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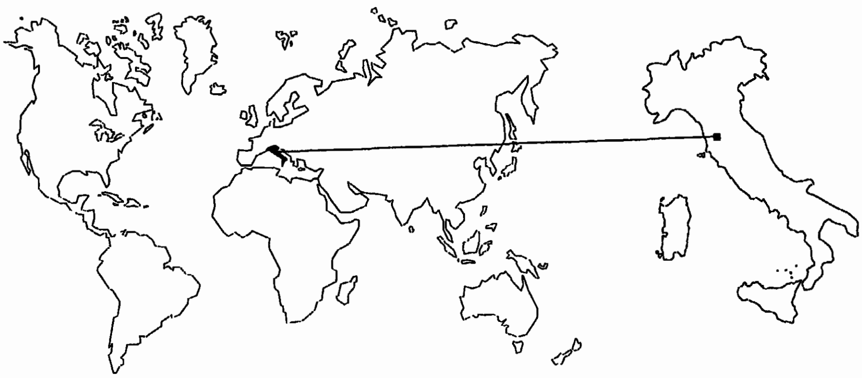


14. Four Centuries of Scientific Investigation at Larderello, from the 16th Century to the 1st International Geothermal Congress in 1928

by
Pier Domenico Burgassi
Raffaele Cataldi
Claudio Donati

Abstract: The chapter describes geoscientific studies and laboratory analyses carried out in the Larderello area of Central Italy, after the Middle Ages until the first International Geothermal Congress in 1928. It examines hypotheses and theories advanced by numerous Italian and foreign scientists explaining the origin of hot fluids, the nature of hydrothermal compounds, and the formation of geothermal fields. During these four centuries, a number of new hydrothermal minerals and some rare gases were identified at Larderello, and many other research activities were undertaken. All of these studies reflect the high level of scientific knowledge, technological advancement, and development reached at Larderello by the beginning of the 20th century.

Historical Background

The description of the principal geothermal manifestations and the formulation of the first hypotheses explaining their occurrence in the Mediterranean area predate the Christian era by many centuries. Hot springs, fumaroles, active volcanoes, earthquakes, and other manifestations of the Earth's heat aroused the interest of many Greek and Latin writers, who described or interpreted them in light of the cosmogonal theories of their time. Thus nearly 1,000 years before the beginning of the Middle Ages, a first and very important nucleus of knowledge was formed concerning geothermal phenomena and the ways that terrestrial heat manifests itself at the surface.

The uses of natural hot water for balneotherapy and the exploitation of hydrothermal products for a wide range of practical applications increased remarkably during the millennium preceding the Christian era and eventually extended over all

Roman territory, reaching an apex during the period of maximum splendor of the Roman Empire, the 3rd century A.D. After the fall of Rome in the 6th century, these uses declined quickly throughout Southern Europe and entered a long period of disuse lasting until the beginning of the second millennium (Cataldi and Burgassi, 1992b).

In a gap of some seven centuries between the collapse of the Roman Empire and the middle of the 12th century, few works can be found referring to geothermal phenomena or describing the uses of the Earth's heat and its by-products. However, the geothermal knowledge gained in Antiquity was not lost and became the basis of a more advanced understanding of terrestrial energy that started in the first centuries of the second millennium (Cataldi and Chiellini, 1995). A reawakened interest in hydrothermal minerals started at Larderello in Central Italy during the first decades of the 12th century. The existence of conspicuous hydrothermal deposits around natural manifestations began to be a matter of contention among some Tuscan communes, lasting about three centuries (Burgassi, 1987; Cataldi and Burgassi, 1992c).

A new literary flowering inspired by geothermal manifestations began in the 13th century. Ristoro d'Arezzo is worthy of mention for the scientific importance that his description of the geothermal phenomena in the Larderello area has had in understanding the evolution through the centuries of the Larderello Geothermal Field. In 1282, he described in detail a huge explosive event that took place in a *lagone* (a natural pool of boiling water) in the southern part of the Larderello area, probably a phreatic explosion. Numerous other authors from Italy and abroad started writing about the natural manifestations: some interested in religious considerations, others in the phenomena and interpretative hypotheses, and others in the therapeutic properties of thermal waters and thermo-mineral muds (see Chapters 11 and 12 in this volume).

16th and 17th Centuries

In the first half of the 16th century, the first important author who dealt systematically with the natural manifestations and hydrothermal products of the Larderello area was Georg Bauer (1494-1555), a German naturalist and medical doctor who translated his family name into Latin and is better known as Agricola. Considered the "father of mineralogy," Agricola wrote detailed descriptions of the manifestations, gases, and hydrothermal compounds at Larderello, explaining them scientifically and comparing them with similar ones in other Italian geothermal areas. He described techniques for extracting and processing hydrothermal minerals (see the initial illustration). The results of his studies are in three general works: *De veteribus et novis metallis* (*Old and New Metals*), 1546; *De natura eorum quae effluent ex terra* (*Nature of Fluids Escaping from the Earth's Surface*), 1546; and *De re metallica* (*Minerals and Mining*), published posthumously in 1556.

Contemporary with Agricola's work is the treatise *De balneis omnia quae extant apud graecos, latinos et arabos* (*All Thermal Stations in Greek, Latin, and Arabian Territories*, 1553). Each monograph in this treatise covers a major geothermal area from these territories and includes a geographic description of the site and detailed information on the therapeutic properties of the thermal waters and thermo-mineral muds. Monographs for the Larderello area include those by Mengo Blanchello Faentino, Franciotti, Savonarola, Bartolomeus Taurinensis, and Ugolino da Montecatini.

The work of naturalist Baccio in 1571 followed shortly afterward. This author was concerned with the fundamental causes of natural manifestations, attributing their formation to the presence of a "subterranean fire." He discussed the origin of sulfurous encrustations associated with fumarolic manifestations.

In 1575, Aldrovandi dealt with natural manifestations and hydrothermal compounds at Larderello. He described the presence of a mineral that he called *nitrum nativum* ("native nitre"). From his description and from later sources (Mercati, 1717; Hoefer, 1777), we know that *nitrum nativum* was boric acid.

In 1606, anatomist and medical doctor Fallopio published an important work describing the characteristics of the manifestations at Larderello. He paid particular attention to the therapeutic properties of different thermal waters and their abilities to enact medical cures. He agreed with Baccio, attributing the formation of the manifestations to the presence of a "subterranean fire."

A little later, the German geographer Phillip Clüver (1580-1622), who took the Latin name of Cluverius and is considered the founder of historical geography, described the Larderello region in detail and prepared the first geographic map of the area with all of the major natural manifestations. His work, with the map, was published posthumously in 1624.

In the second half of the 17th century, the Larderello region attracted the attention of the Danish physician and geologist Nils Steensen, who is better known as Nicolaus Steno (1638-1686).

During his stay in Florence as physician for Grand Duke Ferdinand II, he studied the geological characteristics of many Tuscan areas, including Larderello, which he described in detail because of its geological peculiarities. In his work *De solido intra solidum naturaliter contento dissertationis prodromus* (*Preliminary Dissertation on Natural Solids inside Rocks*), published in 1669, he discussed the nature of volcanoes, maintaining that the natural manifestations at Larderello are "exhalations" of cryptovolcanic activity.

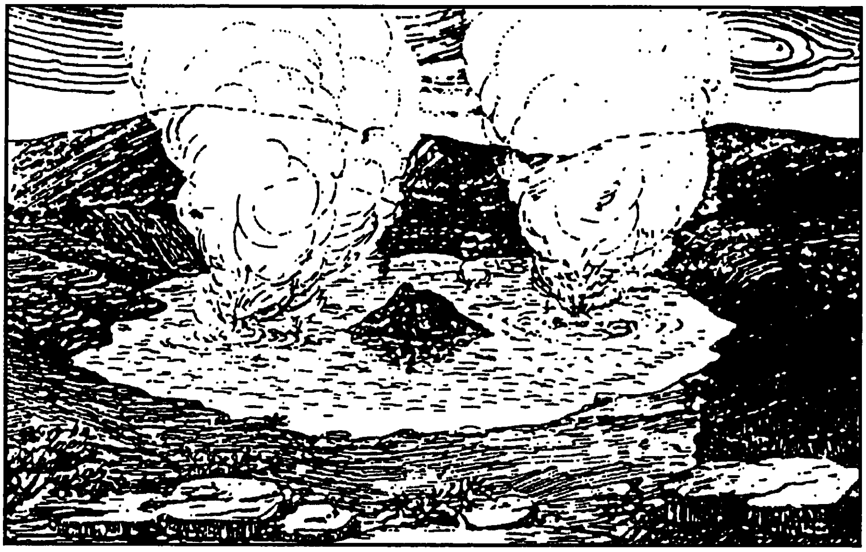
18th Century

Toward the beginning of the 18th century, the mineralogist Mercati began to study systematically the hydrothermal deposits associated with geothermal manifestations in the Larderello region. In a 1717 work, Mercati described many hydrothermal minerals, including what he called *nitrum volaterranum* ("nitre from Volterra"). Based on his indirect description of this mineral *"nitrum nativum scissile ex quo venetis borax conflatur,"* which means "processed native nitre from which Venetians obtain borax," and from Hoefer (1777), we know that he was speaking of boric acid.

A few decades later, the scientist Targioni Tozzetti was appointed by the Grand Duke of Tuscany to evaluate potential development of the agricultural and mineral resources of the Grand Duchy. In 1742, he began 25 years of detailed field surveys in many areas, the results of which were published in 1769. The author did not stop with a simple description of natural manifestations and *lagoni* or with merely listing hydrothermal minerals amenable to extraction and commercialization, such as alum, *nitrum volaterranum*, sulfur, and vitriol (heptahydrated ferrous sulfate); he also discussed critically Larderello's geothermal phenomena in light of theories already proposed. Regarding the natural manifestations and the *lagoni* of the region, Targioni Tozzetti wrote,

> "In all of them, I have identified alum, salt, sulfur and vitriol. Baccio says that a 'subterranean fire' is the cause of heat and boiling; however, if he means 'real fire,' as in the case with volcanoes, he is wrong simply because there is no fire escaping [from those manifestations]. At most, there is a continuous hot fermentation, like certain fermentations that occur chemically with two or more cold liquids....
>
> "Not only the *lagoni*, but all the mineral waters and *mofettes* I have observed, spring out from fractures of primordial mountains, but never from gently-sloped terrains. This means that the minerals formed within rock mountains. As time passed, some small portions of the veins in which the inflammable material was trapped came to outcrop; therefore, this material could come into

contact with outside air and a small amount of [surface] water started to percolate into the veins. This water may be sufficient to trigger off the fermentation process, drive out the air trapped within fractures, release heat, and cause the water to boil. For sure, large masses of inflammable material are scattered within rock mountains, much larger than we might suppose, and one day in the future will come to outcrop and start to ignite [by fermentation]....



Sketch of a *lagone* in the area near Larderello, as seen in 1750. From Targioni Tozzetti, 1769. *Courtesy ENEL SpA/Geothermal Department*

"In other *lagoni*...deep, round-shaped holes are to be seen, like those made by the tarantula; from this type of hole, nothing but very hot air blows out. If you hold a silver coin against the air stream, a veil of condensation forms, much as it happens if you breathe on a mirror. This is an extremely fine coat of water, tasteless but sulfur-smelling; and in less than a minute the coin turns black, as if it were made of iron. On the upper surfaces of many of these holes a substance is deposited similar to pumice. I doubt very much, however, if this substance is that which Aldrovandi calls '*alumen volaterranum...facultatis astringentis*'['alum from Volterra...with astringent properties']."

Targioni Tozzetti even recognized the effects of the self-sealing process; however, he could not fully understand the causes of this phenomenon. He wrote,

"The *lagoni* continually undergo an expansion process, and tend to move toward the mountain top. Areas with fields, which until a few years ago were richly fertile, now yield nothing because they have been crossed by the tortuous fissures created by the spreading *lagoni*. This expansion and encroachment on once fertile fields indicates that this type of *lagoni* eventually reaches and settles in correspondence to large veins of the original material, and this continues until the whole material has been consumed.... However, there is no doubt that the expansion is a process that becomes weaker day by day, and that in certain places it halted a long time ago. The many dried-up and cold, round-shaped lacustrine depressions, which can be seen here and there in the valleys, are evidence of this. These appear as extremely barren places and look like craters, the bottoms of which are filled with collapsed blocks of *alberese* ['marly limestone']; thus, these are to be considered [old *lagoni*] similar to the presently active *lagoni*, the only difference being the fact that no steam is released...."

In 1777, a few years after Targioni Tozzetti concluded his Larderello surveys, a very important scientific finding was made by Hoefer, chief chemist for the pharmacies of the Grand Duke of

Tuscany. Hoefer analytically documented the presence of boric acid in the water of two *lagoni* of the Larderello area, near Monterotondo and Castelnuovo.

At that time, boric acid (then called "Homberg's sedative salt") had not yet been recognized as one of the compounds in the hydrothermal deposits of the Larderello area, nor it had been separated chemically. The confirmation of its presence in the area and the success of Hoefer's chemical separation process opened the way for a flourishing geothermal industry in Southern Tuscany, and the area took on the name of the Boraciferous region.

Boric acid, used widely in the pharmaceutical industry at that time, was obtained from minerals imported overland at great expense from Persia. Hoefer's discovery therefore resulted in immediate plans for industrial production of boric acid at Larderello from hydrothermal minerals. With the support of the Grand Duke of Tuscany, two complementary groups of activities soon began at Larderello: drilling for hot fluids (used for extracting boric acid and as a primary energy source to drive mechanical engines) and systematic scientific research to improve knowledge of geothermal phenomena.

In this regard, we must highlight the scientific contributions made by Mascagni, a professor of chemistry, physiology, and anatomy at several Tuscan universities. In 1779, he published a detailed mineralogical description of hydrothermal products in the Boraciferous region, maintaining in particular that certain "white concretions" that Targioni Tozzetti had thought to be selenite were actually boric acid. In the years that followed, trying to find ways to exploit large quantities of boric acid for industrial production, Mascagni made many more chemical analyses of hydrothermal minerals and conducted site-specific studies on the extension of the manifestations. He proposed that natural heat, rather than wood fire, could be used to evaporate boric brines and designed two different types of metal boilers for this purpose, one to be embedded in hot ground on the edges of the natural manifestations and the other to be partially sunk into the *lagoni* (Burgassi, 1987).

19TH CENTURY

AFTER THE DISCOVERY OF BORIC ACID AND ALONG WITH—AND BECAUSE OF—THE RAPID EXPLOITATION of hydrothermal deposits beginning around 1820, scientific interest in geothermal phenomena at Larderello grew quickly. Many new geological investigations and mineralogical and chemical analyses were undertaken by Italian and foreign scientists. The Frenchman Dumas stated in 1828 that boric acid reaches the surface after interaction between meteoric water and deeply-rooted large masses of hydrothermal minerals, including boric acid and sulfur. In this way, he explained the occurrence of hydrogen sulfide in gas escaping from the *lagoni* and steam jets.

Important geological works were published in 1833 and 1863 by Savi, professor of natural sciences at the University of Pisa. They describe rock formations in the Larderello region and surrounding areas, analyze the characteristics of the solfataras and *lagoni*, and speculate on the patterns of hydrothermal circuits that, rising to the surface, can alter outcropping terrain. Savi recognized the existence of folding and faulting structures in the mountains and hills throughout the Metalliferous Chain, also known as the Metalliferous Hills, due to their rich mineral deposits extending over the whole Boraciferous region and the area to the west (Cataldi and Burgassi, 1992a, 1992c). Savi wrote that a number of anticlines had been formed by the emplacement of intrusive bodies at relatively shallow depth. These could be inferred from outcrops of trachytes and selagites (lamprophyric differentiations from quartz-latitic, alkali-bearing magma) found in areas of Central and Southern Tuscany.

From 1832, several proposals were presented to develop drilling technologies suitable for conditions at Larderello. The one made by Gazzeri (1838 and 1841) is worth mentioning for the geoscientific background on which it was based. Gazzeri dedicated himself to developing drilling methods for Larderello after he had studied the geological situation and the depositional characteristics of hydrothermal minerals in the area. He maintained that the carrier fluids for boric acid were originally contained in one huge, deep, single reservoir. He said that all natural manifestations in the area were nothing but local discharges of deep fluids, "The most elementary notions of geology persuade us that the mineral, whose decomposition gives off the boric acid contained in the ardent vapor of the steam jets, is not distributed in isolated masses at the base of each steam jet or *lagone*, but forms a single and huge deposit, the extension of which is unknown. If we were able to reach the original deposit by means of drilling, a spontaneous blowout of natural fluids should follow, similar to that occurring in artesian wells. Alternatively, [if such a blowout does not occur] we could obtain stimulated production by a judicious injection of [fresh] water or by other methods...." There is no need to stress how modern these concepts are, considering the present knowledge of the geothermal field at Larderello.

In 1838 the French chemist Payen, technical adviser of the Larderello chemical company, began to study the origin of boric acid in the field, first determining the concentration of the compound in the *lagoni* and steam jets as a function of temperatures and flow rates. After some years, noting that both of these parameters and the concentrations of boric acid were decreasing significantly, he wrote that the declines stemmed from the ever-growing extraction of boron-bearing waters from the *lagoni* for chemical production. He thus began seriously to consider Gazzeri's theory of a single, large geothermal reservoir at depth but strongly rejected Gazzeri's idea to drill "deep" wells out of concern for the possibility of uncontrolled blowouts.

To slow the fall of temperatures and boron concentrations of natural *lagoni* and other nearby hot manifestations, Payen developed an ingenious system of connected, cascading, artificial *lagoni* in 1841 (see figure 4 in Chapter 13). The system created a more efficient extraction cycle for boric acid (Burgassi, 1987). Payen's theoretical studies and experimental results on the subject are in an extensive monograph, published in 1847.

At the same time, the Tuscan Boraciferous region was studied by the geologist Pilla. He wrote in 1845 that high-temperature heat is responsible in some areas for forming coal and natural manifestations: "Where partial outlets of igneous rocks occur, the vegetable material that transforms itself into lignite seems elsewhere, [in places it] is baked into lithantrax because of the exceptionally high underground temperature. The famous *lagoni* in Tuscany can be considered the legacy of these underground conditions. One of the characteristics of these is the very high temperatures of the terrain around...." Pilla also discussed the formation of the geothermal field. He was first to maintain that steam jets in the Larderello area result from a regional thermal anomaly caused by recent granitic intrusions and effusions of porphyritic and trachytic rocks.

Pilla claimed that boric acid originates from the decomposition of tourmaline: "The tourmaline found in granitic and porphyritic formations outcropping in the region indicates that the steam jets are related to these.... It is a well-known fact that boric acid is a component of tourmaline, and this clearly points to a connection between the presence of boric acid in the steam jets and the formations just mentioned...."

The geological peculiarities of the manifestations at Larderello and the fame the region gradually acquired after 1830 from the production of boric acid caught the attention of many foreign geologists. Among them were Hamilton, Murchison, and Warington from England, whose works were published in 1844, 1850, and 1854, respectively.

In 1851, the work of Murchison was translated into Italian by Savi and Meneghini, who were studying the geology of Larderello. They wrote an appendix to Murchison's work, with the following comment: "As concerns the numerous steam jets of the area, it should be noted that they seem to spring out from fissures running along northwest-southeast trends.... These regular, parallel, eruptive fissures are clearly the rejuvenation of older fissures that had been formed in preceding eras as a result of violent underground movements caused by the high-temperature regime...."

Murchison visited the Larderello region in 1852 and concluded that the steam jets were not a "phenomenon apart." He maintained that in the framework of the regional geological structure of Tuscany, the steam jets were late manifestations of the same volcanic process that once had affected several areas of Central Italy. Moreover, in agreement with Savi and Meneghini, Murchison pointed out that steam jets and other natural manifestations were all situated along northwest-southeast alignments, corresponding to the main tectonic trend of Tuscany and the whole Italian peninsula.

1818 print showing an alignment of steam jets along a northwest-southeast fault scarp in the southern part of the Larderello region. ***Courtesy ENEL SpA/Geothermal Department***

In 1858 and 1878, the mineralogist Bechi stated that boric acid originates from the decomposition of boron silicates contained in the serpentine rocks that widely outcrop in the Larderello region and are many hundreds of meters thick. He maintained that the decomposition of these rocks is caused by carbon dioxide streams rising from deeper formations. In 1858, Bechi identified a new hydrothermal mineral, which would be called *larderellite,* describing it with the formula $(NH_4)_2 \cdot B_8O_{13} \cdot 4H_2O$. The formula was perfected by D'Achiardi in 1878.

Others, such as Deville from France (1857) and Wagner from England (1875), maintained that boric acid resulted from interactions between hot water and deeply-rooted masses of boron azides. This is how they justified the presence of ammonia in the waters of *lagoni* and thermal springs.

In 1867, Meneghini published a paper dealing with the production of boric acid. He discussed the formation and depositional characteristics of all hydrothermal minerals of the Boraciferous region in light of prevailing ideas in his time on the magmatic origin of geothermal fluids.

Meneghini's paper became a fundamental reference for the Abbot Stoppani, noted naturalist and geographer, who published a notable work in 1874 with an ample dissertation on the geothermal phenomena at Larderello. Using the ideas of his time and many of his own, Stoppani discussed the characteristics of the geothermal field and of the area, such as tectonic control of manifestation alignments, migration of steam jets through time, and thermal anomalies determined by igneous processes, fitting them into a geological framework for all of Tuscany. Not only did he understand the mechanism that controls the occurrence of phreatic explosions, but also the cause of the phenomenon that we call "self-sealing." A passage of Stoppani's work reads,

> "As I have already pointed out, the steam of the manifestations carries not only boric acid but also other compounds, such as ammonia, sulfates, iron, manganese, magnesia, and soda. These crystallize when the steam cools and then they encrust their subterranean passages to the point of closing them completely. Boric acid, for instance, causes the scaling of artificial boreholes.... During drilling, large masses [of hydrothermal minerals] are found, which prevent the steam rising to the surface.... There is nothing more natural than a steam jet closing in by itself, finding no outlet. As a consequence, the closed steam jet gathers all its power before breaching its prison walls and springing out again to the surface like an unshackled prisoner who has just escaped. Sometimes steam jets blow out spontaneously, just like a bomb; the soil is tossed into the air, and a steam cloud blows out.... The steam is accompanied sometimes by a jet of boiling water, which brings to mind a geyser...."

In years to come, several Italian and foreign scientists continued speculating on the origin of boric acid. Dieulafait, from France, proposed in 1877 that boric acid is carried by the steam and that the steam forms by vaporization of meteoric waters when they can percolate through fissures at great depth, reaching very hot formations. The Italian mineralogist D'Achiardi did not support Dieulafait's theory. In 1878, he maintained that the steam escaping from natural manifestations originates in much older rock formations that underlie the Miocene evaporitic sediments and have no intercalated saline layers. In 1888, Dieulafait's theory was again supported by Stohaman and Schwarzerberg from Germany.

In 1897, a few years later, geologist De Stefani strongly opposed Dieulafait's theory on the origin of boric acid from Miocene evaporitic formations. After studying the lithostratigraphic sequence and the geologic setting of all geothermal areas in Tuscany, as well as the hydrogeological conditions and the hydrothermal species occurring in all active and fossil manifestations in these areas, De Stefani stated that boric acid could only form at great depth:

> "The considerable surface area of the territory where these [manifestations] occur, the fact that natural steam carries boric acid everywhere it escapes, the presence of other acids and gases, the high temperature and energy of the steam, are all facts proving that both steam and [boric] acid originate at depth, and that they have nothing to do with shallow sediments and [Miocene] saline deposits.... Since it is widely accepted that temperature increases with depth at an average rate [of some 3° C/100 m], steam with a temperature of about 175° C must come from a depth of some 5 km....
>
> "The geothermal waters have nothing to do with sea water; therefore, they should be of atmospheric origin and percolate underground through the numerous cavities until they reach the deepest recesses of the Earth....
>
> "The presence of boric acid in the steam jets can only be justified if one accepts that its origin is in the depths of the Earth, and that the steam jets are the last legacy of volcanic activity.... This occurred in Tuscany quite recently, and even today the final signs of such activity are quite evident. The steam jets also carry carbonic acid and, as steam rises from underground, it comes into contact with very old borate-bearing rocks; thus, boric acid is drawn from the ensuing decomposition [of the borates].... The volcanic origin of the boric acid contained in the [waters of the] *lagoni* is indirectly confirmed by the fact that the same compound is contained in the steam plumes of active volcanoes and solfatara craters. They, too, just like the *lagoni*, bear witness to the presence of ammoniac substances, sulfurous gases, and carbonic acid...."

Throughout the second half of the 19th century, parallel with geological research and studies on the origin of boric acid, laboratory analyses were made systematically for all hydrothermal minerals from Larderello. Besides confirming the occurrence of alum, boric acid, and sulfur, previously unknown sulfates and borates were discovered as well, such as cerbolite and larderellite. Cerbolite was identified in 1872 by Popp from England and described with the formula $(NH_4)_2 SO_4 \cdot MgSO_4 \cdot 6H_2O$. Larderellite had been identified in 1858 by Bechi, but the formula he wrote for the mineral was incorrect. The formula was perfected by D'Achiardi in 1878 as $(NH_4)_2 \cdot B_{10}O_{16} \cdot 5H_2O$.

In 1895, the chemist Nasini began a systematic study of the gases contained in the steam and dissolved in the hot waters of geothermal manifestations and wells. His series of analyses was repeated for many years. He discovered the presence of helium and argon in geothermal gases at Larderello, quantifying the average amounts in wells and field areas, and the results were published in 1930.

From 1900 to 1930

In the period between the end of the 19th and the beginning of the 20th centuries, other scientists began studying the Larderello region. In 1904, Perrone published an extensive work on the hydrographic conditions of Southern Tuscany. In illustrating the situation of the hydrologic basins in the region around Larderello, he also dealt with the geological characteristics of the geothermal field and presented his own ideas on the genesis of hot fluids. Concerning the origin of boric acid, he again took up the hypothesis advanced by Pilla some 60 years earlier, discussing it in light of recent well data. Considering that the greater drilling depths reached between the end of the 19th and the beginning of the 20th centuries had produced fluids with temperatures above 200° C (not on the order of 175° C, as stated by De Stefani in 1897), Perrone claimed that the original temperature of the primary steam should be at least 250° C; thus, the steam had to come from depths of between 5 and 8 kilometers. At these depths, hot granitic masses containing tourmaline species were likely to exist, as could be inferred by the presence of Late Miocene-Pliocene granitic outcrops in several areas west of Larderello. Perrone concluded that with such temperatures and geological conditions, boric acid could only originate from the decomposition of tourmaline.

Geologist Lotti started in-depth investigations in the Larderello region and wrote many papers about the geothermal field, as well as several general papers on the geology of Tuscany. His most important works were published in 1900, 1907, and 1928. In 1907, Lotti categorically refuted Pilla and Perroni's arguments on the origin of boric acid from tourmaline:

> "Boron, fluorine, and chlorine, along with superheated water, constitute the most energetic dissolvents that contribute to the crystallization of eruptive rocks. Thus, it can be argued that

boric acid is not derived from tourmaline-bearing granites, but forms before, and not after [the eruption of igneous rocks]. Rather, the deep circulation pattern of boron-rich waters must be taken into account because on the one hand, [while percolating downwards, the shallow waters] may reach the granitic stock, interact with it, and facilitate the formation of tourmaline; and on the other hand, [while rising up, the deep fluids] can nourish the steam jets and the fluid produced through drilling...."

From the structural point of view, Lotti recognized that the whole Metalliferous Chain of Tuscany, which includes the Larderello region, has two tectonic styles: one characterized by folding and the other by faulting. Taking up Savi's hypotheses of 1863 and adding many new arguments, Lotti attributed the folded structures to a prolonged phase of igneous activity that began in the Miocene with the sequential intrusion of granitic bodies at the Tyrrhenian islands of Elba, Giglio, and Montecristo, and inland at Gavorrano and Campiglia in Southern Tuscany. During the Quaternary, the granitization process moved upward from great depths until it reached the first shallow formations, resulting in the eruption of trachytic melts in several Tuscan localities, such as Capraia, Montecatini, Orciatico, Roccastrada, and Mt. Amiata. More or less regular anticlines could form in this way, following the uplift of rising igneous bodies: some intrusive, others extrusive.

At Larderello, since no igneous rocks outcrop there or in the surrounding region, Lotti argued that a granitic intrusion, rooted in an active magma chamber, is likely to exist at a relatively shallow depth beneath the field area. He concluded that the cooling magmatic body would have to supply the geothermal system with both heat and steam. In this framework, steam jets and other natural manifestations at Larderello should be regarded as the final stage of an active magmatic process. Lotti speculated that a similar explanation should be given for high-temperature fluids at any other geothermal field in the world, with or without occurrence of recent volcanic activity.

On this basis, he formulated a general theory in 1928 on the formation of geothermal fields, now called "Lotti's theory of the juvenile origin of geothermal fluids," which was accepted worldwide until the end of the 1950s. While making field surveys, Lotti compiled a detailed geologic map of the Larderello area. It was used as a guide for field excursions during the First International Geothermal Congress, held at Larderello in 1928 under the auspices of the Italian Geological Society.

In 1926, the mineralogist D'Achiardi joined Lotti in rejecting Pilla and Perroni's theory on the origin of boric acid. He stated that, even though granitic masses were likely to exist at great depth beneath the geothermal field, their tourmaline content could in no way be sufficient to form the large quantities of boric acid produced at Larderello.

Through the first three decades of the 20th century, besides continuing to study the occurrence and nature of geothermal gases, Nasini and his team of industrial chemists from the Universities of Pisa and Padua conducted a series of research projects, lab tests, and on-site examinations aimed at improving the production processes of all chemical compounds of the Larderello company. These processes resulted from many years of theoretical investigations into the chemistry and thermodynamics of geothermal fluids. In 1930, Nasini's work culminated with the publication of a voluminous monograph that remained a benchmark in geothermal literature until after the 1950s.

Concluding Outlook

Due to geological characteristics, the area around the village presently known as Larderello has attracted the attention of indigenous populations since prehistoric epochs. From Antiquity through the Late Middle Ages, it has aroused the scientific interest of many writers for the same reasons. From the 1470s, this interest grew more quickly when the region came under the rule of Florence and intensive use began of the hydrothermal minerals deposited around the natural manifestations in the area (Cataldi and Burgassi, 1992c). For about three centuries scientific research remained at the level of speculation and was aimed more at understanding geothermal processes than at finding ways to improve development of the rich hydrothermal deposits.

Following the discovery of boric acid at Larderello in 1777-1779 and after new techniques allowed large quantities of this compound to be produced there, applied and scientific research increased, starting in 1830. From then on, advances in scientific research paralleled achievements in the technological sector (see Chapter 13), and the two become interdependent. To better evaluate the former, it is necessary to have in mind the latter and vice versa.

In summary, the principal advances in scientific research at Larderello from the 16th century to the early 20th century include the following:

- Identification and characterization of hydrothermal minerals
- Igneous and hydrothermal processes

- Structural control of manifestations
- Presence of a strong thermal anomaly as a result of relatively young igneous processes
- Formation of anticlines and creation of rock fractures by granitic intrusions or magmatic extrusions
- Percolation of meteoric water along fractures and/or through outcrops of permeable formations
- Presence of reservoir rocks
- At-depth interaction of meteoric water with reservoir rocks and hydrothermal minerals
- Self-sealing processes and evolution of natural manifestations over time
- Underground circulation patterns and interaction of meteoric water with deep, hot fluids
- Origin of noncondensable gases associated with geothermal steam and waters
- Accumulation at shallow depth of over-pressured hot fluids, resulting in phreatic explosions and/or steam jets

Knowledge of these aspects accrued gradually, evolving slowly over 400 years and leading to the first structured theories on the formation of Larderello Geothermal Field between 1890 and 1930. If we consider all of the above in light of the practical achievements—the technological innovations, the chemical production of many compounds, the use of natural heat for space heating, the first experiment of geothermal-electrical generation in 1904, and the industrial production of electrical power from 1913 on—then we can realize why the knowledge of Larderello Geothermal Field and ways to exploit its resources for many uses became familiar to many Italian and foreign scientists and engineers by the first decades of the 20th century. These technological achievements and scientific discoveries formed the basis for future development of the Earth's heat, not only at Larderello and other geothermal areas in Italy but in many other geothermal fields around the world.

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The Authors:

Pier Domenico Burgassi
2, Via G. Galile
56044 Larderello (Pisa), Italy
Telephone: 39.0588.86.74.89

Raffaele Cataldi
55, Via del Borghetto
56124 Pisa, Italy
Telephone/Fax: 39.050.59.81.07
E-mail: rafcat@tin.it

Claudio Donati
33, Pod. Bufalona-Zona Belvedere
58024 Massa M.ma (Grosseto), Italy
Telephone: 39.0566.90.33.89

The indoor pool with geothermal waters, designed around 1900 for the Hotel Gellert in Budapest. *J. Lund*