

# The paleo-lacustrine diatomaceous deposits of Monte Amiata volcano (Tuscany, Italy) and the Ezio Tongiorgi paleontological collection in the Museum of Natural History of the University of Pisa

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## Abstract

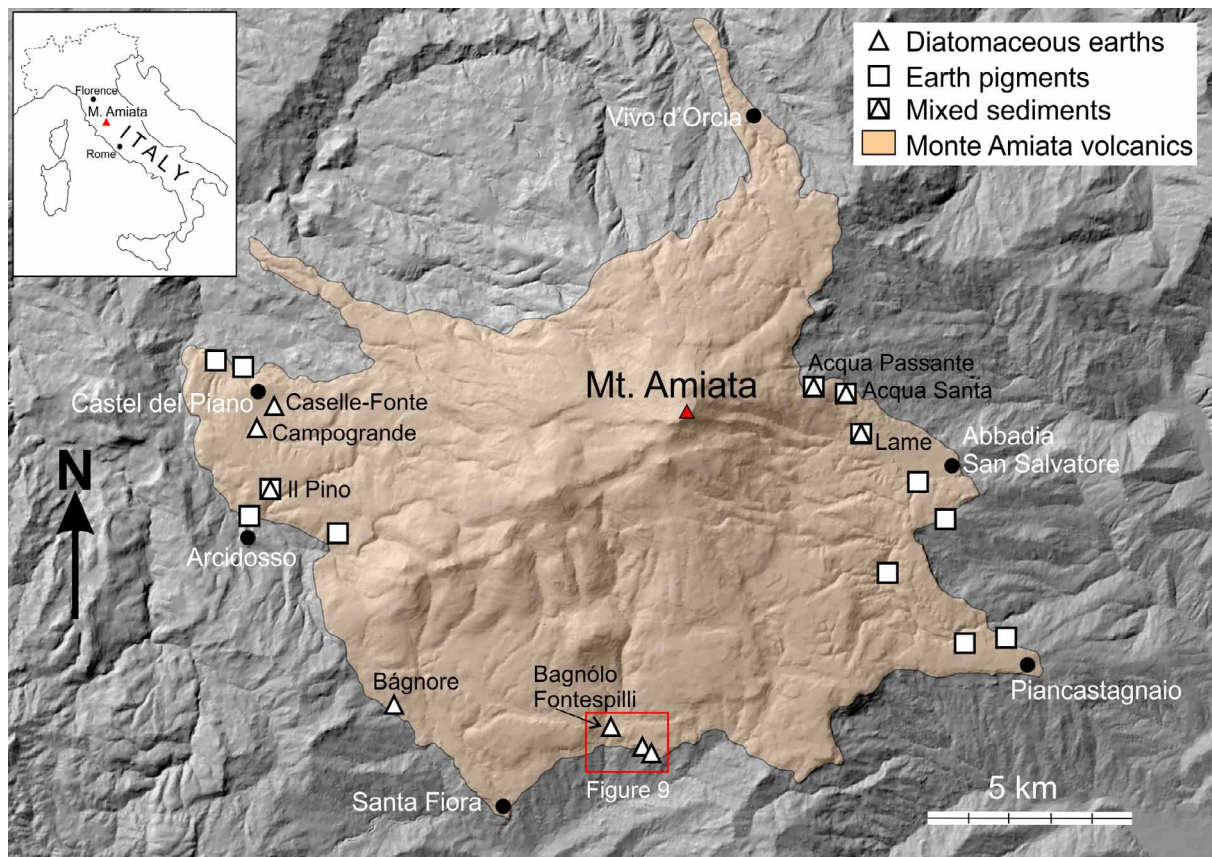
At the foothill of Monte Amiata volcano (southern Tuscany, Italy), small extinct lake basins of late Pleistocene age are documented. These lake basins were characterized by the deposition of two very different types of sediment: a) derived from the authigenic precipitation of iron oxides (goethite) and exploited as earth pigments; b) biogenic siliceous sediment composed of fossil diatoms and named diatomaceous earth or diatomite. The lacustrine sediments of Mount Amiata volcano were widely exploited for various applications since ancient times. Literary documents begin in the 16th century, with the descriptions of Cesalpino, Gesner, Agricola, and Imperato. Specific references to the diatomites of Monte Amiata are quoted in the 17th century by Boccone and Bonanno. The quarrying activity was described by Micheli in 1733. During the 18th and 19th centuries, the diatomaceous earths of Monte Amiata are part of the important geological collections of Micheli, Targioni Tozzetti, Baldassarri, Campani, and Tommi. A particular significance has the collection of botanic and ichthyologic fossils collected by Ezio Tongiorgi, and now preserved in the Museum of Natural History of the University of Pisa sited at the Charterhouse of Pisa in the Calci village. These paleontological samples preserve the biological and physical testimonies of the environmental and climatic changes of the late Pleistocene and are now particularly valuable because they are the only remaining evidence of the diatomaceous lacustrine deposits of the paleo-lakes of Monte Amiata. For these reasons, they represent geological materials with a fundamental cultural value.

Keywords: Paleo-lake; Diatomite; Late Pleistocene; Ichthyologic fossil; History of Earth sciences.

## 1. Introduction

Monte Amiata is a middle Pleistocene [305-231 ka BP; Laurenzi et al., 2015, Laurenzi and La Felice, 2017] silicic effusive volcano culminating at 1738 m above sea level (a.s.l.) located in southern Tuscany (Italy; 43°43'18.84"N - 10°31'24.77"E, Figure 1). Monte Amiata activity was dominated by the emplacement of trachydacite and subordinate trachyandesite [La Felice et al., 2017; Landi et al., 2019; and references therein] lava flows and exogenous lava domes, that were produced during two main periods of activity [Principe et al., 2017, 2018; Vezzoli and Principe, 2017; Principe and Vezzoli, 2021; and references therein].

Around the base of Monte Amiata volcano, lacustrine sedimentary deposits of late Pleistocene age were formed in small presently extinct lake basins, located near the boundary between the volcanic rocks and the sedimentary substrate units (Figure 1) [Vezzoli et al., 2017].



**Figure 1.** Map with the location of the late Pleistocene paleo-lakes in the region of Monte Amiata volcano (Tuscany, Italy) differentiated according to prevailing types of lake sedimentation: earth pigments, diatomaceous earths, or mixed. The inset shows the location of Monte Amiata in Italy.

According to different environmental, chemical-physical, and biological conditions, these paleo-lakes were characterized by the deposition of two very different types of sediments (Figure 1) [Vezzoli et al., 2017]. The first type is derived from the authigenic chemical precipitation of iron oxides-hydroxides, assisted by the presence of ferro-bacteria. These sediments were used as earth pigments, such as the famous *terra di Siena*, due to the bright and permanent colors ranging from light yellow to red and brown [Vezzoli and Principe, 2021]. The second type is named diatomaceous earth or diatomite, is siliceous in composition and biogenic in origin, being formed by the accumulation of fossil unicellular algae of the Bacillariophyceae class (diatoms). Overall, sedimentation in Monte Amiata paleo-lakes has been of a single type, even in areas very close to each other. In particular, the lake deposits with earth pigments were in the municipality of Castel del Piano, Arcidosso, Piancastagnaio, and Abbadia San

Salvatore; and the main lake deposits with diatomaceous earths were in the municipality of Castel del Piano and Santa Fiora (Figure 1). In few basins, both types of sediment were found superimposed or in alternating layers, such as in Abbazia San Salvatore and Arcidosso (Figure 1), to indicate cyclical variations in environmental and genetic conditions within the same basin.

Both diatomaceous earths and earth pigments are minerals with economic importance and therefore the lake sediments of Mount Amiata have been the subject of extensive industrial exploitation, especially in the nineteenth century [Fei, 1997]. The identification of the ancient lake basins and the study of their sediments are today made difficult due to the deposit's exploitation until exhaustion, and their complete anthropic transformation. For these reasons, the field evidence of the existence of the Monte Amiata paleo-lakes is currently minimal, and we must base their study on past literary documents and survived mineral sample collections.

While the Monte Amiata lacustrine sediments made up of iron oxides and hydroxides are generally devoid of biological remains, diatomaceous earth deposits, in addition to their intrinsic biogenic composition, resulted to be rich in pollens and microfossils such as fishes, insects, leaves, fruits, seeds, and woods. These fossils have been collected and studied by various scholars since the nineteenth century.

The most important paleontological collection regarding the diatomaceous earth deposits of Monte Amiata is the one collected from a quarry in locality Fontespilli (Bagnólo, Santa Fiora; Figure 1) during the years 1953-1956 by the botanist, geologist, paleontologist and geochemist Ezio Tongiorgi (1912-1987; see Section 3.1). Some of the Tongiorgi's findings have been studied and published in Bradley and Landini [1982]. The complete Tongiorgi's collection is currently preserved in the Museum of Natural History of the University of Pisa based inside the ancient Charterhouse of Pisa in Calci (Italy; see Section 3.2).

This work is dedicated to the geological contextualization and description of historical mineral sample collections of the diatomaceous earth ores of Monte Amiata collected during the 18th and 19th centuries, and in particular of the paleontological collection of Professor Ezio Tongiorgi. These collections are particularly valuable because they are the only remaining evidence of the diatomaceous deposits from the extinct lakes of Monte Amiata volcano, and of their paleontological content.

## 2. The diatomaceous earths of Monte Amiata

### 2.1 Documents and collections of the 18th and 19th centuries

The pure white, fine, and light material forming the diatomaceous earths is a very particular mineral deposit that has aroused curiosity in scholars since ancient times. It was described above all in medical treatises until the 18th century [e.g.; Hill, 1751], and it was named by old authors with several terms, such as: *creta Seleneusiaca* [Osbaldeston, 2000, Agricola, 1546], *Agaricum saxatile* [Gesner, 1565], *Lac Lunae* (moon's milk) [Gesner, 1565; Boetius De Boodt, 1609; Lang, 1708; Micheli 1733; 1754a], *Bolus candidus* [Cesalpino, 1596; Bonanno, 1709], *Agarico minerale* [Imperato, 1599; Baldassarri, 1750], *Galactite* [Boetius De Boodt, 1609; Worm, 1655], *Lapis Morochtus* [Boetius De Boodt, 1609; De Laet, 1647], *Marga candida* [Dale, 1693], and finally *Paretonium* [Targioni Tozzetti, 1750] (Figure 2). It should be noted that in the treatises of these ancient scholars, mineral materials of different composition (i.e.; calcareous, clayey, or siliceous) and genesis (i.e.; biogenic or chemical) have been often compared as similar and included under the same classification, or at the same mineral have been attributed different names on the basis of the distinct geographical provenance.

A first mention of the origin of a mineral material named *Lac Lunae* from the region generically called *Aetruria* (Tuscany) is by the Flemish natural philosopher Anselmus Boetius De Boodt (1550-1632) [Boetius De Boodt, 1609].

The diatomaceous earths of Monte Amiata, and in particular the one of Bagnólo near Santa Fiora, were described for the first time in 1697 by the Sicilian scholar Paolo Boccone (1633-1704), botanist at the Medici court in the Grand Duchy of Tuscany [Boccone, 1697]:

“Lemnia Earth of the Sienna Mountains. ... Near Santa Fiora, the Abbey of S. Salvatore, and in Monte Tinni, or Monte Amiata, at about a palm under the ground, there is an earth fat and oily like lard or butter, white in color, and when it has just been extracted from its Mine it is characterized by its softness, and to be greasy over solid bodies. Which becomes whiter as it dries, and sticks to the tongue; in addition, that earth is abundant near the Chestnut Forest, and easy to find”. [Boccone, 1697]

“Terra Lemnia delle Montagne di Siena. ... Vicino Santa Fiora, l'Abbadia di S. Salvatore, e nel Monte Tinni, o Monte d'Amiata si trova un palmo sotto il suolo in circa una Terra grassa, untuosa come Lardo, o Butiro, di color bianco, ed essendo frescamente cavata dalla sua Miniera si distingue per la sua morbidezza, e grassezza sopra i corpi solidi. Che asciugandosi diventa più bianca, e si attacca alla lingua; e che vicino la Selva di Castagni è copiosa, e facile a rinvenire essa Terra”. [Boccone, 1697]

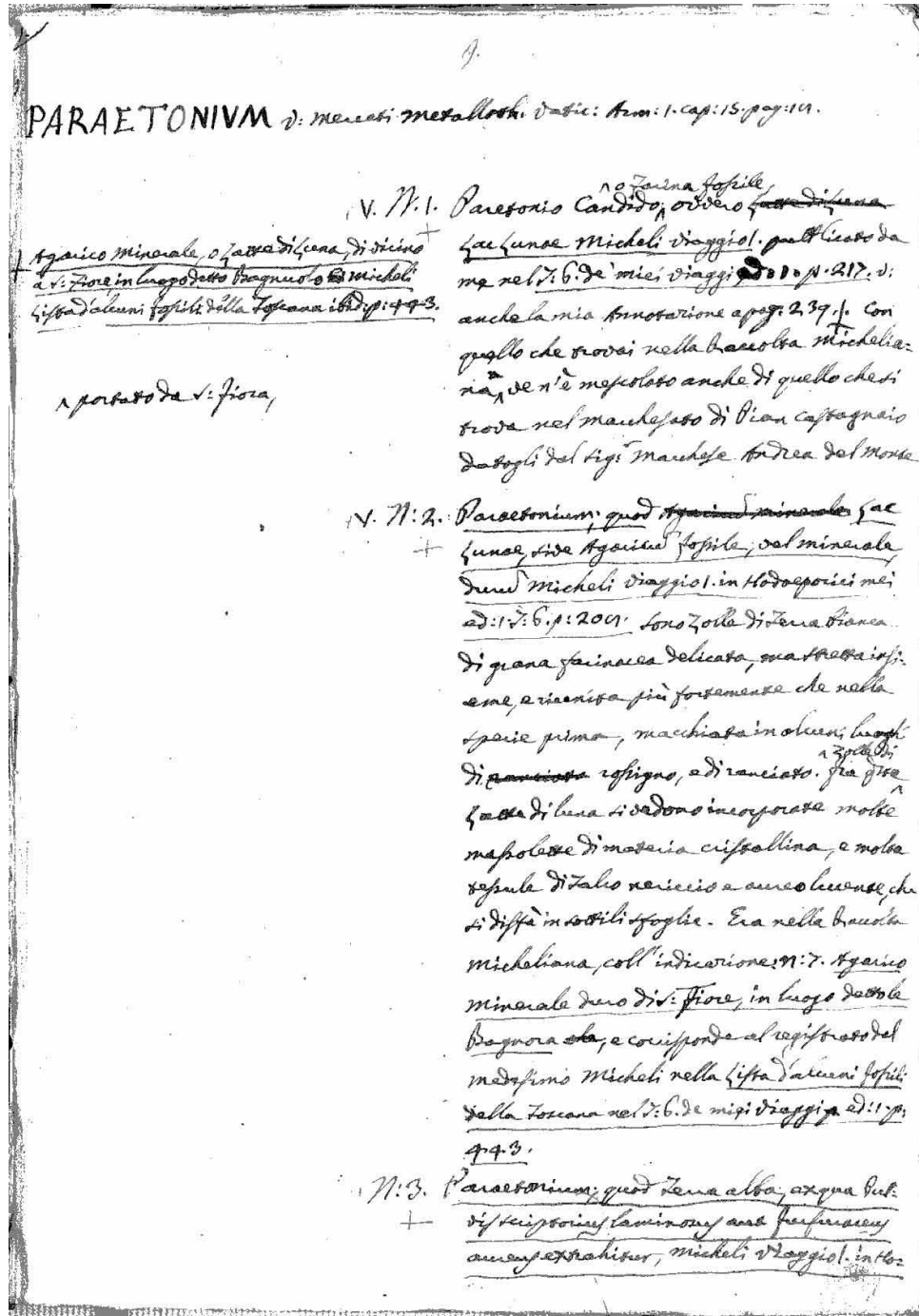


Figure 2. A page of the manuscript catalog of the private collection of Giovanni Targioni Tozzetti, [Targioni Tozzetti, 1750] showing the descriptions of the samples of diatomaceous earths of Santa Fiora (classified as *Paraetonium*) collected by Pier Antonio Micheli during his travel of 1733. <http://www.museogalileo.it/istituto/biblioteca-digitale-tematica/targionitozzetti/catalogo.html>



## Diatomaceous earths of Monte Amiata volcano

A few years later, the description of a similar earthy material that was found in the territory of the city-state of Siena was reported under the name *Agarici fossilis* by the Jesuit Filippo Bonanno (or Buonanno; 1638-1725), curator of the *wunderkammer* at the Roman College of the scholar and polymath Athanasius Kircher (1602-1680) [Bonanno, 1709]:

“To this is added another earth, which I believe can be understood under the name of white bolus, this earth is very white and very light, and does not dirty the hand in the slightest if touched, braced between the teeth proves to be very juicy like the Samia earth. The use of this earth is very useful against fevers and poisonings. ... From the countryside of Sienna, such an earth is found with the name of *Agarici fossilis*. That is a light, white, crumbly, but not bitter substance similar to Agaric. Thus this agaric was described by Imperato. ... The earth so called is similar in its whiteness to lime, but dissimilar in its lightness, which in the Agaric usually is maximum, it is found in the top of caves, with a soft consistency if dissolved in water, it has a fibrous behavior, but finally liquefies like other earths, nor does its origin seem entirely different from the true Agaric, as in the appearance it completely resembles it; it adheres to the tongue, for which reason it feels like the Samian earth and by many physicians is used in its place. It is useful for the repulsions of blood by mouth, and generally in all other things it is used as Samia. Called by some moon’s milk, for the whiteness, and tenderness it has, while it is collected in its own places”. [Bonanno, 1709]

“*His adde terram aliam, quam sub nomine boli candidi comprehendere posse judico, nam terra est candidissima, & levissima tangentium manus nequaquam inficiens, dentibus confricata succosam admodum se praebet ut terra samia. Huic simile terra felicissimo eventu se usum esse adversus febres, quae ex venenata qualitate in humoribus existente ortum trahunt, ... Ex agro Senensi similem terram recepi sub nomine Agarici fossilis. Substantiam enim Agarico similem habet levem albam, sed friabilem, non tamen amaram. Tale agaricum descripsit Imperator, ... Terram ait existere ita vocatam, candore calci similem, levitate dissimilem, quae in Agarico summa esse solet, in specuum fornicibus inveniri, consistentiae mollis dum solvitur, fibrosi aliquid praeferre; sed denique terrarum aliarum instar liquescere, nec ejus ortum a veri Agarici ortu diversum videri, quemadmodum etiam effigie omnino ipsum refert; linguae adhaerescere, quapropter, & credi, esse terram samiam, & pro ea a multis peritis medicis usurpari. Sanguinis per os rejectionibus prodesse, generatim ad ea omnia adhiberi, quibus Samia terra est conducibilis. Lac Lunae nonnulli appellant ob mollitiem, & candorem, quam praefert, dum in propriis locis colligitur*”. [Bonanno, 1709]

The physician Michele Mercati (1541-1593), who was superintendent of the Vatican Botanical Garden under several Popes, in his work *Metallotheca Vaticana*, written probably between 1570 and 1593 but published posthumously in 1717 [Mercati, 1717], quoted an earth mineral named “*Argilla*” (clay), coming from the county of Santa Fiora and used in the smelting of precious metals due to its refractory properties:

“*Argilla* ... Some are found leaner and some fatter, one that resists fire well, others not at all. The one that resists fire, called by Pliny (33.4) Talc, none like this one tolerates burning breath, flame and matter. This is used by the goldsmith to melt gold and silver, which is located in the county of Santa Fiora not far from the mountain called Laterone, and from other parts of Italy”. [Mercati, 1717]

“*Argilla* ... *Verum alia tenuior reperitur, alia crassior: quaedam ignem fert, quaedam vero minime. Ea, quae fert ignem, Tasconium a [c 33.4] Plinio appellatur; neque enim alia (de Tasconio loquens ait) afflatum, ignemque, & ardentem materiam tolerat. Hae utuntur auri Fabri ad fundendum aurum, atque argentum, quae in Comitatu Sanctae Florae reperitur non longe a monte Laterone vocato, aliisque Italiae locis*”. [Mercati, 1717]

The Florentine botanist Pier Antonio Micheli (1679-1737) in his diary of the *Viaggio fatto l'Anno 1733 per diversi luoghi dello Stato Senese* (Journey made the year 1733 for different places of the Siennese State; Micheli, 1733; 1754a) referred to quarries in the *latte di Luna* (Moon’s milk) near Arcidosso and at Bagnólo (Santa Fiora):

“Not far from the aforementioned quarry [at the Bagnora near Arcidosso], there is that of the hard *Latte di Luna*, that is “*Lac Lunae*”, or a *Agaricum fossile* or a hard mineral”. [Micheli, 1754a] ... “I walked towards the Bagnuolo, ... and when I arrived there I found, just past the last houses below, and on the edge of the chestnut groves, the open quarry of a white, very fine and very light earth, which when chewed does not screech under the tooth, called by Latins *Lac Lunae*”. [Micheli, 1754a]

“*In poca distanza dalla suddetta Cava [alla Bagnora vicino Arcidosso], vi è quella del Latte di Luna duro cioè “Lac Lunae”, sive Agaricum fossile vel minerale durum*”. [Micheli, 1754a] ... “*m’incamminai alla volta del Bagnuolo, ... e giuntovi trovai, giusto passate l’ultime case di sotto, e a confini de’ castagneti, la Cava aperta di una Terra candida, finissima, e leggerissima, la quale masticata non stride sotto il dente, detta da Latini Lac Lunae*”. [Micheli, 1754a]

More than a hundred rock samples collected by Micheli during his 1733 travel at Monte Amiata were part of his private museum in Florence [Vezzoli and Principe, 2020] including two samples of *Agarico Minerale* or *Latte di Luna* from Santa Fiora [Micheli, 1754b]. At the premature death of Micheli in 1737, this collection was purchased by his disciple Giovanni Targioni Tozzetti (1712-1783). The private collection of Targioni Tozzetti, including also Micheli's samples, comprised more than 9000 samples of rocks and minerals and was described in a manuscript catalog [Targioni Tozzetti, 1750] (Figure 2).

Giuseppe Baldassarri (1705-1785), physician of the main Camaldolese convent of Monte Oliveto Maggiore (Tuscany, Italy), professor of natural history at the University of Siena, and president of the *Accademia delle Scienze di Siena detta de' Fisiocritici* (Fisiocritici's Academy of Science in Siena), compiled a catalog of natural products that are found in the territory of the city-state of Siena and that are into the private museum of Giovanni Venturi Gallerani [Baldassarri, 1750; <http://www.museofisiocritici.it/catalogobaldassarri.asp>] (Figure 3a), comprising 130 samples of rocks and minerals, and 37 samples of *testacei* (fossils). Until 1765, the samples described in the Baldassarri's catalog were exposed in the Museum of the Fisiocritici Academy in Siena as quoted by Targioni Tozzetti [1774], but their current location is unknown. The first mineral product described in this catalog was the diatomaceous earth of Monte Amiata named *Agarico minerale* following Imperato [1599] (Figure 3b):

"1. MINERAL AGARIC, also called Moon's milk; it is found in several places near Castel del Piano, at the foot of the Mount of S. Fiora. ANNOTATION. Called from Gesner Moon's milk, from Agricola *Medulla Saxorum*, and from Ferrante Imperato *Agarico minerale*, due to the similarity it has with a mushroom, called Agaric, i.e. *Fungus Laricis* C. B. Pin. This is a fungal, light, rare, candid, and insipid earth, and can be referred to *Marghe* genus. It dissolves easily in water, and dyes it white. It has much uses in medicine, and it is attributed the faculty to be refreshing, astringent, and stopping the loss of blood, and the uterine discharges; it is prescribed in tenesmus, and in dysentery with much profit. When pulverized and sprinkles over the ulcers it dries them admirably". [Baldassarri, 1750]

"1. AGARICO MINERALE, detto anco Latte di Luna; si trova alle falde della Montagna di S. Fiora presso a Castel del Piano in più luoghi. ANNOTAZIONE. Chiamasi dal Gesnero Latte di Luna, dall'Agricola *Medulla Saxorum*, e da Ferrante Imperato *Agarico Minerale*, per la simiglianza, che ha col Fongo, detto *Agaricum*, seu *Fungus Laricis* C. B. Pin. Questa è una terra fongosa, leggiera, rara, candida, e insipida, e si riduce al genere delle Marghe. Si scioglie facilmente nell'acqua, e la tinge di bianco. Hà molto uso nella medicina, e li si attribuisce la facultà di rinfrescare, astringere, e fermare le perdite di sangue, ed i fluori uterini; si prescrive nel Tenesmo, e nella Disenteria con molto profitto. Polverizzata si asperge sopra le ulcere, e le risicca mirabilmente". [Baldassarri, 1750]

The Florentine naturalist, agronomist and chemist Giovanni Fabbroni (1752-1822) was among the first to discuss the difference between the various types of earthy mineral materials hitherto united under the names of *Lac Lunae* (*Latte di Luna*, moon's milk, *guhr*), which is a plastic clayey earth, and Agaric (*Agarico minerale*), which is a calcareous earth, and to underline how the soft, light, and flaky white earth found at Monte Amiata is different from the both. For this reason, he proposed to name the diatomaceous earth of Monte Amiata as *Farina Fossile* (fossil flour, *bergmehl*) [Fabbroni, 1794], and with this name it continued to be locally known since then.

During the 19th century, diatomaceous earth samples from Monte Amiata were comprised in the collection of Giovanni Campani [Campani, 1860] and in the mineralogical catalogs of Cesare Tommi [Tommi, 1890] [Vezzoli et al., 2017]. Giovanni Campani was professor of general chemistry at the University of Siena and director of the Museum of the Fisiocritici's Academy. He donated in 1860 to the museum itself a collection of rock samples with the title *Collezione Geognostica e Oritognostica del Monte Amiata e sue vicinanze* (Geognostic and Orthognostic Collection of Monte Amiata and its vicinity), originally including 124 samples, 116 of which were stored and 109 are still on display at the Museum of Natural History of the Fisiocritici Accademy (MUSNAF) in Siena. Among the Campani's collection, a sample of *farina fossile* comes from Castel del Piano (Campani [1860]; Figure 4).

Cesare Tommi was the secretary-speaker of the Chamber of Commerce and Arts of Siena and Grosseto and compiled the catalog *Elenco dei minerali delle provincie di Siena e Grosseto dei quali la Camera di Commercio possiede un campione* (List of minerals from the provinces of Siena and Grosseto of which the Chamber of Commerce has a sample) [Tommi, 1890]. In the Tommi's book 203 samples are described, inclusive of a sample of diatomaceous earth of Monte Amiata (*farina fossile*) from the quarry of Santa Fiora (Bagnólo) [Tommi 1890, inventory number 35; Vezzoli et al., 2017] and a refractory brick made with the *farina fossile* of Bagnólo [Tommi 1890, inventory number 36; Vezzoli et al., 2017]. Attached to this catalog is also a large table called *Elenchi dei minerali esistenti nelle Provincie di Siena e Grosseto* (Lists of existing minerals in the Provinces of Siena and Grosseto), consisting of 8 sheets (86 x 64 cm large),



Figure 3. a) The frontispiece of the catalog of Baldassari [1750]. b) The description of the *Agarico Minerale* of Castel del Piano in Baldassari [1750].



Figure 4. The sample of *Farina Fossile* from Castel del Piano in the collection of Giovanni Campani [1860]. Museum of the Fisiocritici's Academy in Siena (Italy), inventory number 3581.



in which 528 samples of rocks are described. Among them are three samples of diatomaceous earths from the quarries of Abbadia San Salvatore (Acqua Santa), Castel del Piano (Fonte), and Santa Fiora (Bagnólo) [Tommi, 1890, inventory numbers 222, 383, and 409, respectively; Vezzoli et al, 2017]. The Tommi's collection was kept until the first half of the twentieth century at the Chamber of Commerce in Siena, but was subsequently dispersed due to a flooding in the building.

Descriptions or brief references to the diatomaceous earth of Monte Amiata can be found in Santi [1795], Repetti [1830], Giannetti [1873], Lotti [1878], Clerici [1903a], Verri [1903], and De Castro [1914]. Above all, Lotti [1910] makes a detailed description of the quarries and sediment stratigraphy.

The first hypotheses on the genesis of the diatomaceous earth of Monte Amiata formulated in the eighteenth century suggested that it was the result of the alteration of the Monte Amiata siliceous volcanic rocks (called by the local people as *peperino*; Vezzoli and Principe, 2020), transported by water and deposited in small depressions [Targioni Tozzetti, 1776-1777; Santi, 1795; Tasselli, 1890]. The problem of the origin of this lacustrine sediment was solved by the first modern analyses on the deposits of Santa Fiora basin made by Klaproth [1814], which demonstrated its siliceous chemical composition and proposed the name *Kieselguhr*, and by Ehrenberg [1836; 1838], which recognized its biogenic composition due to siliceous skeletons of Infusoria (including diatoms) (Figure 5).

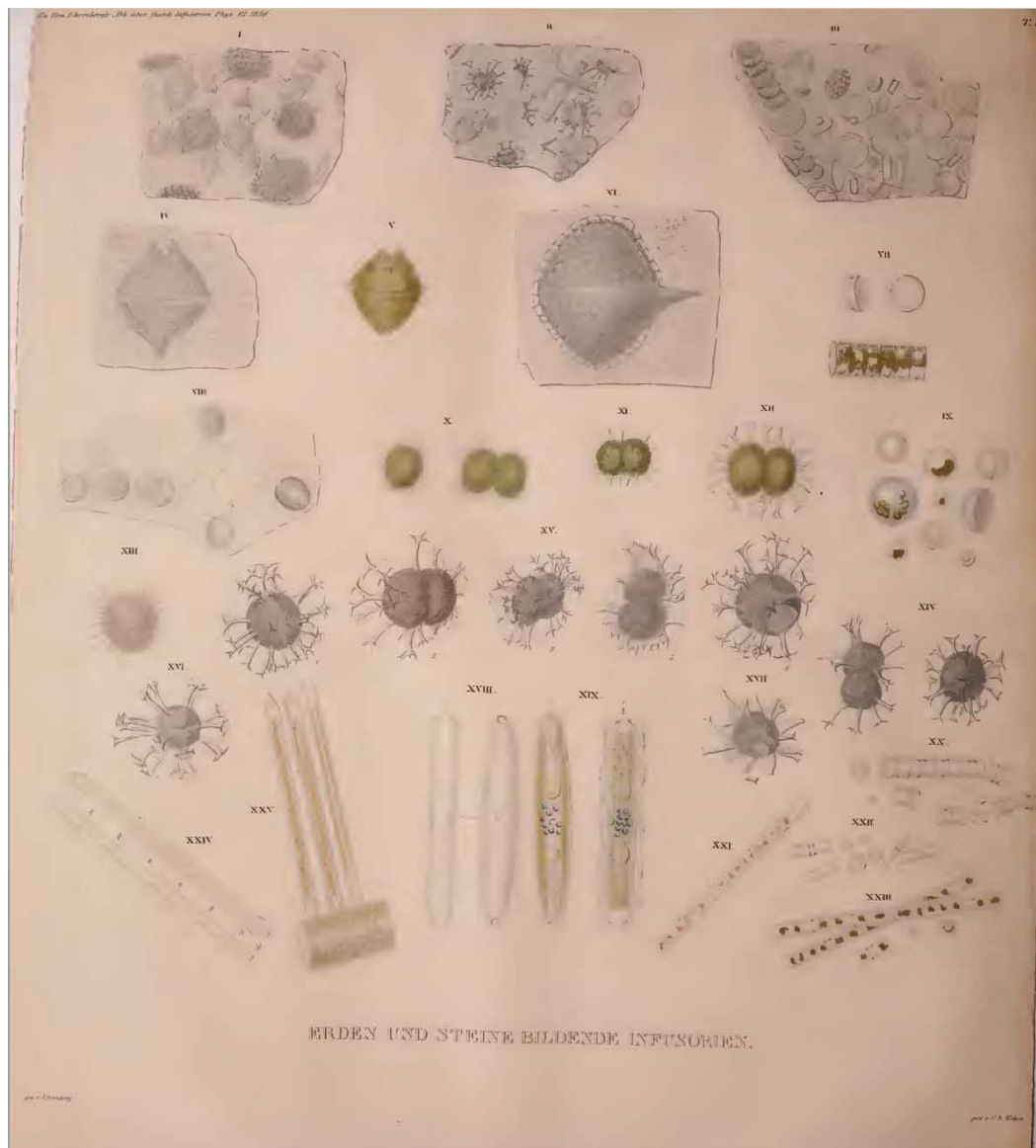


Figure 5. Plate 1 from Ehrenberg [1838], the figure XXIV depicts the diatom *Synedra capitata*, identified as the main species forming a sample of *Kieselschaale* (diatomite) from Santa Fiora.



## 2.2 Lithological, chemical, and paleontological characteristics

Diatomaceous earths are composed of the fossil microscopic unicellular algae of the Bacillariophyceae class (diatoms), they have an ultra-fine grain size, and are soft and crumbly, with an earthy texture and a pure white color.

Diatoms are microscopic unicellular brown algae, with an internal skeleton, called “frustule”, composed of amorphous hydrated silica (opal;  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ). The average dimensions are between 10 and 200  $\mu\text{m}$ . To develop diatoms need light (for photosynthesis, because they contain chlorophyll) and humidity. They inhabit all aquatic environments: freshwater (springs, streams, rivers, lakes, swamps, and peat bogs), brackish (estuaries), and salty water (seas and oceans). The frustules of the dead diatoms accumulate in large quantities at the bottom of the marine or continental basins, where they remain unaltered and fossilized, forming the deposits known as diatomaceous earth (or diatomite) [Taliaferro, 1933; Cressman, 1962].

Diatomaceous fossils are useful both for biostratigraphy, as based on their evolutionary sequence it is possible to date the sediment in which they are imbedded, and for paleoecology, as they give us indications on the conditions of the habitats of the past. Indeed, they are excellent biological indicators as they are very sensitive to changes in environmental physical parameters such as light intensity, temperature, pH, salinity, and currents velocity, and in chemical parameters such as nutrients (nitrates and phosphates), dissolved oxygen, and abundance of organic matter and silica.

Also the chemical composition of Monte Amiata diatomaceous earths is dominated by silica. The first chemical analysis was that announced by Giovanni Fabbroni in 1791 [Fabbroni, 1794] quoted also by Santi [1795]. Subsequently, more modern analyzes were performed by Klaproth [1814], Lotti [1878], Tasselli [1890], and Lotti [1910]. All analyses agreed on very high values of  $\text{SiO}_2$  (79-94 wt%), less presence of iron oxides (<5%), alumina (<5%), magnesium (0-12 wt%), and water.

The Monte Amiata lacustrine diatomaceous deposits have been described by Clerici [1903a] as a series of alternating white and gray layers parallel to each other, some thick a few decimeters, others thinner than a millimeter (Figure 6). These layers remained perfectly horizontal in the middle of the lake basin, whereas at the margins they curved following the morphology of the basin coast. Intercalations of thin layers of clay or fine sands are also present. The thickness of the deposit never exceeded 5-6 meters. Monte Amiata diatomaceous earth deposits also contain fossils of fishes and insect, macro-plant remains, pollen, and perfectly preserved large wood fragments.



**Figure 6.** Sample of diatomaceous earth from the Fontespilli quarry (Bagnólo, Santa Fiora), showing well developed laminae of sediment (Tongiorgi Collection, Museum of Natural History, University of Pisa; inventory number I-17753).

From the fundamental work of the German zoologist Christian Gottfried Ehrenberg (1795-1876) [Ehrenberg 1836; 1838] on the same sample from the Santa Fiora basin analyzed by Klaproth (Figure 5), we know that the diatomaceous earth of Monte Amiata is formed almost exclusively by the siliceous frustules of diatoms, with lower concentrations of opal, and impurities such as aluminum silicates (clays), calcium carbonates, and organic matter.

Ehrenberg recognized in the sample of Santa Fiora 6 genera and 18 species of diatoms, many of which are still unknown, and among which the *Synedra capitata* is an exclusive species that forms the main mass of the deposit [Ehrenberg, 1836].

The systematic microbiological analyses that were made by Forti [1899] on samples from the Castel del Piano quarry recognized 12 genera and 35 species of diatoms, all still living today. Other analyses on diatoms were carried out by Clerici [1903a] in the diatomaceous earths of Castel del Piano (La Fonte), Abbadia San Salvatore (Acqua Passante) and Santa Fiora (Bagnólo); by Bradley and Landini [1982] in the diatomaceous earths of the Fontespilli quarry (Bagnólo, Santa Fiora), and more recently by Crawford et al. [2003] in the collection of Ehrenberg's samples preserved in Berlin [Ehrenberg 1836; 1838].

The plant macro-remains were studied by Clerici [1903b], Blanc and Tongiorgi [1937], and Tongiorgi [1938, 1939] who revealed the presence of leaves, fruits, seeds, and woods representing the genera *Abies*, *Pinus*, *Quercus*, *Alnus*, *Fagus*, *Populus*, *Picea*, and *Betula* (Figure 7). Pollen analysis was done by Bertolani Marchetti and Jacopi [1962]



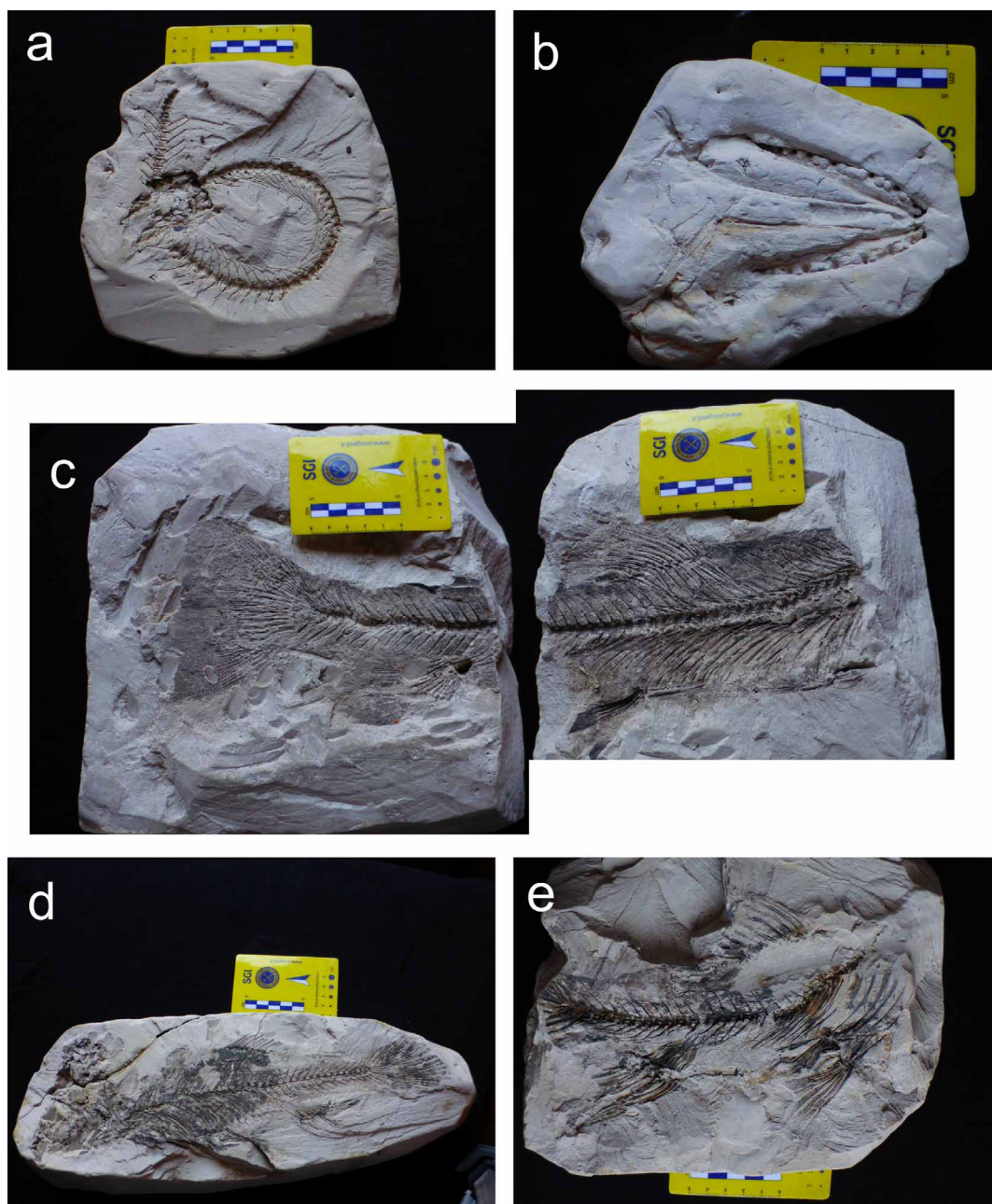
**Figure 7.** Pictures of plant fossils found inside the diatomaceous earth from the Fontespilli quarry (Bagnólo, Santa Fiora). a) and b) leaf impressions; c) and d) wood fragments; e) branch impression; f) conifer's cone mould (Tongiorgi Collection, Museum of Natural History, University of Pisa; inventory numbers: a) = I-17588; b) = I-17754; c) = I-17755; d) = I-17756; e) = I-17593; f) = I-17595).



## Diatomaceous earths of Monte Amiata volcano

on the deposits of a paleo-lake basin of Abbadia San Salvatore (Lame) and by Bertolani Marchetti and Soletti [1972] on the diatomaceous earths of the Fontespilli quarry (Bagnólo, Santa Fiora).

The fossil fishes from the Fontespilli quarry belonging to the Ezio Tongiorgi collection have been studied by Bradley and Landini [1982]. They recognized the species *Salmo trutta*, *Leuciscus cephalus*, and *Barbus barbus plebejus* (Figure 8). This fossil fauna is contained in the lower part of the diatomaceous deposit, richer in clay and organic matter. The specimens generally appear as imprints of the skeletal structure, the fossilized bones are almost totally missing, and the soft parts are preserved as a carbonaceous patina. This indicates that burial and fossilization took place in a reducing environment, poor in oxygen, and devoid of necrophagous organisms [Bradley and Landini, 1982].



**Figure 8.** Pictures of the fish fossils found inside the diatomaceous earth from the Fontespilli quarry (Bagnólo Santa Fiora). *Salmo trutta*: a) incomplete specimen; b) impression of the lower jaw; c) abdominal and caudal region. *Squalius cephalus*: d) almost complete specimen; e) abdominal and caudal region. Samples also published in Bradley and Landini (1982), from the Tongiorgi Collection at the Museum of Natural History of the University of Pisa (inventory numbers: a) = I-17569; b) = I-17570; c) = I-17560; d) = I-17562; e) = I-17565).

### 2.3 The industrial production

Diatomaceous earths have been used at least since the eighteenth century as abrasive to clean metals, as building material, and as medical remedy [Baldassarri, 1750; Santi, 1795]. Subsequently, this material was used for several other applications. Fabbroni (1794) thought of making floating bricks, and Campani [1865] suggested using it for the preparation of soluble alkaline silicates. At the beginning of the nineteenth century, with the advent of industry, the diatomaceous earths (in German *kieselgur*, *bergmehl* = fossil flour, or *kieselschaale* = diatomite) were used for industrial applications after their accidental discovery during a well drilling in Lower Saxony (North Germany). An important pulse for a massive extraction of this material, all over the world and also at Monte Amiata, was given by Alfred Nobel's dynamite discover in 1867 and by the consequent use of diatomaceous earths as a stabilizer of nitroglycerin.

Diatomaceous earths have a great economic importance because of their physical characteristics: they are microporous (they can absorb up to 3 times their weight in water) and chemically inert in many liquids and gases, and have very low density (0.32-0.64 kg/l against 1.00 kg/l of water), a very homogeneous composition (containing 80-95% of silica, SiO<sub>2</sub>), low thermal conductivity, and high melting point (1000-1750°C). Currently uses of diatomaceous earths are as filter in enology or for drinking water, abrasive for polishing soft metals, insulator in construction and in ceramics, and absorbent in the preparation of soaps and in particular chromatographic analyses.

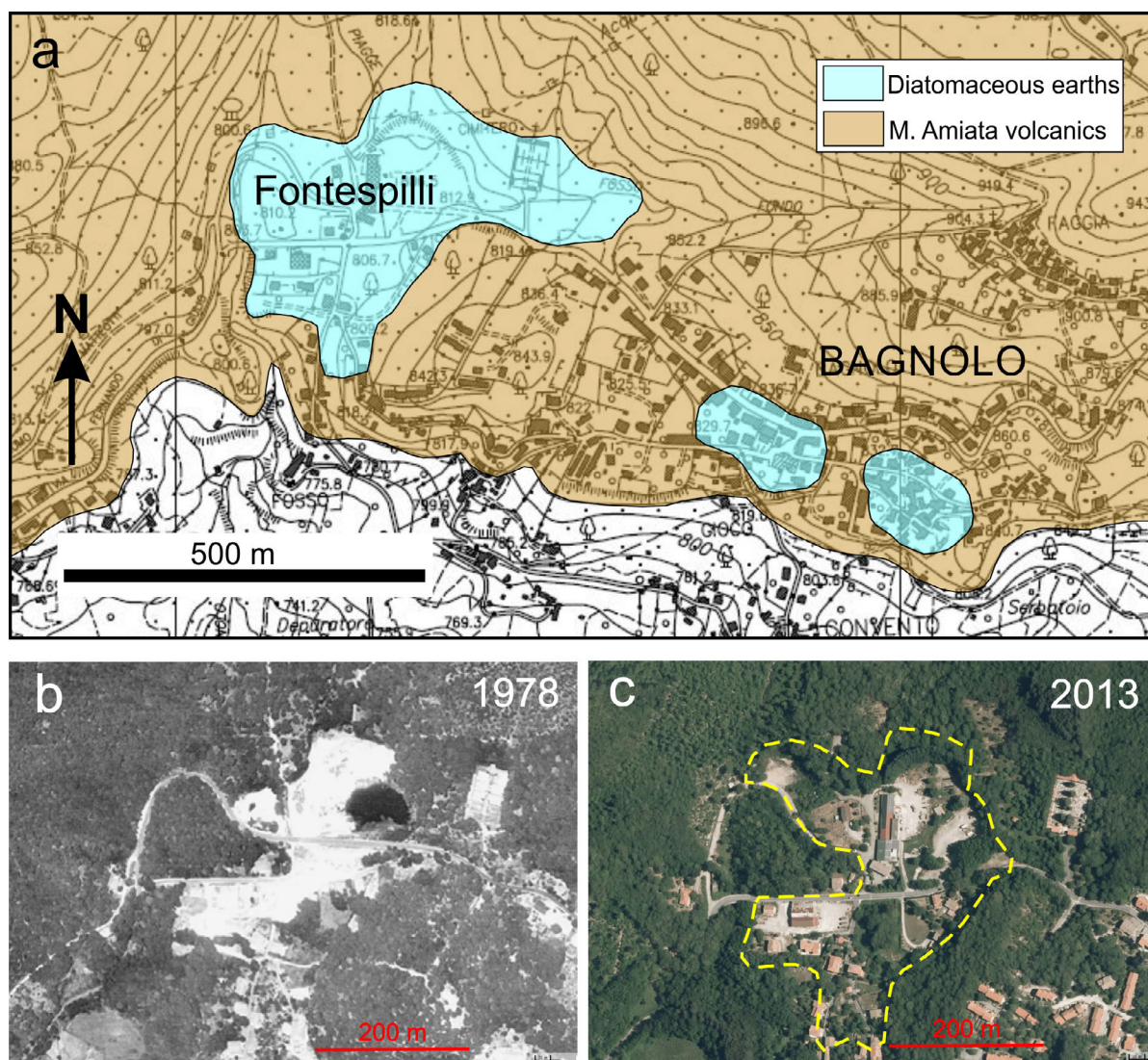
At Monte Amiata, quarry cultivation was carried out by cutting the mineral deposit into parallelepipeds on a front comprising all its thickness, and proceeding by progressive cuts, so that the waste went to fill the void left by the removal of the blocks previously cut [Clerici, 1903a; De Castro, 1914]. Diatomaceous earths were extracted wet, placed to dry in the air under shelters, disintegrated and sieved, and finally packed in bags. Transportation was by rail from the Monte Amiata Scalo station, located on the valley of the River Orcia about 5 km north of Castel del Piano. Two commercial qualities of diatomaceous earths were distinguished, based on color and purity, a very white with a density of 0.08 g/cm<sup>3</sup> and a light green with a density of 0.30 g/cm<sup>3</sup> [Clerici, 1903a]. A technical improvement concerned the use of drying ovens, which allowed the reduction of the residual water content from 30% to 5%.

The mining areas of diatomaceous earths at Monte Amiata were mainly in Castel del Piano and Santa Fiora [Fei, 1997] (Figure 1). In the municipality of Castel del Piano (Figure 1) the quarry "Fonte" [Santi, 1795; Lotti, 1878; Tasselli, 1890; Tommi, 1890; Forti, 1899; Clerici, 1903a, Manasse, 1915; Pompei, 1924], also known as Caselle [Lotti, 1910; De Castro, 1914; Blanc and Tongiorgi, 1937], was active. Its activity has been reported since 1872 by the *Società anonima terre bolari e gialle del Monte Amiata* [Giannetti, 1873]. Subsequently the production underwent considerable vicissitudes, passing into the ownership of various companies including the *Società du Kieselguhr Toscan Hemmeler, Tournier & C.ie* [Clerici 1903a] and, from 1929, the company Winkelmann & Crida, which in 1934 had a monopoly on all the quarries of Monte Amiata diatomaceous earths (Fei, 1997). Another quarry at Castel del Piano was the Campogrande (Figure 1) [Blanc and Tongiorgi [1937], whose deposit was exhausted in 1956.

In the municipality of Santa Fiora (Figures 1 and 9) the most known and documented diatomaceous earths deposit was in Bagnólo [Micheli, 1754a; Lotti, 1878; Tommi, 1890; Clerici, 1903a; De Castro, 1914; Blanc and Tongiorgi, 1937; Bertolani Marchetti and Soletti, 1972; Bradley and Landini, 1982]. Although its presence had been identified as early as the beginning of the eighteenth century, its industrial exploitation was active only from 1911 and until total exhaustion in 1977, in at least three large and two smaller quarries [Fei, 1997]. Among them are the quarries named Fontespilli (Figure 9) [Clerici, 1903a; De Castro, 1914; Blanc and Tongiorgi, 1937; Bertolani Marchetti and Soletti, 1972; Bradley and Landini, 1982], Pratuccio [Fei, 1997], and Piano al Camposanto [Clerici, 1903a; Lotti, 1910; De Castro, 1914]. In Bagnólo, other more modest quarries were in the area of Gioco and Convento [Blanc and Tongiorgi, 1937]. In the territory of Santa Fiora mining activity of diatomaceous earths is reported also at Bagnore in the locality of Prati [Clerici, 1903a; De Castro, 1914].

In the municipality of Abbadia San Salvatore (Figure 1), there are numerous paleo-lakes with mixed sedimentation, such as near Acqua Santa - Lame [Santi, 1795; Tommi, 1890; Clerici, 1903a, b; Bertolani Marchetti and Jacopi, 1962], and in the Vallone locality, from which an acorn of *Quercus aegilops* was found [Tongiorgi 1939].





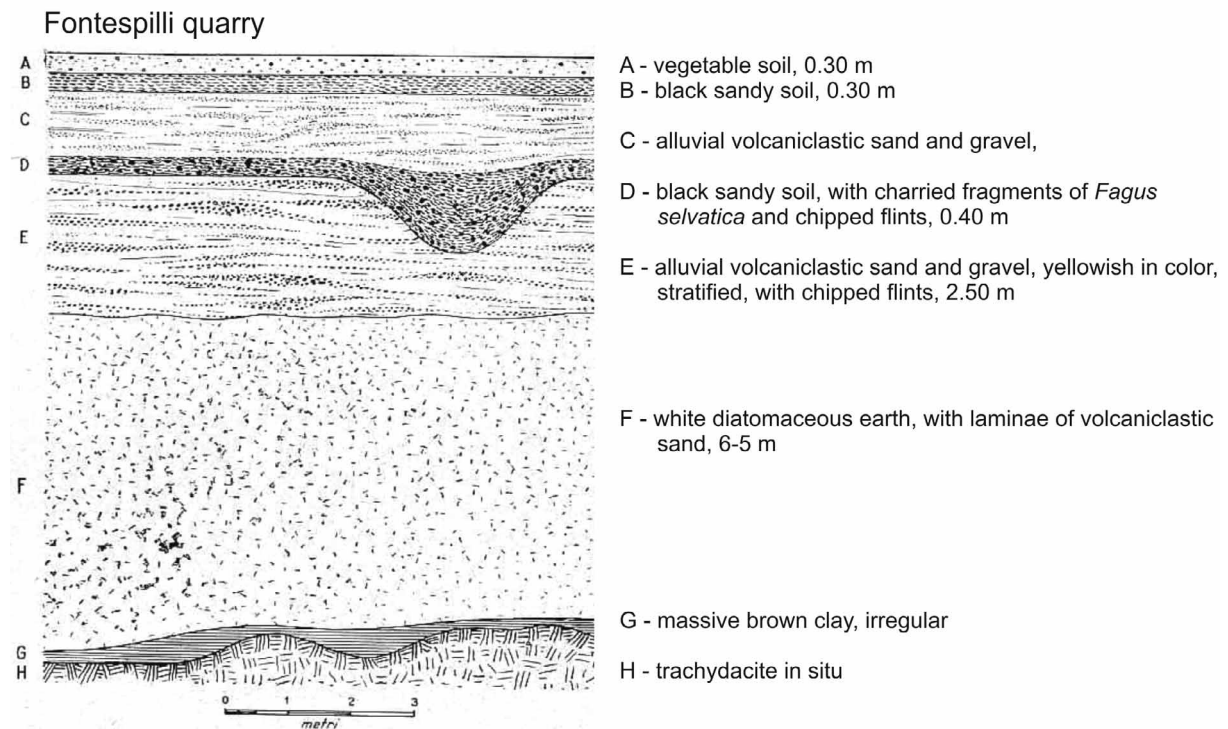
**Figure 9.** a) Map of the extinct lake basins with diatomaceous earth deposit in the area of Bagnólo (Santa Fiora). b) The diatomaceous earth quarry of Fontespilli in an orthophoto obtained from aerial photographs that were taken in 1978, immediately after the ore deposit exhaustion and the end of the mining activity, compared with c) a 2013 orthophoto of the same area. Hatched yellow line indicates the area affected by the mining activity. Images provided by the Regione Toscana.

## 2.4 The Fontespilli basin

The lake deposits of diatomaceous earths of Fontespilli (Bagnólo, Santa Fiora) were those most affected by the exploitation activity and those most studied from a geological point of view, due to their extension and mineral abundance. Presently, the area affected by the mining activity is occupied by various artisan and residential settlements, but the depressions of the two main quarry areas are still visible, bounded towards the mountain by slopes of 3-4 m height corresponding to the ancient quarry fronts (Figure 9). No diatomaceous materials are possible to find in these areas nowadays, as all the strata of diatomaceous earths have been completely removed during the past mining activity [Vezzoli et al., 2017].

The stratigraphic sequence of the Fontespilli diatomaceous basin has been described by De Castro [1914], Blanc and Tongiorgi [1937] (Figure 10), Bertolani Marchetti and Soletti [1972] and Vezzoli et al. [2017]. On the active quarry fronts the following layers have been identified, from the bottom upwards (Figure 10): (H) *in situ* trachydacite

lava; (G) compact, dark gray to brown, plastic clay bench, with scattered carbonaceous remains and a pedogenized top, of irregular thickness from 0.30 m to 1.50 m; (F) two diatomaceous deposits, the lower one gray or hazel in color, with widespread blackish organic matter and intercalations of thin beds of black peat with leaves; and the upper one pure white in color, with intercalations of siliceous fine sands; their total thickness ranges from a minimum of 0.30 m to a maximum of 5 meters; (E-B) stratified volcaniclastic sands and gravels, of alluvial deposition, with abundant carbonaceous plant remains, and intercalation of pedogenized beds, with a maximum thickness of about 6 meters; and (A) the present soil with variable thickness from 0.70 m to 3.35 meters.



**Figure 10.** The stratigraphic log of the excavation front of the Fontespilli quarry (Bagnólo, Santa Fiora), redrawn from Blanc and Tongiorgi [1937].

## 2.5 Paleoenvironment and evolution of the paleo-lakes of Monte Amiata

The geological observations made by scholars who visited the diatomaceous earths and earth pigments quarries at the time of their activity, together with the available chemical and paleontological analyses, can give us indications on the paleo-environmental characteristics of the Monte Amiata paleo-lakes formation, evolution and extinction.

Even if from an industrial point of view the diatomaceous earths and earth pigments of Monte Amiata represented two completely different and independent materials, they are closely connected to each other by genetic and geological relationships. Bargagli Petrucci [1914] had already noticed the coexistence of colonies of *Bacillus ferrugineus* and diatoms in the current spring and marsh areas of Monte Amiata. This is an association that favors the mutual development of micro-organisms and the deposition of iron oxides-hydroxides and diatomites. In addition, in some of the extinct lake and marsh basins of Monte Amiata, layers of iron oxides-hydroxides (limonite/goethite), clays, and diatomites were superposed or alternated, as in the deposits of Castel del Piano (Mazzarelle), Arcidosso (Il Pino), and Abbadia San Salvatore (Acqua Passante, Acqua Santa, and Lame) (Figure 1).

## Diatomaceous earths of Monte Amiata volcano

Both in the case of earth pigments and diatomaceous earth, the purity and very fine grainsize of the minerals indicate that during the sedimentation process the contribution of terrigenous pollutants, deriving from erosion and runoff of detrital materials on the slopes of the volcano, was practically absent in the lake basins. This fact, besides favoring a permanent clearness of the water, indirectly suggests the concomitance of a relatively warm and little rainy climate and the development of a thick vegetation mantle to protect the soil. In fact, the fossil remains of macrophytic plants, which lived around the basins, testify to a covering of mixed mountain vegetation of broad-leaved and coniferous trees in a period of temperate-warm climate with a prominent oceanic character [Blanc and Tongiorgi 1937; Tongiorgi 1938, 1939].

The feeding of the basins could take place above all from springs. The water of the springs had to be strongly mineralized with iron oxides and/or colloidal silica to provide respectively the raw material for the deposition of limonite/goethite in the case of earth pigments, or for the development of diatoms in the case of diatomaceous earth. If in some cases we can hypothesize the presence of real lake basins, such as in Bagnólo (Santa Fiora), probably in others cases it was just marshy areas or encrustations around mineralizing springs, such as the Lama and Acqua Santa (Abbadia San Salvatore), or pools of limited extension above the surface of lava flows, as in Piancastagnaio.

The stratigraphic sequence of the sediments that made up the filling of the main lacustrine basins (Figure 10) gives us indications on the succession of different lithologies and therefore on the evolution over time of the geological and environmental dynamics [Lotti 1910; Blanc and Tongiorgi 1937]. Abundant vegetal, ichthyologic, and entomological remains have been found both in the peat and diatomaceous layers [Forti, 1899; Blanc and Tongiorgi, 1937; Bertolani Marchetti and Jacopi, 1962; Bertolani Marchetti and Soletti, 1972; Bradley and Landini, 1982] and indicate some changes in ecological conditions.

The reconstructed evolution of these paleo-lakes includes a first phase in which there is deposition of clays and iron oxides, as in the deposits of Bagnólo (Santa Fiora), Caselle and La Sega (Castel del Piano). The paleontological analysis indicates for this initial phase conditions of cold climate due to the predominant presence of *Pinus*, with *Picea* and *Betula* [Clerici, 1903b; Lotti, 1910; Blanc and Tongiorgi, 1937; Bertolani Marchetti and Soletti, 1972]. During a second phase, the lower diatomaceous layers were deposited, with contamination of terrigenous material and abundance of organic matter [Bradley and Landini, 1982]. These diatoms layers are characterized by an oligotypic association of the planktonic genus *Ciclotella* and very few benthic diatoms. The sedimentation environment that can be reconstructed for this second phase is that of a lake sufficiently large and deep (15-20 m) to accommodate typical limnetic forms [Forti, 1899], with a bottom below the photic zone and poorly oxygenated [Bradley and Landini, 1982]. The water was not clear due to the suspended terrigenous material and the abundant production of phytoplankton. The fishes lived in the intermediate-shallow zone. The climate was continental warm with great development of *Fagus*, *Abies*, and *Castanea* [Tongiorgi, 1939]. Relatively cooler and drier conditions were suggested by the presence of *Pinus*, *Betula* and *Carpinus* into the thicker peat layer interstratified with diatomites at Bagnólo (Santa Fiora) and Lama (Abbadia San Salvatore) [Bertolani Marchetti and Jacopi, 1962; Bertolani Marchetti and Soletti, 1972].

In a third phase, a climatic change induces an increase in temperature, but not an increase in water influx, with related absence or scarcity of meteoric precipitations. This fact leads to initially optimal environmental conditions for the proliferation of diatoms within a clear water body. Moreover, the relatively high concentrations of dissolved silica generate conditions close to saturation in opal, which further promotes the growth of diatoms. However, the gradual loss of water by evaporation causes the depth of the lake to be reduced to a few meters, turning it into a pool of algae covered with epiphytic diatoms [Forti, 1899]. The environment is no longer favorable to the community of fishes, which die in mass. With the end of the evaporation process also the diatoms die and settle down to the bottom of the almost dried up basin, generating the layers of pure diatomite, white and powdery, consisting of predominantly benthic diatoms, such as the genus *Frigilaria* [Bradley and Landini, 1982], contrary to what happened in the second phase of paleo-lake evolution in which planktonic diatoms prevailed.

The pollen remains of *Pinus* in the highest part of the diatomite sequence indicate the transition to cool and wet climate [Bertolani Marchetti and Soletti, 1972] that foreshadows the cold-climate peak characterizing the overlying sedimentary complex that represents the fourth phase. During this last phase, the lake deposition is interrupted, simultaneously in all basins, by a complex of sediments composed of alluvial volcanoclastic sands and gravels, with intercalations of clays and peats (Figure 10) [Blanc and Tongiorgi, 1937]. These sediments are generally sterile of fossil remains. The sudden change of sedimentation style suggests a considerable and general change in the feeding regime of the basins, which can be interpreted as the effect of having arrived a cold and rainy climate [Blanc and



Tongiorgi, 1937]. This climatic variation has had as consequence a thinning of the vegetation surrounding the basins, colder temperatures, a more active thermo-clastic breakup of the rocks, an intense and widespread runoff on the slopes, and the increase of waters turbidity.

Finally, the younger sediment complex is represented by sands and silts more or less rich in organic matter (even coals fragments deeply altered in soil), and by vegetable soil (Figure 10). It indicates a scarce colluvial and alluvial sedimentation with a substantial stability of the topographic surface that has favored the development of intense processes of weathering.

## 2.6 Age of lake deposits and relations with the volcanic activity of Monte Amiata

In order to define the age of the lacustrine deposition of earth pigments and diatomaceous earths of Monte Amiata, and their relationship with volcanic activity, we can use geological, paleontological, paleoenvironmental, and archaeological tools.

All previous authors agree in considering the formation of lake basins as a phase completely subsequent the activity of the Monte Amiata volcano [dated at 305-231 ka by Laurenzi et al., 2015, Laurenzi and La Felice, 2017]. On the basis of the thickness (about 11.5 m) of diatomite strata in the quarry of Fontespilli (Bagnólo, Santa Fiora) and the mean thickness (1-3 mm) of laminae (equated to varves) that compose it, Fornaca Rinaldi [1968] formulated the hypothesis that the duration of the environmental conditions in which it was possible to form the diatomaceous deposits of Monte Amiata was of about 20,000 years. The only radiometric age available on the Monte Amiata lake deposits is that performed by Fornaca Rinaldi [1968] with the  $^{230}\text{Th}/^{238}\text{U}$  method on the diatomaceous deposit of Fontespilli (Bagnólo, Santa Fiora) which provided an age of 130-140 ka before present.

From the stratigraphic point of view, the lake deposits of Monte Amiata are superimposed on the trachydacitic lavas belonging to the first phase of activity of the volcano [Principe et al., 2017]. There are no direct geological relationships between the lake deposits and the volcanic products of the second, most recent, phase of activity [Principe et al., 2017], due to their different areas of distribution. However, the lake deposits are never covered by primary volcanic units, but only by later alluvial or colluvial volcanoclastic deposits derived from the exogenous weathering of volcanic rocks.

From the paleontological point of view, the fossil species of diatoms, macrovegetation and fauna found in Monte Amiata paleo-lake sediments are identical to those currently living.

From the paleoenvironmental and paleoclimatic point of view, the main phase of Monte Amiata lacustrine sedimentation refers to a period of temperate-warm climate with a prominent oceanic character bordered, both at top and bottom, by deposits evidencing a colder and wetter climate [Blanc and Tongiorgi, 1937; Tongiorgi, 1938; 1939]. This period of temperate-warm climate possibly corresponds to the last interglacial period [the Eemian or Marine oxygen Isotope Stage MIS 5e; Regattieri et al., 2016], which developed between 140-130 ka and 115-110 ka before present [Adams et al., 1999; Shackleton et al. 2003; NEEM, 2013] in agreement with the age of 130-140 ka of the sediments and a lifetime of 20,000 years of the lacustrine basins suggested by Fornaca Rinaldi [1968]. The end of the lake sedimentation and the beginning of the alluvial progradation is attributable to the intervention of a colder climate coinciding with the beginning of the last glacial period at about 115-110 ka BP. Subsequently, during the last phase of colluvial sedimentation and pedogenesis, the presence of *Fagus* and *Picea* carbons gives us testimony of the vegetation corresponding to the return to an oceanic climate, occurred with the current postglacial period at 14 ka ago [Tongiorgi, 1938].

From the archaeological point of view, within the lacustrine sediments any lithic industry is absent; while in the overlying alluvial layers the archaeological findings are significant. D'Achiardi [1872] reported the findings in the Mazzarelle quarry (Castel del Piano) of artifacts (scraper and arrows) and flint and jasper shards, in the lower part of the alluvial deposit, and of objects in bronze or copper in the upper part. In the Caselle quarry (Castel del Piano), worked oak poles, probably of huts, were found on the surface separating the diatomaceous earths from younger volcanoclastic debris [Blanc and Tongiorgi 1937]. According to Grifoni Cremonesi [1971] other archaeological artifacts (such as polished stone axes, arrow cusps, copper axes and small daggers, bronze axes, bronze age ceramics) were found in the diatomaceous earth quarries of Castel del Piano (Campogrande and Caselle), and Santa Fiora (Bagnólo) [Sestini 1934, 1936; Blanc and Tongiorgi 1937], without the description of a precise stratigraphic position, and are preserved in the Archaeological Museums of Rome, Siena, Perugia, and at the



University of Pisa. In summary, at the contact with the diatomaceous deposits, in the deeper alluvial layers, there is a typical industry of the Middle Paleolithic [Mousterian; lasted roughly from 160 ka to 40 ka BP in Europe; Shaw and Jameson 1999]. An Upper Paleolithic industry follows towards the top of the alluvial and peaty sediments. In the uppermost layers a Neolithic and Bronze Age industry was found accompanied by a rough ceramic, with abundant remains of fireplaces containing *Fagus* and *Abies* coals [Tongiorgi 1938].

### 3. The Ezio Tongiorgi Collection

#### 3.1 Ezio Tongiorgi (Milano 1912 - Pisa 1987) - biographical notes

Born on March 12, 1912 in Milano, Ezio Tongiorgi [<https://suisa.archivi.beniculturali.it>; Alabiso and Tongiorgi, 2010] was student at the *Scuola Normale Superiore* and at the University of Pisa, where he graduated in Natural Sciences in 1934 (Figure 11). After few years as assistant at the Botanical Institute of the University of Pisa, in 1938 the research carried out on the history of the vegetation of the Apennines earned him the prize of the *Società Italiana per il Progresso delle Scienze*, and in 1939 he obtained the qualification for the university teaching.



**Figure 11.** Portrait of Ezio Tongiorgi in the 1930s. Photograph from the web page of the Istituto Italiano di Paleontologia Umara, Rome (<http://www.isipu.org/storia-isipu/protagonisti/?nggpage=4>).

At the end of the Second World War - during which he served as a second lieutenant in artillery, before moving into the ranks of the Roman Resistance - Tongiorgi resumed his scientific activity at the Botanical Institute of Pisa University first as assistant, then as director of the *Istituto e Giardino Botanico*.

In the following years Ezio Tongiorgi gradually expanded his fields of interest from botany to paleobotany, from anthropology to paleontology, from nuclear geology to scientific museology. In these areas he promoted numerous institutions and initiatives of considerable importance for the city and the University of Pisa and for the Italian scientific research as a whole. First of all, he founded the Pisa section of the Italian Institute of Human Paleontology, which was created in Rome by the eminent Quaternary scholar, and his friend, Carlo Alberto Blanc, and later merged into the Institute of Anthropology of the University of Pisa. Since 1946, he promoted and personally conducted important paleontological excavations in the Pisa hinterland, into the high valley of the river Serchio, in Latium and Liguria. Of particular importance was the excavation of the Grotta del Leone, at Agnano, near Pisa. The rich Neolithic findings from this excavation are now preserved in the Museum of Natural History of the University of Pisa (inside the ancient Charterhouse of Pisa in Calci) that is also executor of the renewed prospecting starting from 2019. In 1953, on the occasion of the International Congress on the Quaternary organized in Italy by Alberto Carlo Blanc, Livio Trevisan and Ezio Tongiorgi himself, he set up an important exhibition in Pisa on the cultures from Paleolithic to the Bronze Age. This significant cultural event contributed to spreading the conviction that the study of man constitutes a historical discipline that cannot ignore the aid of the natural sciences, a methodological conviction that Tongiorgi would never have renounced.

The need to accurately date the archeological finds from Grotta del Leone led Tongiorgi to the creation, in 1958, of a pioneering laboratory of nuclear geology (*Laboratorio di Geologia Nucleare*) in the framework of the Italian Consiglio Nazionale delle Ricerche (National Researches Council - CNR for short), that becomes a very advanced research center frequented by scientists from all over the world. It is here that the first Italian mass spectrometer instrument was built, for dating ancient artifacts through the analyses on the decay of <sup>14</sup>Carbon isotope [Ferrara et al., 1959]. Tongiorgi was the first director of this Institute and in 1965 became also full professor of nuclear geology at the University of Pisa. The Laboratory of Nuclear Geology was transformed during the 1980s into the CNR Institute of Geochronology and Isotope Geochemistry (*Istituto di Geocronologia e Geochimica Isotopica*), that in turn during the 2010s merged with another CNR scientific institution created by Ezio Tongiorgi, the International Institute for Geothermal Researches (*Istituto Internazionale di Ricerche Geotermiche*), to form the present Institute of Geosciences and Earth Resources (*Istituto di Geoscienze e Georisorse*).

Considering the importance of Italian geothermal resources for the production of electricity, starting from 1966, Ezio Tongiorgi promoted the formation of a group of expert CNR researchers, which in 1969 resulted in the establishment of the International Institute for Geothermal Research based in Pisa and of which he was the first director. As part of this Institute, periodic international courses of specialization in geothermal energy were held in the 1970s for researchers coming from developing countries. As a matter of fact, the ruling class of the institutions involved in the research and development of geothermal energy in Latin America in the following decades has all passed through this school. In 1972, Tongiorgi started the still existing “Geothermics” scientific journal.

As an application of his interest in Earth Sciences to the cultural heritage, Ezio Tongiorgi applied also to the study of ancient pottery (in particular the medieval earthenware bowl inserted in the facades of many of the Romanesque churches of Pisa) by means of innovative techniques. In relation to this cultural sector, Ezio Tongiorgi developed the sciences subsidiary to archeology in Pisa, creating a laboratory for paleomagnetic measurements and giving life to a specialization school for archaeologists. For his effort in this study sector, the educational section of the Montelupo Ceramics Museum near Florence has been dedicated to Ezio Tongiorgi and many of these bowls are now exhibited at the National Museum of San Matteo in Pisa in a room dedicated to Ezio Tongiorgi and his wife and collaborator Liana Strenta.

As president from the 1950s until 1977 of the appointed provincial commission, Ezio Tongiorgi also studied the problems of subsidence of the Pisa’s underground, controlling the course of the water table by leveling the topographical surface and the wells of the plain, and started the reorganization plan of the coastal area of Marina di Pisa to safeguard it from erosion. He also gave the hydrogeological suggestions that were decisive to limit the inclination of the bell tower of the city’s cathedral, the famous “Leaning Tower” of Pisa, in the 1960s, stopping the extraction of the water table on which the Leaning Tower rests.

To these scientific interests, Tongiorgi accompanied constant interests of a historical-humanistic matrix, anticipating that union between scientific knowledge and humanistic knowledge that today constitutes a salient aspect of the most advanced culture not only in Italy. Of solid republican convictions, from 1956 he was president of the *Domus Mazziniana* in Pisa, an institution devoted to researches on Italian *Risorgimento*. In 1976 Ezio Tongiorgi received the “A. Feltrinelli” award from *Accademia dei Lincei* for research in the geo-mineralogical sector, and the insignia of the *Ordine del Cherubino*, the highest honor of the University of Pisa.

Ezio Tongiorgi was also a passionate bibliophile and collector of prints and iconography of the city of Pisa and was the creator and editor-in-chief of the journal *Antichità Pisane*, a quarterly of “Archeology and Historical Topography”, published between 1974 and 1975. He left a vast library of 20,000 volumes, on humanities, which is currently preserved by his nephews Fabio and Duccio. In the last phase of his life, he mainly devoted himself to the transcription and study of works by Pisan and Florentine chroniclers and historians of the late fifteenth and early sixteenth centuries.

Ezio Tongiorgi died in Pisa on August 28, 1987, at the age of 74. In recognition of his high human and cultural qualities, in 1997 the Municipality of Pisa wanted to honor his memory by dedicating to Ezio Tongiorgi a town square.

### **3.2 The Museum of Natural History of the University of Pisa inside the Charterhouse of Pisa in Calci**

The Charterhouse of Pisa in Calci (Figure 12) is a vast monumental complex that rises on the slopes of Monte Pisano, a few kilometers from the city of Pisa. It was a cloistered monastery of the Carthusian order of San Bruno

## Diatomaceous earths of Monte Amiata volcano

founded in 1366 at the behest of the Archbishop of Pisa Francesco Moricotti and thanks to the financial support of illustrious Pisa families. The convent assumed also a political importance, in particular after the annexation of the ancient Benedictine monastery of the island of Gorgona, which took place in 1425. It was suppressed first in the Napoleonic era, and then by the Savoy, but it was once again inhabited by the monks until 1969 when they definitively abandoned it. It was enlarged between the seventeenth and eighteenth centuries and today is a splendid baroque monument set in a highly suggestive landscape (Figure 12). It is following the foundation of the monastic complex that the Calci valley, originally called “dark”, was renamed *Val Graziosa* (“full of grace” valley).

After the last monks abandoned the Charterhouse complex, Ezio Tongiorgi did his utmost to ensure that the prestigious monumental building was entrusted to the University of Pisa in order to establish a Museum of Natural History and the Territory (*Museo di Storia Naturale e del Territorio*). In fact, the grandiose building was passed to the Italian state property, and in 1972 it became the place of the “National Museum of the Monumental Charterhouse of Calci” (*Museo Nazionale della Certosa di Calci*). But Ezio Tongiorgi, with his frequent contacts with the competent ministry, was responsible for obtaining in 1979 that part of the building was transferred to the University of Pisa for its educational and scientific purposes. The more strictly artistic and religious portions were left to the Superintendence of Monuments, while the other part was initially used as a warehouse for finds from the naturalistic institutes of the University of Pisa and, after the necessary restorations, was prepared to host the new “Museum of Natural History and the Territory”. In the Tongiorgi idea, the name of the museum (today shortened in “Natural History Museum”) recalls the founding concept of a natural history in close connection with the history of its territory. Ezio Tongiorgi was the director of the Calci’s Museum from 1977 to 1985.



**Figure 12.** The Charterhouse of Pisa in Calci, place of the Museum of Natural History of the University of Pisa. Associazione Amici della Certosa (<https://www.facebook.com/amificertosa>).

The Naturalistic Gallery of Pisa, the initial nucleus of the Museum, was established in the late 16th century as part of the Botanical Garden. In 1814, the Gallery became independent of the Botanical Garden, and, in the late 19th century, its naturalistic collections were divided into three separate museums: the Museum of Zoology and Comparative Anatomy, the Museum of Geology and Palaeontology, and the Museum of Mineralogy and Petrology [Landini, 2011]. The Second World War marked the beginning of a phase of decline and isolation that ended when the three museums were rejoined and relocated into the Charterhouse of Pisa in Calci in the late 1970s. A Centre for Environmental Education (CEA) was established in 1997, and since 2008 the museum has assumed the role of “Hub of Environmental Education” for the Pisa area. Various institutions promoting the cultural and scientific dissemination have their headquarters at the Museum of Calci. The exhibitions have been expanded with new galleries and the services to the public have been improved [Landini, 2011]. Today the Museum offers also temporary scientific exhibition in addition to the permanent ones based on both historical and recently acquired specimens.

### 3.3 The paleontological collection

The paleontological collections of the Natural History Museum of the University of Pisa consist of over 200,000 specimens that, with the exception of the very few fossils mentioned in the seventeenth-century catalogues of the Granduke’s Gallery and no longer preserved, were collected by the scholars of the Pisa University during almost two centuries of research.

Giuseppe Meneghini, director of the old Museum of Mineralogy and Geology from 1849 to 1889, started both the Pisan geological school and the paleontology collections that were subsequently greatly increased firstly by his student and successor Mario Canavari and then by all the following museum’s directors. The Museum of Geology and Paleontology was located in Pisa in the same building of the Department of Earth Sciences and since its beginning it represented the repository of the collections actively studied by the earth sciences professors of the university. This close relationship producing the continuous increase of the specimens housed, continued even when the geological collections were moved to the Charterhouse of Pisa to join the zoological ones in the newly unified Museum of Natural History.

The Monte Amiata paleontological specimens collected by Ezio Tongiorgi between 1953 and 1956 arrived at the Museum of Natural History of the University of Pisa in Calci in two phases: the first one involved the ichthyologic remains which Ezio Tongiorgi himself entrusted to Walter Landini for a specialist study and which were deposited in the museum after the publication [Bradley and Landini, 1982]; the second one regarded all the other materials stored in the Department of Archeology of the University of Pisa and arrived in the museum at the turn of the first decade of 2000s.

The collection of fossils preserved in the diatomites of Monte Amiata presently housed at the Museum of Natural History of the University of Pisa consists of: 386 plant fossil remains, mainly comprising the so called “*fillite*” [Italian generic name indicating a plant fossil; Clerici, 1903a], 61 ichthyologic specimens, 2 mammalian teeth preserved in a glass vial, and 5 samples of sediment.

The ichthyologic specimens include all those published by Bradley and Landini [1982] and referred to *Salmo trutta* (Figures 8a, 8b and 8c) and *Squalius cephalus* [named *Leuciscus cephalus* in Bradley and Landini, 1982] (Figures 8d and 8e), in addition to 30 specimens extremely fragmentary but that, to a first examination, appear to be comparable to the species already reported. The fauna is completed by two teeth referable to carnivores.

Plant remains are the numerically dominant element of the collection and different types have been recognized. The leave impressions (Figure 7a and 7b), sometimes accompanied by fragile remains of carbonaceous material or even of the cuticle, are the most frequent with over 90% of the specimens. There are also wood fragments (Figure 7c and 7d), branch impressions (Figure 7e), conifer’s cones or their moulds (Figure 7f), and several coal pieces. Among the samples of *fillite*, generally with a base smaller than 10 x 10 cm, it is remarkable the presence of a well preserved single specimen with a base of about 16 x 27 cm, packed in a paper envelope with the annotation “Bagnolo”.

In the collection are also some sediment samples, the most interesting being: a series of samples of diatomite in continuous stratigraphic succession for a total thickness of about 45 cm, a sample of diatomite with evident lamination (Figure 6), a glass ampoule with diatomite powder, a clay sample with a partially unreadable note referring to the locality “Pratucci”, and a partially consolidated coarse sediment.



All the published ichthyologic specimens, as well as the other sufficiently complete fish remains, have been catalogued individually. On the contrary, only the most significant plant specimens have been given an individual inventory number; while for the others, pending a specialist study, a cumulative inventory number has been attributed to each of the original boxes in which the material reached the museum (labeled as belonging to the old “Institute of Human Paleontology of the University of Pisa”), for each boxes the number of specimen is reported. The photographs and a summary descriptive table of the inventoried paleontological samples of the Tongiorgi collection are available on the website of the Tuscany Region: <https://www.regione.toscana.it/-/documentazione-relativa-al-volume-il-vulcano-di-monte-amiata>.

### 4. Concluding remarks

The extinct lacustrine basins at the foothill of Monte Amiata volcano have been the place for the exploitation up to the exhaustion of the diatomaceous earth and earth pigments here sedimented during the late Pleistocene. Both the earth pigments and diatomaceous earth deposits are closely related to the high availability of colloidal silica and ferrous solutes from low temperature hydrothermal springs draining the volcanic edifice. The age of the lacustrine sedimentation (140 - 130 ka) is consistently younger than the volcanic activity of the Monte Amiata volcano (305 - 231 ka).

Diatomaceous earths represented a richness of this territory, and experienced different uses during centuries, but from the geological point of view they were the witnesses of the evolutive history of Monte Amiata lacustrine basins. This history has been reconstructed on the basis of the previous geological and paleontological studies and can be summarized in a number of sedimentation episodes mainly driven by climatic changes:

- 1) The first phase is represented by the sedimentation of clay and iron hydroxides in well-developed lacustrine basins, during cold climate conditions, as suggested by the pollen predominance of *Pinus*, *Picea*, and *Betula*.
- 2) During the second phase, the sedimentation of the diatomaceous earth begins. The abundant plant, ichthyologic, and entomologic fossils indicate a warm continental climate with great development of *Fagus*, *Abies*, and *Castanea*. The lithological and paleontological characteristics of the diatomaceous earth suggest a gradual drying of the lake and the final transition to a humid fresh climate. The quite significant thickness and the purity of the deposit are due to the environmental situation of the lake basins. It has probably remained stable for hundreds or thousands of years to allow diatoms to develop exclusively, continuously, and without polluting of terrigenous sediments.
- 3) The third phase is characterized by the simultaneous end of the lacustrine deposition in all the basins. Its upper limit is coincident with the end of the last inter-glacial period (at about 110-115 ka ago). The alluvial sedimentation of volcaniclastic sands and gravel is the result of a sharp environmental change that is interpreted as the effect of a climate change and the establishment of cold and rainy conditions.
- 4) The last stage shows a low colluvial and alluvial sedimentation with a substantial stability of the topographic surface until the present times.

The diatomaceous earth of Monte Amiata and its fossil content have been the subject of important geological collections during the eighteenth and nineteenth centuries: Micheli [1733], Targioni Tozzetti [1750], Baldassarri [1750], Campani [1860], and Tommi [1890]. They also constitute the paleontological collection formed between 1953 and 1956 by Professor Ezio Tongiorgi, now preserved in the Museum of Natural History of the University of Pisa.

The Tongiorgi collection consists of: 386 plant remains, 61 ichthyologic specimens, 2 mammalian teeth, and 5 samples of sediment. The fish remains were deposited in the museum after their publication by Bradley and Landini [1982], who recognized the living species *Salmo trutta* and *Squalius cephalus*, while all the other materials arrived around 2010. Among plant remains, the numerically dominant element of the collection, different types have been recognized: leaf impressions, wood fragments, branch impressions, conifer's cones or their moulds, and several coal pieces but a detailed study of this material is still pending.

These paleontological samples represent the biological and physical testimonies of the environmental and climatic changes of the late Pleistocene and are now particularly valuable because they are the only remaining evidence of the ore deposition occurred in the lacustrine sediments of Monte Amiata. For these reasons, they represent geological materials with a fundamental cultural value and merit to continue to be accurately preserved and better known.

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