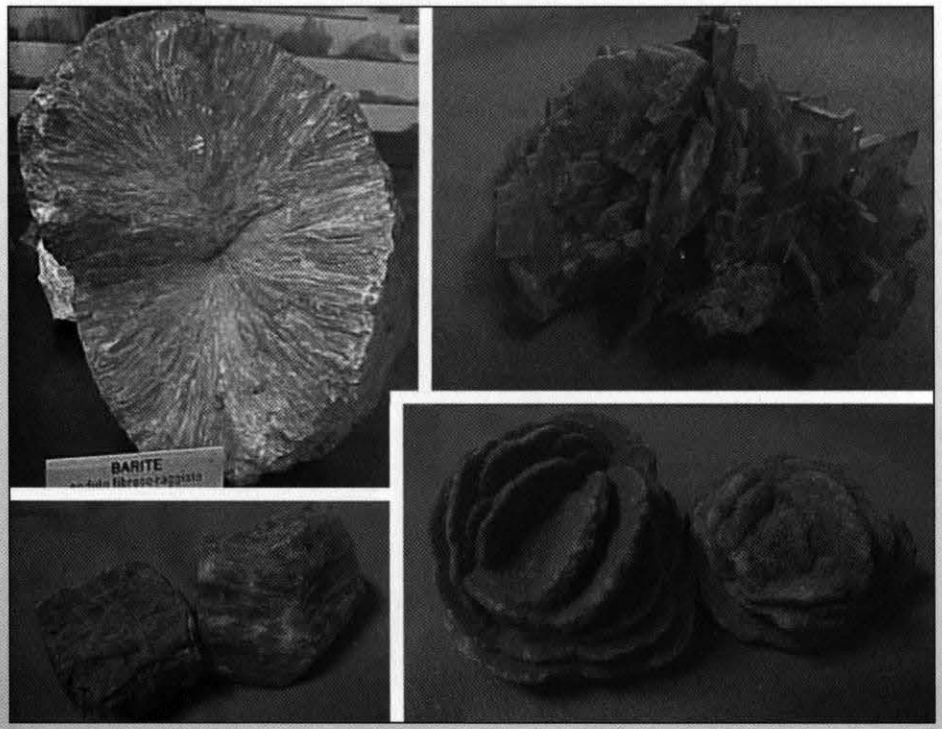

Figure 5. Specimens of various forms of barite, $BaSO_4$. Upper-left: a "tubercule of radiating fibers," the "Bologna stone," exhibited in the Museo Bombicci, University of Bologna. During the crystallization process, the differentiation has created a core of calcium sulfate and an outer layer of barium sulfate. Lower-right: pieces of "Bologna stone" found by the authors at Monte Padern; sometimes the shards were light (calcium sulfate) and other times heavy (barium sulfate). Upper-right: most common form of barite, in the form of plates, collected by the authors in Colorado. Lower-right: famous barite roses of Oklahoma, collected by the authors.