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NEW MATERIALS AND TECHNIQUES FOR THE STRENGTHENING OF STONEWARE AND PLASTERS

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To all people that supported me during this work

Preface

SANDSTONES CONSERVATION. *STATUS QUAESTIONIS*

1. *Sandstones deterioration*

Sandstone is a sedimentary rock that contains quartz as main element, together with clay matrix and low calcite cement, and shows parallel lamination structure. This compact rock was formed by "lithification" (consolidation, compaction, cementation) of sandy incoherent materials (clasts from 2 mm to 0.0625 mm [Pettijohn *et al.* 1987]), deposited in sedimentary basins by turbidity current effects. In the eves, the new materials carried to the sedimentary basins in continuous mode create new sedimentary sequences.

Since the antiquity sandstones have been used to build monuments and buildings with civil (castles, medieval walls, private houses, etc.) and religious (temples, monasteries and churches) aims, and to make sculptures and other architectonical and decorative elements (columns, capitals, architraves, cornices, etc.) all over the world, due to the great amount of natural sandstone quarries.

The choice of this rock as building material depends on the specific artistic techniques used and by logistic requests, such as the final esthetic aspect of the monument, stonework resistance, and presence of natural quarries near the working and building places.

Sandstones are extracted in blocks and they are used in natural, semi-finished or finished shapes, according to the final destination of the objects and to the people's working culture.

The ageing of sandstone surfaces may bring to their degradation, due to different environmental (wet and dry cycles, freezing-thawing cycles, humidity, temperature, biological activity, salts transport, etc.), and pollution actions, as they produce [Martuscelli 2007]:

1. *scaling, flaking, exfoliation, granular disaggregation and cracks* [described in NORMAL 1/88] in surface layers made by:
    a. water action, such as humidity and water absorption. Water enters into the pores, interstices and cracks of the stones and fills the free space. In the freezing and thawing cycles, when the temperature decrease below 0 °C, water solidifies increasing its volume, and consequently the pressure on the internal walls increases: this may lead to disaggregation of the rock.

b. wind action, which shows a double effect: it increases the evaporation rate and thus water flow from inside to outside of the stone, and produces erosion and abrasion. Recent studies made in the archeological site of Petra in Jordan showed that wind speed strongly influences the rate of damage and pattern of soluble salts distribution [Balaawi 2008];

c. vegetal action, for example lichens provoke mechanical and chemical damages into the stone. The first is caused by hyphae penetration and thallus expansion and contraction, under changes of humidity, while the second may arise by secretion of oxalic acid, or generation of carbonic acid or other acidid substances able to chelate ions such as calcium [Doehne-Price 2010];

d. temperature changes, that produce continuous expansion and contraction phenomena into the stone structure during daytime or seasons, especially in objects exposed directly to sunlight. Stones composed of minerals with big and disordered crystals (i.e. marble and granite) show thermal expansion dependence with the direction of the crystals (anisotropic properties). In presence of water and acidic substances, this expansion may give rise to decohesive processes of the crystalline structure [Torraca 2002].

2. *hydraulic swelling and shrinkage* of the surface layers in clay-rich rocks [NORMAL 1/88; Wendler 2000]. For instance, after a brief rain the wet surface of a clay stone swells while its interior remains dry. These effects are found in stone corners [Doehne *et al.* 2005]. Important studies on clay swelling of Portland brownstone were made by Scherer at Princeton University, finding that shear forces can cause buckling of wetted stone surfaces and that the primary mode of swelling operates at the intracrystalline level, despite of the proportion of swellable clay of only 1 percent. Thus, the clay is present as a cement at sand-grain boundaries, allowing a sufficient leverage in brownstone [Duffus *et al.* 2008; Wangler-Scherer 2008; Jiménez Gonzalez *et al.* 2008; Doehne-Price 2010]. Moreover, soluble salts have a role in the decay of this stones because of the swelling increase of clay minerals [for overview of these studies: Doehne-Price 2010];
3. *formation of black-crusts* [NORMAL 1/88] through the action of lichens, mosses, bacteria or polluting agents (NO_x, SO_x and CO_2), creating a chemical interaction with the sandstone surface [Simao *et al.* 2006; Schiavon 2007; Doehne-Price 2010];
4. *formation of efflorescences and inorganic salts* (nitrates, sulfates, chlorides, etc.) [NORMAL 1/88; Charola 2000] into the pores of the stones, through crystallization due to water evaporation or cooling of salt solutions. Water on the surface and into the stone,

induces reactions and easy transport of different ions and molecules. These phenomena change the chemical equilibrium into the rock and may show their effects on the stone surface. In severe cases this can cause fragmentation, lamination or even pulverization of the stone. The transformation in a powder is due to the growth of salts into the stone, which generates internal stresses that are sufficient to overcome the stone tensile strength. One of the most damaging soluble salts is sodium sulfate, present in the anhydrous (Na_2SO_4) or decahydrated form ($Na_2SO_4 \cdot 10H_2O$); the transformation of the anhydrous phase into the hydrated one produces a volume increase that cause the so-called "hydration damage", a special case of crystallization damage. Salt damages can occur both in outdoor and indoor environments, *i.e.* museums environments.

The resistance of sandstone to all these degradation elements depends on physico-chemical structure, porosity, pore size and water absorption capacity of the stone. For example, stones with a given porosity and small pore size is mostly susceptible to degradation due to frost damage. Frost resistance decreases when porosity increases, especially when pore volume is accessible to water. The frost resistance of a stone is often evaluated from the saturation coefficient, which indicates the ratio between the volumetric amount of water retention and the total volume of empty pores present in the rock, while the degree of saturation is expressed by the percentage of empty pores present in a rock, which are filled by imbibition water. If saturation coefficient has value less than 0.8, the stone is considered safe from frost damage.
Moreover, in the case of salt damage, the resistance of the stone depends on the pore size distribution, and it decreases when the concentration of pores with small size increases [Martuscelli 2007].
In the presence of a deep deterioration, the stone artifacts show severe damages, and in the case of cultural heritage this may cause the complete alteration of art work or buildings.

2. *History of the conservation studies*

Already in the past centuries, the characteristics of the stones (such as morphology, mechanical properties, easy working, shape of degradation and durability) were known and studied by scientists, artists and quarrymen.
Some very important books were written on this topic in the past centuries, such as: *i*) XXXVI book of *"Naturalis Historia"* by Plinio The Older in roman age, *ii*) the eighth chapter of the "*De*

re aedificatoria" of Leon Battista Alberti in the XVI century, and *iii*) the "*Vite"* wrote by Giorgio Vasari in XVI century.

Leon Battista Alberti connects morphology with characteristics of the stones and he remembers: "*Estrarrai la pietra d'estate; la terrai sotto l'aperto cielo; non l' adopererai prima di due anni.*" (translation: *you will extract the stone during summer; you will keep it outside, you will not use it before two years*). Thus means that, if the stone is just extracted from the quarry and it is exposed to the violence of the wind and frost actions, this may produce flaking and granular disaggregation. The advice of not using the stone for two year after the extraction is a good method to identify the weak stones, since this allows to point out differences between stone and stone: some becomes hard in the presence of air, other gives rise to rusting and disaggregation in presence of humidity, etc. . Again, Alberti observed that the presence of a great number of veins in a stone means a poor cohesion of the matrix and then a short durability [Gurrieri 2002].

Vasari speak of sandstones used in Tuscan monuments and buildings, i.e. Pietra Serena, Macigno stone, and Pietra Forte. He remembers the quarries of extraction (such as Firenzuola, Arezzo, Fiesole and many other places in Apennine layer), and the relationship between materials and monuments.

In the case of Pietra Serena, he mentions the characteristics (such as color, aspect, durability), and the causes of the deterioration under environment conditions (mainly humidity and rains). He observes that this decay was often visible on buildings and sculptures put in outdoor places and exposed to weathering agents.

Moreover, Vasari says that for law Pietra Serena was employed only in public buildings of Florence, and he reports some examples of this use, such as San Lorenzo and Santo Spirito churches (projected by Filippo Brunelleschi), and in the library and sacristy of San Lorenzo Church (created by Michelangelo) [Gurrieri 2002, Massi 2002].

In the past there was the tendency to replace the degraded stones on buildings with new good ones. Only from the beginning of XIX century, with the development of organic-chemistry, many scientists began to study and propose different solutions for the conservation and the restoration of the stones such as silicate rocks (as sandstones and calcarenites), carbonate rocks (as calcareous and dolomitic stones), marbles (i.e., travertine and granite), volcanic tuffs and lavas.

In this context, the first concepts of consolidation and protection treatments of the stone were asserted.

Consolidation process is an impregnation treatment with a product which, penetrating in depth, improves cohesion of the altered material and its adhesion to the good substrate. After this treatment, the stone will show an increase of resistance to the alteration.
Protective treatment is a technique that involves the application of materials which determinate an increase of surface proprieties, to prevent further degradation of the stone.
The function of a protective treatment is, mainly, to prevent the penetration of water into the stone, and thus its degradation action, but without creating an obstacle to the gas exchange between the inside and outside of the material [Borgioli 2002].
The products used in conservative operations are inorganic and organic materials: on them and on their application there is a very large and consolidated literature [for overview of these studies: Price 1996; Wheeler 2005; Doehne-Price 2010].
The development of synthetic polymers has been very important for stone conservation, since there are different kinds of materials that can be classified as [Borgioli 2002]:

1. *Adhesives* (polyester, epoxy and acrylic resins),
2. *Consolidants* (acrylic resin, silicate/alkylalkoxysilanes),
3. *Protectives* (silicone resin, waxes, resin base on fluoride compounds).

This classification is not absolute, and some products can be used with different purposes. For instance, epoxy resins are applied both as adhesives and consolidants, while acrylic resins exhibit low adhesive and hydrophobic proprieties, which are lost after short time and may be reduced faster in the presence of light and water.
Researches in the field of conservation have developed different chemical products for the experimental application on stones, with good or bad results.
In the case of failure, the applied product is considered ineffective for the conservation of this type of rock, because it has reduced the life of a monument that it had been survived for centuries [Borgioli 2002].
Hydrophobic protectives and consolidants can be classified in two classes[Borgioli 2002]:

1. *monomeric products*, that are applied after their dissolution in appropriate solvents. Their polymerization occur during or after solvent evaporation.
   Ethyl silicate, polyester, epoxy resins, and oligomeric siloxanes belong to this group.

2. *polymeric products*, that are applied by solvent solutions or water emulsions and they are deposited on the stone by evaporation of the solvent. In this case, polymerization reaction occurs during the production phase of polymeric product.
   Acrylic resins, microcrystalline waxes, and fluorinated resins are members of this group.

The development of semi-inorganic polymers bases on silica, deriving from monomeric molecules of silane (SiH_4), has been very important for stone conservation.
The chemistry of silicon-based organic compounds was developed by F.S. Kipling between 1899 and 1937. He discovered how to make silicon similar to carbon, with consequently the possibility of synthesizing new organic compounds. Indeed, silicon possesses proprieties similar to those of carbon, since the two elements belong to the same chemical group 14. Nevertheless, silicon is present also in substances like quartz and glasses, whose main characteristics are to be inert materials, resistant to the effects of heat or atmospheric influences [Martuscelli 2007].
An important group of silicones for stone conservation is the alkoxysilane compounds. The history of the development of these materials for stones conservation was summarized by G. Wheeler in the book "*Alkoxysilanes and the consolidation of stone"* [Wheeler 2005] and in the article "*Alkoxysilanes and the consolidation of stone: where we are now"* [Wheeler 2008]. While, the more recent studies were reported by E. Doehne and C.A. Price in the book "*Stone Conservation. An Overview of Current Research"* [Doehne-Price 2010].
In its works, Wheeler remembers three important event for the developed of alkoxysilanes as stone consolidants [Wheeler 2005, 2008]:

1. *the synthesis of ethyl silicate* in 1846, followed soon after by A. W. von Hoffman's suggestion that it can be used as a stone consolidant in 1861;
2. *the development and use of ethyl silicate products for stone consolidation* by A. P. Laurie in the 1920s;
3. *the invention of Wacker OH* in the late 1960s.

While distinctly separated in the time, these three developments are strictly connected.
The half of XIX century was characterized by syntheses of many silicon-based compounds, such as tetraethoxysilane (TEOS, Ebelmen in 1846), methyltriethoxysilane (MTEOS, Ladenberg in 1874), and methyltrimethoxysilane (MTMOS, probably synthesized by Kipping in 1904) [Wheeler 2005]. In 1861, A. W. von Hoffman suggested "silicic ether", a form of tetraethoxysilane (TEOS) called also ethyl silicate, as a consolidant for stone. In this particular

case, he proposed of using TEOS on deteriorated stones of House of Parliament in London, but these stones were not a good candidate for treatment with this type of consolidant: first, they have a chemical composition (the calcite in limestone) which, as shown by Laurie, produces a gel less suitable for consolidation, and second, they have a physical composition (large, pocket-like pores) which cannot be bridged by ethyl silicate derived gels [Wheeler 2005, 2008].

In 1920s, Laurie experimented several ethyl silicate formulations. His work was fundamental for understanding the relationship between stone mineralogy and TEOS catalysis. He remember: "*I have now found that if silicic ester is slightly acid before it begins to hydrolyze, the hydrated silica which is deposited forms a hard glassy layer that constitutes an excellent preservative or cement layer within the pores and on the surface of the stone. If the silicic ester is slightly alkaline, however, the hydrated silica is deposited as a soft gelatinous precipitate, which is useless as a cement or preservative. Limestones and calcareous sandstones are generally sufficiently alkaline to render the silicic ester alkaline and so to make the precipitate soft and useless"* [Wheeler 2008].

Laurie's research established the use of ethyl silicate as a treatment material for restoration and conservation, starting the development of ethyl silicate as product for stone consolidation.

For instance, the creation of the Wacker commercial products is the direct connection between Laurie's work and the developed of modern conservation chemistry.

Indeed, as mentioned above, Laurie indicated that if the ethyl silicate solution is acid-catalyzed the resulting gel is more glassy and better suited as a consolidant, but the consequent problem was how the reactions can be given a glassy gel without employing acid catalysts. The solution came by neutral catalysis through dibutyltindilaurate (organotin compound), worked out from resin industry during the 1940s and 1950s [Wheeler 2008].

In the same time, the first mention of alkylalkoxysilanes for stone preservation appears to be a U.K. patent application of the British Thomson-Houston Company (1947). In 1956, Wagner averred that silicic acid esters were being replaced by silicones, and General Electric (1959) patented water repellents based on methyl- and ethylalkoxysilanes. Stone consolidants consisting of mixtures of ethyl silicate and methyltrialkoxysilanes were suggested by Blasej in 1959. In the following years, Sneyers and de Henau (1963, 1968) reported on the consolidation of damaged calcareous and dolomitic stone with mixed alkoxy- and alkylalkoxysilanes, and Larner and Anderson (1967) used similar materials as water repellents [Wheeler 2005].

The 1960s represent an important moment for the study and use of alkoxysilanes on stone. These years are marked by Lewin's research (1966) on a treatment system for carbonate rocks based on

barium hydroxide and the next year he experimented with a new formulation base on ethyl silicate for siliceous rocks [Wheeler 2005].

In the same years, Wacker industry employed the discovery of neutral catalysis through dibutyltindilaurate for development of Wacker OH consolidant base on TEOS partially polymerized and solvents (usually ketones). The first application of this product was on sandstones [Wheeler 2008].

After fifty years, an evolution of Wacker OH, known as Wacker OH 100, was presented and applied in different types of stones: volcanic and plutonic igneous rocks (basalt, granite, etc.) siliceous and calcareous sedimentary rocks (sandstone, limestone, etc.), foliated and massive metamorphic rocks (gneiss, marble, etc.) [Wheeler 2008].

The expansion of the applications was due to the gradually experimentation of different alkoxysilane products on different type of rocks, beginning in the late 1960s. The first application of silicate products on a substrate not made in sandstones belongs to Hempel and Moncrieff that experimented a catalyzed MTMOS on marble sculptures, as a stone consolidant.

A few years later, Arnold and Price developed BRETHANE, a catalyzed stone consolidant base on MTMOS. In the 1970s and 1980s, the application of these products began into the museum environment by the initiative of Hempel and Larson, leading to extensive treatment programs on Egyptian limestone objects, with a catastrophic deterioration, at both the British Museum and the Metropolitan Museum of Art. After that BRETHANE and other consolidants were employed outdoors on sandstone and limestone sculptures, monuments and buildings (i.e. medieval cathedrals in England), but since the 1990s their application has been diminished both indoor and outdoor [Wheeler 2008].

The first application of alkoxysilanes on historic carbonate rocks and marble was on deteriorated sculptures in Venice and Bernini's Triton at the Victoria and Albert Museum, made in Carrara marble [Wheeler 2008].

Through the 1980s and 1990s, few museum marble objects were treated with alkoxysilanes;
while outdoor sculptures, monuments and buildings made with different varieties of marble were treated with ethyl silicate consolidants in Italy, France and United States [Wheeler 2008].

On the end of XX century, many alkoxysilane treatments were based on catalyzed TEOS and mixed TEOS-MTEOS systems (i.e. Wacker or Conservare H and OH, Tegovakon V and T), catalyzed MTMOS systems (i.e. BRETHANE), and uncatalyzed MTMOS systems. The uncatalyzed system often contained dissolved organic resins [Wheeler 2005].

Ethyl silicate formulations with or without MTEOS were commonly applied on sandstone or as sandstone strengthening agents, and MTMOS formulations saw a wide use on limestone and marble [Wheeler 2005].

In the early 1980s TEOS products began to be used with increasing frequency on limestone and marble, a practice that is common today [Wheeler 2005].

MTEOS and MTMOS-based consolidants had the ability to stabilize or provide strength increase to weakened stone, together with water repellency. This last feature became available in the 1970s, with the development of hydrophobic commercial products (H products), such as Wacker H, Keim H, Tegovakon H and Conservare H. Through the 1980s other water repellent components replaced MTEOS, such as dimethyl- and phenylsilicones that were added to ethyl silicate to make up RC80 and RC90 consolidants. The water repellent consolidants are used less frequently than their non-hydrophobic counterparts (Ohne Hydrophobie products so called OH, i.e., Wacker OH).

Other product currently used by conservators is Funcosil 500 STE that reduces both the brittleness of the gels formed from ethyl silicate and the brittleness that unmodified ethyl silicate impact on treated stone. This product does not appear to be used extensively in comparison to the Wacker OH 100 and other manufacturers.

In the studies of stone conservation, inorganic materials (as calcium, barium, sodium, titanium, lithium, aluminum hydroxides and hydroxyapatite) represented another evolution, employed only or combined with organic polymers (such as TEOS-based products) as consolidants. These compounds form inorganic salts which improve the binder properties of TEOS in calcareous limestones and sandstones [Lambropoulos *et al.* 2000, Laurenzi Tabasso 2002, Boriani *et al.* 2007, Sassoni *et al.* 2011, Murdock *et al.* 2012, Daniele *et al.* 2012, Messori *et al.* 2000, Naidu *et al*. 2012, Luvidi *et al.* 2012, Perez *et al* 2012, Sassoni *et al* 2012., Thorn 2012, Ziegenbalg-Piaszczynski 2012, Zornoza-Indart *et al* 2012].

In particular calcium and barium have been more studied than others. Here we report a brief summary of current researches dealing with either these materials, as overviewed by Doehne and Price [Doehne-Price 2010]. A saturated solution of calcium hydroxide was used to consolidate limestone because it easy penetrates into the stone and after water evaporation it is deposited into the stone. Calcium hydroxide reacts with carbon dioxide present in the air to produce calcium carbonate that leads to the hardening within the stone. Between the new products now commercially available there are nanoparticles of calcium hydroxide in alcoholic solutions (or suspensions) that permit their deep penetration into limestone surfaces and consequently a good consolidation.

Instead, barium compounds, even if chemically similar to calcium compounds and with the same characteristics, are employed as consolidants because of the insolubility of barium sulfate, compared to the sparing solubility of calcium sulfate. Therefore, barium sulfate was employed on calcareous surface for reducing damages due to the dissolution and recrystallization of calcium sulfate. In this context, after carbonation, a coating of barium carbonate is deposit, which will be more resistant than calcium carbonate to acidic rain, and they may serve to consolidate the stone through the formation of solid solutions of barium calcium carbonate [Lewin-Baer 1974].

The characteristics of barium treatments and the different application techniques on limestone and marble were studied by many authors [Schnabel 1992; Toniolo *et al.* 2001; Hansen *et al.* 2003, Bracci *et al.* 2008]. An application of barium hydroxide was proposed on wall paintings as pre-treatment before the application of ammonium carbonate to dissolve the calcium sulfate [Matteini 1991; Ambrosi *et al.* 2000]; while, barium oxalates and aluminates have been tested on calcareous stones and paintings [Messori et al. 2000, Matteini-Zannini 2004].

3. *Why this thesis?*

In this work we decided to study new chemical treatments and new method for strengthening and conservation of sandstones.

We have chosen this type of stone because its conservation is very difficult for the problems explained in the *par. 1*, and since XIX Century A.D., many scientists have proposed and tried different solutions for blocking its degradation (*par.2*).

Another important element that helped for the choice of this stone was its widespread all over the World and in particular in our country. Indeed, sandstone quarries are present in different part of Italy, in particular in the Alpine and Apennine layers: South Tyrol (Grödener Sandstone) [Franzen *et al.* 2000], near Pavia [Carò *et al.* 2002] and near Bergamo (Sarnico and Molera's sandstones) [Carlessi 2012], in Lunigiana and Parma lands [Di Battistini *et al.* 2003], near Bologna city and in Bologna Apennine. Little quarries are present also in Modena Apennine [for instance, Lugli *et al.* 2010], in Firenzuola (currently home of the only active quarries of Pietra Serena) [Gurrieri 2002, Massi 2002], in Fiesole (where the quarrymen took the stone for Florence buildings) [Gurrieri 2002, Massi 2002], other quarries were present in Marche, Umbria and Sardegna (near Alghero) Regiones. Each of these places is characterized by a specific type of sandstone that varies by its composition and genesis.

The sandstone samples used for our research came from Firenzuola quarries in Toscana (modern samples, natural ageing samples and historic samples were taken for laboratory analysis) and from local quarries present on the hills of the Modena district (historic samples preserved in Montegibbio archaeological site for outdoor analysis).

In the next paragraphs, I will present the situation of Italian sandstones and an example of architectonical diffusion of sandstone. We will extensively speak about chemical treatments chosen for the conservation of the sandstone samples in the chapter III. As anticipation, for the conservative treatments different commercially available ethyl silicates, used by only or combined with barium hydroxide in water solution, were employed. The choice of TEOS as consolidant agent is depended by the practice of its use and widespread in the restoration field [on its behavior: Wheeler 2005, 2008], while the combined use of silicate products and barium hydroxide was made by properties of this last compound that leads to the strengthening of the binders materials present into the stone with the formation of salts.

4. *Italian Sandstones*

Many works on Italian sandstone deterioration were reported in the literature, in particular sandstones from Lombardia, Liguria, Emilia Romagna and Toscana regions have been studied, because of their characteristic conservative conditions due to the natural petrographic composition. These contexts are important for creating new materials and techniques for restoration and conservation.

In Lombardia, the uses of different types of sandstone have characterized the building trade of this land for many centuries. The effects of the choices between Sarnico, Pavia, Flysh of Bergamo or Molera sandstones are visible in architectonical elements (cornices, doors, etc.) on the external facades of buildings and churches. Many of these ornamental pieces show the typical expressions of decay of sedimentary rocks (scaling, exfoliation, granular disgregation), which may lead to complete loss of the artistic motives [Carlessi 2012].

In Emilia Romagna, sandstone quarries were present in the south of Bologna: in the place called “alle Grotte”, in Santa Margherita al Colle and Barbiano areas. These materials do not show good characteristics like yellowish color, low cement and easy granular disaggregation.

Good materials were instead extracted in quarries across Via Emilia (i.e. Varignana, used since Medieval age), Reno Valley, Sasso Marconi, Monte Mario, Montovolo, Monte Vigese and Porretta (i.e. Madonna del Ponte, Costa, Puzzola, San Rocco) [Del Monte 2005].

Other sandstone quarries were present in Lunigiana (Liguria Region) and in Parma district (in Magra Valley); in these places, sandstones were extracted since Medieval age and employed to build towers, castles and churches or architectonical elements for these buildings. These quarries were characterized by Macigno stone (upper Val Magra), or similar sandstones (Monte Gottero), and turbidite sandstones characterized by quartz and feldspars composition with medium-fine grains (Monte Molino and Monte Cervarola) [Di Battistini *et al.* 2003].

Other little and local sandstone quarries were present in Emilia Romagna, mainly near the Apennine layer or across the rivers, where small pieces of sandstones are transported from mountain formations by natural erosion action. These stones were used for local buildings but, under environment conditions, they showed scaling, exfoliation, granular disaggregation and consequently, they had a short durability in the time.

For instance, there are two different types of sandstones employed in Montegibbio archaeological site (Modena): biocalcareous sandstones from Pantano formation emerged near the site and peat sandstones with fossil traces from Termina formation, which emerged under the Montegibbio's Castle (ca. 2 km far from the archaeological site) [Lugli *et al.* 2010].

In Toscana, two types of sandstones are mainly diffuse, Macigno stone and Pietra Serena, that they are extracted from Apennine layer.

A great number of historic monuments and buildings were made with these stones, as we can see in Florence, Arezzo, Siena and in other cities. These types of stones were employed also in some cities of Emilia Romagna, Marche and Umbria Regions, placed near Apennine layer where the quarries of sandstones are diffused.

In "*Istoria delle Pietre"*, Agostino Del Riccio speak about some Florence monuments and reports the place of origin of different sandstones used to build these monuments (such as Macigno, Pietra Serena, Pietra Bigia, etc.). For instance, he mentions the Macigno stone extracted at Fiesole quarries used for different architectonical decorative elements, like the columns placed in Santo Spirito, Santa Croce and San Lorenzo churches and in Mercato Nuovo in Florence. Also, Francesco Rodolico in "*Le pietre delle città d'Italia"* (1953) describes the position of these quarries in Fiesole hills, in the Mesola Valley, and near Maiano and Settignano [Massi 2002].

Pietra Serena sandstone employed in Florence was extracted at Gonfalina quarries near Signa, and at Montebuoni quarries, between Greve and San Casciano. At the moment, only the Firenzuola querries are used for the extraction of this type of stone [Massi 2002].

In outdoor environment, Pietra Serena and Macigno stone can easily deteriorate because of different causes (weathering agents, salts solutions, biological agents), and consequently they

show surface damages (cracks, scaling, exfoliation, granular disaggregation, etc.) and on artistic artifacts that employed these types of stones [Gurrieri 2002].

5. Architectonical diffusion. The Case of Florence

In Florence, only in XV Century A.D., the use of the Pietra Serena as material for building and architectural decoration began with the work of the architect Filippo Brunelleschi. He used this material for obtaining large monolithic columns employed in Ospedale degli Innocenti, and others architectonical elements for Santo Spirito and San Lorenzo churches.

In the introduction of the "*Vite",* Vasari described the different types of Pietra Serena and the different uses made until his time.

Vasari remembers that Brunelleschi employed Pietra Serena extracted at Fiesole quarries in all buildings he projected in Florence, including Santo Spirito and San Lorenzo churches. Instead, Michelangelo used Fossato Sandstone in the library and sacristy of San Lorenzo Church for Pope Clemente.

In Mercato Vecchio of Florence, Donatello employed Pietra Serena for creating Dovizia's sculpture [Massi 2002].

Moreover, Vasari remembers that in Firenzuola the use of extracted Pietra Serena only for public buildings was ordered by law [Massi 2002].

Also Agostino Del Riccio remembers that the Macigno stone of Fiesole was used in Gaddi Chapel into Santa Maria Novella and in the doors of Palazzo Ducale of Florence [Massi 2002].

In Florence, generally, Pietra Serena was employed in indoor environments, where it is more stable to weathering agents, and less subject to easy decay with respect to outdoor environments, like Michelangelo's sculptures in the library of San Lorenzo and Ammannati's stairway of Santo Stefano Church [Massi 2002].

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Chapter 1

SANDSTONES. GEOLOGICAL AND PETROGRAPHIC ASPECTS

1.1. *Fundamental properties: mineral and chemical composition, texture*

Sandstone is a clastic sedimentary rock formed by deposition of loose and incoherent granular materials called “Sands”, with grains size from 2 mm to 0.0625 mm [Pettijohn *et al.* 1987], and their subsequent compaction to create a coherent rock [Bargossi *et al.* 2002].

These sands have been formed by weathering on different kinds of rocks (magmatic, igneous and sedimentary). Thus, sandstone mineralogy depends on the composition of these sands made by minerals and rock fragments. Generally, this composition is in large part similar to source rock, but it can be modified by weathering actions, during transportation to the site of sedimentation and, in this last place, by diagenesis processes.

Knowing the mineral composition of sandstone provides information on origin of the grains or rock fragments (including tectonics and climate), on effects of transport (such as distance and direction), and on additional chemically-deposited minerals during sedimentation and diagenesis.

Mineralogical composition of a sedimentary rock is altered by weathering processes, which lead to disintegration into minerals and fragments detritus. For instance, feldspar may alter to kaolinite or intermediate products, while pyroxenes and amphiboles may dissolve and be transported as ions. Conversely, some minerals (such as quartz) are not soluble and they remain unchanged in amount and composition during transport.

The mineral transport, from the source area to the sedimentary basin, is made normally by wind and water actions, and only in the case of a sedimentary basin placed near to an active continental margins of the Earth's crust (orogeny processes), the deposition occurs by tubidity current effects [Bargossi *et al.* 2002]. Transport has two important effects: reduction of the sizes and shapes of minerals, and influence on the basin shape. In the first case, soft minerals present a higher degree in the dimension reduction compared to hard ones, and very soft minerals may not even survive as sand grains. In the second case, it is possible to find sands derived from the same source materials with different mineralogy and textural composition in different parts of the basin.

In a sedimentary basin the lithification and the diagenesis processes (i.e., consolidation, compaction and cementation) occur on sandy incoherent materials.

Lithification occurs over long time and only after this process the clastic sediments are compact and coherent enough to be defined sedimentary rocks. In the eves, the materials deposited in sedimentary basins in continuous mode give rise to new sedimentary sequences.

Diagenesis occurs during lithification, and consists in the drastically alteration of mineral composition through dissolution, precipitation or alteration. During this process unstable minerals may be completely or partially lost, while new components may be added by precipitation from solution, like carbonates.

Sandstones show a chemical composition that reflect the degree of maturity, i.e. the degree of evolution toward the stable final rock of the formation process. Chemical composition also reflects the mineralogical differences among the main groups of sandstones, the arenites and wackes, as well as the specific origin. Moreover, the mineral species in a sandstone determine its composition and characteristics, for instance, in the same rock minerals slightly soluble (i.e. detrital silicate) or completely soluble in water (i.e. chemical carbonates) can be present.

Also the surface appearance of sandstones is strongly influenced by mineral composition and consequently, one kind of stone can be identified by its color surface. In nature there are different cases such as: quartz arenites, that virtually contain only quartz, tend to be white or very light gray in color; sandstones rich in rock fragments and clay show different shades of gray, from greenish gray to dark gray; graywackes appear to be very dark. Instead, iron oxides confer reddish or brownish colors to sandstones, due to the presence of coatings of hematite or limonite on silicate grains.

A good summarization on the types, origin and characteristics of minerals found in sandstones was made by Pettijohn, Potter and Siever in the book *Sand and Sandstone* [Pettijohn *et al.* 1987]. They distinguished between detrital minerals, the main components of the sandstones derived by the source rock, and chemical minerals belonging to the environment of deposition and diagenesis.

Detrital minerals are silica, feldspar, mica, chlorite, clay, heavy minerals, and rock fragments.

Silica minerals are amorphous and polymorphous minerals based on silica crystals. Amorphous silica can be found in sandstones and may be derived by radiolarians and frustules of diatoms, opaline silica, silica glasses, cherts, or other materials. Instead silica polymorphs include low quartz (stable polymorph, and the most common mineral present in sand and sandstones), tridymite, and cristobalite (well-crystallized polymorphs, and rarely included in sandstones).

Quartz compounds are also distinguished in monocrystalline (made by single crystals) and polycrystalline (an aggregates of crystals) forms. This last includes quartz grains from igneous and metamorphic rocks, quartzite, sandstones and cherts.

The study of detrital quartz grains can lead to understand the type of weathering, fracture textures and specific transport agents, such as wind or glacial, that has occurred during rock formation. Quartz is also ubiquitous as chemical cement, almost everywhere deposited in optical continuity with the original detrital grains.

Instead, feldspars are abundant constituents of different sands and sandstones, and they can be divided in K-, Na-, and Ca-feldspars. Generally, K-feldspars (such as orthoclase and microcline, both with the same mineral composition, i.e. $KAlSi_3O_8$) are the most abundant in sandstones, while Na-feldspars (such as sodic plagioclases like albite, $NaAlSi_3O_8$) far outweigh calcic ones.

Orthoclase is found in all sandstones and its quantity is higher than microcline. Instead, microcline is characteristic of arkoses and feldspathic sandstones, especially those of continental block origin. Sodic plagioclases are the only feldspars present in many graywackes; aside from these, there are few sandstones with appreciable quantities of Ca-feldspars, such as anorthite, $CaAl_2Si_2O_8$. Feldspars with intermediate compositions between sodium and potassium silicate, sanidine ($(Na,K)(Si,Al)_4O_8$) and anorthoclase ($(Na,K)AlSi_3O_8$), are also found in sandstones.

The amount of feldspar found in a stones is related to: source rock composition, chemical weathering in the source area, abrasion and solution during the transport and solution and precipitation during diagenesis. The chemical conditions for the precipitation of feldspars are given by relative amounts of their components in solution (potassium, sodium and calcium ions; and also silica), by pH, and by reaction temperature. For instance, ions precipitation is influenced by a slightly elevated temperatures associated with moderate deep burial of the mineral sediments.

In the case of clay minerals, they are closely related in chemical composition (hydrated aluminosilicates) and crystal structure (sheet structures). These compounds are formed to micas (mainly muscovite and biotite), chlorite, and other minerals.

In sandstones it is often impossible to note any discontinuity in size between large flakes of micas and very fine-grained interstitial clay. In these stones, fresh or altered large grains of micas and chlorite are common, and normally they are a minor constituent in most sandstones, with an exception given by some shaly sandstone where they may be abundant [Pettijohn *et al.* 1987].

In turbidite sandstones, micas are associated to rocks generated in subsea deposits, where micas are abundant. Moreover, muscovite is much more resistant to chemical weathering than biotite or chlorite, while chlorite has tendency to degrade to finer particles than biotite, and it is frequently coupled with the fine clay fraction in sandstones. The alteration of biotite to chlorite is common, and often the pattern of this alteration is visible in a single grain [Pettijohn *et al.* 1987]. Also, biotite can alter to glauconite [Galliher 1939].

Clays are the essential constituent of the sandstone matrix and argillaceous rock fragments. They are classified in different groups on the basis of their structural and chemical composition, such as kaolin (kaolinite and others similar clay minerals), micas (muscovite, biotite, glauconite, and illite), smectite (montmorillonite and many others), chlorite, and mixed layer group. All these groups show a structure made by sheets of allumina octhaedra and silica tetrahedra.

Clay mineralogy is connected to source rock composition, climate and topography, environments and condition of deposition, and following diagenesis. The majority of clay minerals originate as subaereal weathering products of silicate minerals or as alteration of preexisting clays. All of the major clay groups are found in weathered residues and soils. This deposition is also influenced by interactions between climate, geomorphology, and source rock. For instance, feldspars and their silicates are altered to kaolinite in humid climates. Moreover, in the same environments are formed illite products.

In low temperature and pressure conditions, clay minerals are altered in water solutions. After few hours or days, chemical changes take place in the environment of deposition and the origin clay minerals will appear partly dissolved or precipitated. During this alteration, clays will absorb silica from solution in conjunction with cations to transform to somewhat different composition; these changes are strongly influenced by pH and as well as by activity of dissolved cations.

In sandstone can be found small quantities of heavy minerals and rock fragments.

Heavy mineral are composed by various silicates and oxides, such as tourmalite, zircon, amphiboles and pyroxenes. These minerals show different grains size distributions and resistance to decay. For instance, some have high resistance to mechanical and chemical attack as zircon, while others have little resistance to decay like amphiboles. Normally, heavy minerals are found in placer deposits.

In the case of rock fragments, they belong to argillaceous rocks (such as shale, slate, phyllite, and schist), volcanic rocks (including glass and pyroclastic debris), silica (i.e. quartz and cherts), and rarely carbonate rocks. Diagenesis process causes deformation, alteration and loss of rock fragments. For instance in older sandstones, argillaceous fragments are not identified as such because they blend into or appear as clay matrix. Besides, it may be possible that abundant argillaceous rock fragments in a sandstone indicate a nearby source of silt or clay.

Chemical minerals found in sandstones are carbonates, sulfates, sulfides, phosphates, iron silicates and oxides, zeolites and organic material.

Carbonates minerals are calcite, aragonite, dolomite, and iron-magnesium carbonates. These mineral derived by detrital and chemically precipitated.

Detrital carbonate is abundant in calcareous sands and its grains derived from source regions outside the basin are also found in some sandstones (i.e. molasse sandstone).

Instead, calcite and dolomite are abundant in sandstones as pore-filling and replacement cements of post-depositional origin. Some pore-filling cement may be recrystallized from originally detrital carbonate grains or may be a precipitate from an aqueous solution in an originally empty pore space. Moreover, the early diagenetic cement carbonate may include magnesian calcite, while the later diagenetic cements are relatively pure calcite and dolomite. Aragonite is not found as precipitated cement in ancient sandstones, though it is present in modern sands, probably because it was inverted to calcite during early or middle diagenetic recrystallization process.

Calcite may be derived by primary cement or recrystallized from earlier detrital origin, while dolomite appears almost always as a replacement of a calcite precursor. The difference lies in replacement textures and in crystal habit: calcite is anhedral, while dolomite is rhombohedral. Another difference is showed by the presence of stains in dolomite that indicates small amount of iron.

Moreover, some sandstones show abundant presence of iron-rich carbonates such as siderite ($FeCO_3$), ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$, found as concretionary accumulation), and rhodochrosite ($MnCO_3$, found in some concretionary forms but rarely in cements).

The precipitation of calcite and dolomite is primarily influenced by calcium and magnesium activities and pH, whereas that of the iron and manganese carbonates has an additional dependence on the oxidation-reduction balance environment. In carbonate minerals, iron and manganese can be found only in their reduced state.

In sandstone, common sulfates found as cementing agents are gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and barite ($BaSO_4$), while sulfides are represented by pyrite (FeS_2).

Gypsum is found as the first crystallized mineral in almost all natural environments. In a stone, the presence of gypsum or anhydrite depends on pressure, temperature and salinity conditions of environment. When one of these properties increases, gypsum will be converted in anhydrite. This change is predictable by relationship between volume and density of two minerals.

In the case of barite, it is a mineral with low solubility and its origin seems to be related to volcanism on the sea floor. In sandstones, it was found in concretions and cements.

Whereas, pyrite is a iron-sulfide that show in sandstones both detrital and diagenetic origins. Also, it is possible to find pyrite as constituent of the heavy minerals in most modern sands.

Phosphates are present in sedimentary stones where their presence is related to organic productivity. These minerals show a complex mineralogy made by hydroxides, fluorides,

carbonates, and phosphates. The main phosphate is calcium hydroxyapatite ($Ca_5(PO_4)_3OH$). In some sandstones, the precipitation of phosphates appears to be related to phosphatic bones or shells.

Moreover, in sandstones are present iron-rich minerals such as iron silicates and iron oxides.

Iron silicates are clay minerals rich in iron. The most common mineral is glauconite ($(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$), a mica related to illite in structure but with a higher amount of ferric ions, that is found in arenites (lithic and quartz) and in some other sandstones (as feldspatic sandstone). Instead, iron oxides are hematite (Fe_2O_3), limonite ($FeO(OH)\cdot nH_2O$), goethite ($Fe^{3+}O(OH)$), and lepidocrocite (γ-FeO(OH)). These are present mainly in red sandstones but also in lower amount in other sandstones.

The most likely origin of iron silicates and oxides in sedimentary environments is the diagenetic transformation of ferric hydroxide in water environments. The ferric hydroxide, when mixed with detrital clay minerals (such as chlorites or illites), may spontaneously reorganize and, if sufficient organic matter is present, may enter the clay mineral structure and form the iron silicate.

Other minerals can be present in sandstones such as minor compounds, i.e. titanium oxides and zeolites.

In the case of titanium oxides and iron-titanium oxides, they are found as minor components of the heavy minerals. These oxides are resistant to chemical and mechanical decompositions so they tend to persist for long times throughout the sedimentary cycle.

Zeolites are widespread and abundant in sandstones, especially those associates with voulcaniclastic in subduction zone environments. These minerals were found in hydrotermal alteration zones and hot spring deposits that affect surrounding sandstones.

Also organic material can be present in sandstones as biochemical precipitate characteristic of the environment which is altered by diagenesis. It derives from breakdown of plant and animal tissues in the sedimentary environment; later the decomposition products may be solubilized, transported and re-precipitated during stages of diagenesis. Generally, sandstones show small amounts of organic matter (less than 0.1%). Some graywackes are an exception and may contain up to several percent of organic matter.

On the bases of chemical composition, sandstones can be classified in [Pettijohn *et al.* 1987]:

1. *Quartz arenites* that show nearly pure quartz content, aluminum oxide (from clay) and calcium oxide (from calcite cement).

2. *Lithic arenites* that have a higher content in aluminum, ferrous and ferric, calcium, and potassium oxides (derived by argillaceous rock fragments).
3. *Graywackes* that show lower quartz than most of sandstones, more aluminum oxide, and dominance of sodium over potassium oxide and magnesium over calcium oxide.
4. *Arkoses* that have high aluminum, potassium, and sodium oxides contents (from the high amount of feldspars).

Texture is another important property of sandstones, it describes the granulometric characteristics of particles and pores that form a stone such as shape, roundness, surface features, grain size, and fabric.

Shape and roundness of a particles are employed for the study of the effect of the transport process on the debris came from the source area. These properties reveal the modification of angular grains of many shapes by abrasion, solution and current sorting.

Shape determines the ratio between surface area and volume of a grain. If this ratio is high, the grain will be entrained more easily by hydraulic forces acting on the surface and it will settle slowly. Shape is also defined by various ratios with a classification in long, intermediate and short particles.

Instead, roundness reflects abrasion history, which depends by different factors such as relief, kinds of source rocks, transport process and the mineralogy of the grains. In a stone the degree of rounding of a detrital particle depends on its size, physical characteristics and history of abrasion.

In the case of surface textures, it is the study of the great variety of microstructures that occur on sand grains, such as fractures of different shapes, striae, isolated depressions, and many others. All of these microstructures may be polished, weathered or fresh. Generally, this study is mostly applicable to environmental discrimination of modern sands.

The different dimensions between the grains that form a rock is called grain size. This property is studied by granulometric analysis where the different grains that form a sand or stone are separated by means of sieves with meshes of different sizes, in decreasing order.

Fabric is called the way in which the grains aggregate together. It is dependent on the currents that deposit large numbers of grains of different sizes, shapes and roundnesses, and on how the aggregate is then compacted by physical and chemical processes. Fabric is described by two parameters: grain contacts and orientation. Spatial distribution of grain contacts allows knowing the origin and ages of the cementing agents and diagenetic processes involving the formation of

the sandstone. Whereas, orientation of grains is related to the permeability and correlated with sedimentary structures of the stones.

Moreover, texture influences physical properties such as bulk density, porosity, crushing strength, and permeability.

Porosity is the ratio between the voids, i.e. portion of stone not occupied by its solid components, and the total volume of the solid material. Voids may either be connected or isolated. There are four types of porosity in sandstones [Pettijohn *et al.* 1987]: interparticulate (i.e. voids between framework grains, small detrital grains and/or dense authigenic materials), intraparticulate (within grains as in most authigenic clays), fracture porosity (such as micro- and macro-fractures), and solution porosity (related to the solution of framework grains or cements).

Porosity is reduced by mechanical compaction of the framework, pressure solution at points of contact and cementation, while it is increased by solution in depth and outcrop. This last is the pore system that permits sandstone to store and transmit fluid; the size, shape and pattern of this pore system is very difficult to specify owing to lack of geometric regularity and small size of pores.

Permeability of a rock measures its ability to be permeated by a fluid. This property is influenced by grain sizes, sorting, orientation and packing of framework grains, cementation, and bedding. For instance, permeability decreases with increasing grain thinness and poorer the sorting of loose sand, because of increasing internal surface area which increases the surface drag on the flowing fluid. Conversely, porosity increases with better sorting because fewer small grains occur between the larger grains. In ancient sandstones, porosity and permeability distribution depend on depositional process.

In a sandstone, orientation and packing of the framework grains show a weak control on permeability in the plane of the bedding but a strong control in sections perpendicular to bedding. Permeability is also influenced by bedding, i.e. when a slight pauses in sand deposition is present, grain fabric and laminations inhibits the vertical flow of fluid. Thus grain orientation imparts weak anisotropy to permeability in the plane of the bedding. As a consequence, permeability is a directional property and is correctly described in three dimensions.

In sandstones permeability is also influenced by the drag of the fluid on the walls of the pore system and by the path length that fluid must flow to go between any two points in the sandstone.

1.2. *Petrography of common sandstones*

On Earth many different sandstones types exist, and they can be distinguished in two main groups (arenites and wackes) and in their subgroups on the bases of mineralogical composition and matrix/cement ratio. This classification depends on source rocks and all the phenomena that influence the grains after weathering, such as transport, environment deposition and diagenetic processes. Thus, it is possible find the origin and tectonic of source rock knowing the mineral composition of the grains present in a sandstone [Pettijohn *et al.* 1987].Therefore, sandstones are classified in:

1. *Arenites*, with less than 15% of matrix:
    a. *quartz arenites*, that show a content of feldspar and rock fragments less than 5%;
    b. *feldspar arenites*, that contain more of 5% of feldspars and rock fragments, such as:
        - *arkosic arenites*, with 25% or more feldspar and a smaller percent of rock fragments;
        - *lithic arenites*, with 25% or more of rock fragments and lower amounts of feldspars.

2. *Wackes*, with more than 15% of matrix:
    a. *subgreywackes*, with a matrix content between 15 and 50%;
    b. *greywackes*, between 50 and 75%;
    c. *pelites*, with matrix higher than 75%.

Pettijohn, Potter and Siever in their book *"Sand and Sandstone"* [Pettijohn *et al.* 1987] have described the principal families of sandstones and some of the more important species present in each group. Also they have pointed out some of the problems of origin of each group, to summarize what is known about their relative abundance and the principal theories on sandstone petrogenesis. They have grouped sandstones into genetic classes, namely those based on maturity as expressed by composition and sorting: *immature sandstones*, that are those closest in composition to the parent rock; *mature sandstones*, which are nearest at theoretical end-product; various hybrid types (such as tuffaceous sandstones or hybrid types with a significant fraction of sand formed by chemical or biochemical process); few rare types of sand which do not fit readily in any of the above categories.

A brief summary of the descriptions of sandstones families is reported in the next paragraphs.

1.2.1. *Quartz arenites*

Quartz arenites are the most common and best known type of sandstones. They are sands with more than 95% of quartz content in the detrital fraction and less than 5% of other constituents.

These arenites are generally white rocks, but some exhibits pink or reddish coloration due to a film or coating of hematite on the grains. In this case, the iron oxide content represents a small amount of the rock.

Quartz arenites possess sands with excellent sorting, where the quartz grains are characterized by high roundness, that in some cases approaching perfection. Other constituents of these stones are heavy mineral (such as tourmalite, zircon and rarely ilmenite), and grains of chert or other equally durable rock particles, these latter may be the clue to the provenance of the stone.

The chemical composition of quartz arenites may be altered by the addition of the cement. The silica-cemented sands are not so altered, but those with calcite or anhydrite will show a silica percentage depressed by the addition of calcium oxides, carbon dioxide and sulfur trioxide. Silica is the most common cementing agent, but there are some quartz arenites cemented with other forms of silica, such as opal or chalcedony or both.

Some quartz arenites exhibit carbonate cement, such as calcite, siderite and dolomite. Other cements made by anhydrite, barite and celestite have been found, but they are much less common of the other types. In the case of barite, the quartz grains enclosed in this cement show markedly less corrosion than those cemented with carbonates.

Quartz arenites are sandstones almost pure in silica content (Qz > 95%), consequently the only possible distinction can be made on the kind of cement they contain. Moreover, it appears very difficult to distinguish between quartz arenites derived directly from a plutonic sources rock and those derived from pre-existing sandstones.

Quartz arenite are found in many places of the world, such as North America, Europe and Africa. In Europe the main quarries are in Sweden (Hardeberga Sandstone), England (Malvern Quartzite), Germany (Sandstones of Harz), and France (Fontainebleau Sandstone); while in Africa, quarries are present in Egipt (Nubian Sandstone).

1.2.2. *Arkose*

Arkose includes sandstones that contain 25% or more of feldspars, which can be derived from disintegration of acid igneous rocks of granitoid texture. These stones are made by a coarse-grained rock and have a pinkish to reddish color, due to feldspar amount, or in some cases white or gray color, from granitic or gneissic rocks containing gray or white feldspar.

The mineral constituents of this class of sandstones are quartz, feldspars, mica and clay (usually kaolinitic). The dominant mineral of this group is quartz that shows irregular and poorly rounded grains. Exceptionally, feldspar may exceed quartz in volume, and it is present as K-feldspar (microcline), from extremely fresh to weathered. In arkose with carbonate cement, the feldspar may show varying degrees of replacement. Other minerals found in arkoses are micas, both muscovite and biotite. The mica flakes tend to lie parallel to the bedding and hence to one another, and they may be bent or deformed by pressure or adjacent grains. Biotite may show chloritization or more commonly, alteration and oxidation.

Some arkoses sandstones contain clay matrix (such as kaolinitic and ironstained), while other varieties have little quantities of such matrix and are generally carbonate cemented.

Arkose is a chemically homogeneous group, that is rich in aluminum and potassium oxides, the latter generally exceeding to sodium oxide. Most of these stones have an excess of ferrous and ferric oxides, while those with a carbonate cement have high values of calcium and carbon dioxide.

Arkoses sandstones can be distinguished in arkosic arenites, with little matrix, or arkosic wackes, with significant clay contents. Some of the latter are produced by the in-situ disintegration of granite and related rocks.

Residual arkose is another group, that may contain more quartz than normally found in granite. Many of these stones contain an abundant clay-rich matrix, and an example is given by redstones that show a deep red-stained matrix.

Arkoses with a prominent matrix are probably sedentary or residual or a product of limited transport, others may be the result of post depositional alteration that can be an important part of the diagenesis of continental bend. So altered arkosic sands show pseudomorphs of kaolin after feldspar.

Older deposits of arkosic arenites may show normal mineral cement precipitated in the pore system. Usually this cement is made by calcium carbonate, which may marginally replace or embay the framework grains. In these arkoses the grains may be characterized by good rounding.

In addition to the textural variations, which distinguish the arkosic wackes from the arkosic arenites, there are mineralogical variation in the composition of the framework components. Arkose is the product of disintegration of granite, i.e., a coarse-grained plutonic rock of which K-feldspar is the dominant or at least the major constituent. Some volcaniclastic sands resemble arkose in external appearance although they contain little feldspar. These sandstones are derived from extrusive and intrusive rocks erupted from vulcanoes, where the more acidic flow provides an undue share of the debris from such regions.

Arkoses form no more than 15% of all sandstone. For instance, two kinds of arkoses are Molasses sandstone from Switzerland, which shows a granitic source and contains between 50-60% of feldspar [Gasser 1968], and Old Red Sandstone of Scotland that contains up to 60% feldspar [Mackie 1899].

1.2.3. *Lithic arenites*

Lithic arenites (or litharenites) have light gray color and 25% or more of rock fragments and lesser amount of feldspar.

Of all sandstones, litharenites show the greatest diversity on both mineralogical and chemical composition points of view. This variability reflects the importance and relative abundance of the diverse rock particles, which these sands may contain. If the rock particle content is small, these sands pass over into the quartz arenites or orthoquartzites. However, rock particles may form more than half of the framework, and in few rare cases all of it.

Rock particles of litharenites are themselves diverse and belonging to volcanic rock (i.e. particles of extrusive rocks), metamorphic rock (that include slate, phyllite, and mica schist), and sedimentary rock (such as various kinds of shale, siltstone, argillite, pelitic material, some detrital chert and, in some cases, micritic limestone and dolomite. Also, there are sandstones in which chert and micritic limestone become dominant).

The unique character of the lithic sandstones (volcanic arenites excluded) is due to abundance and variety of sand-sized particles of pelitic derivation such as shale, siltstone, slate, phyllite and mica schist.

Litharenites have a main mineralogical composition made by quartz as dominant and detrital component (from sedimentary, low-rank metamorphic and volcanic rocks). Quartz can be derived by disintegration of older sandstones that show original rounded detrital grains; or in some cases by some metamorphic rocks. Particles derived from this source will contain little feldspar. Another significant constituent of litharenites is detrital mica, both biotite and muscovite, the latter being the most common.

The lithic arenites may be cemented either with carbonates or with silica or both. Little or no matrix material is present, though some of the weaker argillaceous rock particles may be deformed between adjacent harder quartz grains in such a manner as to resemble a matrix filled pore. They appear to fill some pores, and the matrix would be distributed among all pores.

Mineral charcoal and carbonaceous plant fragments are common in younger lithic arenites. While, shale pebbles may be present.

Chemical analysis of litharenites indicates high values of aluminum and potassium oxides (such as in the case of pelitic particles), low values of sodium and magnesium oxides, and high amount of calcium oxide and carbon dioxide. In these arenites, chert or micritic limestone particles are dominant and show respectively an unusual quantity of silica or calcium oxide and carbon dioxide. A high calcite content can denote a calcite cement rather than limestone detritus, while high value of magnesium oxide is due to detrital dolomite.

The silica content is depressed by addition of carbonate cement or by the abundance of detrital limestone and dolomite particles, and is augmented by added quartz cement or by the abundance of detrital chert.

Some special types of lithic arenite are:

a. s*chist arenites*, with dominant metamorphic rock particles (as phyllite and mica schist);
b. *chert arenites*, where the detrital chert grains form a considerable or even the major part of the sands detritus. Chert sands are more inclined to diagenetic change than quartz, because of the higher solubility. Moreover, chert is more susceptible to carbonate replacement than quartz. In general, chert is derived by sedimentary rocks but there are also cherts with volcanic affinities, as an alteration product of volcanic glass;
c. *calclithites*, sandstones in which detrital carbonate is derived from preexisting carbonate rocks, and it forms a large and significant part of the rock. Detrital carbonate occurs in modern sands, and it is found rarely in ancient sandstones.

Lithic sandstones are immature sands and their composition reflects their provenance. Moreover, they are very common and widespread in each age. For instance, Lower Old Red Sandstones from England [Allen 1962] and Molasse sandstones from northern Alps (as those extract by Swiss quarries) [Füchtbauer 1964] are litharenites.

1.2.4. *Graywackes*

Graywackes are dark gray or black and well-indured stones, with a matrix that is included between 50 and 75%.

The matrix is the essential characteristic of these stones and it is attributed to transport and deposition of the sediments. Many graywackes show turbidites origin, where, the deposition of sand and suspended mud were made by turbidity currents action in sedimentary basins. The matrix of these stones is made by recrystallized material and it consists of chlorite, serecite and quartz in the oldest graywackes, and zeolites and montmorillonite in the youngest ones.

Graywackes show a mineralogical composition rich in quartz, with a varying proportion of feldspar and rock particles, and little detrital mica. Quartz is varied in size and shape and it is quite angular. Usually, it constitutes half or less of the sand fraction. Instead, feldspar is largely sodic plagioclase (albite), while K-feldspar may be completely absent. These minerals are generally fresh, and some contain inclusions such as chlorite.

Rock particles are mudstone, shale, siltstone, slate and argillite, phyllite and mica schist. Also, chert, micritic limestone, polycrystalline quartz and fine-grained quartzite may be present in large amount. Many graywackes contain particles of fine-grained igneous rocks, some with microlites of feldspar. For instance, common are acid igneous flow of rocks, whereas less common is andesitic debris and rarely is found serpentine ($Mg_3(Si_2O_5)(OH)_4$).

Detrital micas, both biotite and muscovite, are common though not abundant constituents. Minor accessories minerals include carbonates (probably iron-rich such as ankerite, $Ca(Fe^{2+},Mg,Mn)(CO_3)_2$), sulfides (as pyrite), and also some rock particles and feldspar grains. Graywackes are bound by fine-grained matrix consisting of an intimate intergrowth of chlorite, and minute silt size particles of quartz and feldspar. This content seems to be linked with the size of sand fraction.

The graywackes are a chemically homogeneous group, rich in aluminum oxide, ferrous and ferric oxides, sodium oxide and magnesium oxide. The high value of magnesium and ferrous oxides are related to the chloritic matrix.

There are different types of graywackes, such as: lithic graywackes, rich in rock fragments; feldspatic graywackes, rich in feldspar; volcanic graywackes, poor in quartz and rich in volcanic compounds and with an appreciable content of ferromagnesian minerals; Fischer, i.e., graywackes abnormally rich in quartz and lacking feldspar.

In 1970, Crook recognized three major classes of graywackes on the basis of their different provenance [Crook 1970]:

a. *quartz poor* (Qz < 15%), that owns volcanic provenance by island arc environment;
b. *quartz rich* (Qz > 65%, often near 80%), which shows sedimentary provenance from tectonically inactive continental margins;
c. *intermediate class* (15 < Qz < 65%), with a mixed provenance from tectonically active margins of continents or microcontinents.

Graywackes are found in many different places of the world, for instance in England (Walles, Cornowall and Devon) and Scotland. Also, graywackes are found in Italy along the Apennines, and some of these stones are Pietra Forte and Pietra Serena from quarries in Toscana Region.

1.2.5. *Hybrid sandstones*

Hybrid sandstones are formed by sands in which a significant proportion of the framework shows another origin, such as formed in basin or deposited by chemical or biochemical precipitation or produced elsewhere by volcanic action. Examples of these stones are greensands (such as glauconite), phosphatic sandstones, calcarenaceous sandstones, and tuffaceous sandstones.

In the case of greensands, they contain over 50% of glauconite (that normally occurs in some nearly-pure quartz arenites), less mature feldspathic, and micaceous sands. Greensands show high variable composition which depends on the ratio between clastic material, interstitial calcite and secondary siderite. These sandstones are characterized by high values of iron oxides (ferric oxide) and potassium oxide.

Phosphatic sandstones are characterized by sand cemented by calcium phosphate or sandstone that contain an appreciable amount of phosphatic debris, precipitated granules or oolites of phosphate. In these sandstones, phosphate compounds may be mixed in different ratio with detrital quartz.

Calcarenaceous sandstones consist of a mixture of detrital quartz and sand-sized chemical or biochemical carbonate. Thus, these sandstones exhibit a mineralogical composition made by carbonate detritus (as foraminiferal tests, shell and other skeletal fragments), carbonate intraclasts, pellets and carbonate oolites, mixed in different proportion with quartz and other epiclastic debris. The cement is given by calcite.

Tuffaceous sandstones were formed by erosion, reworking and redistribution of pyroclastic materials, such as tuff. During the redeposition, this vulcanic debris may be mixed with other sands in all proportions to produce hybrid rock or tuffaceous sandstone. Tuffaceous stones contain minerals rare in ordinary sands, such as olivine and pyroxene, and show low quartz content.

1.3. *Stone samples: Italian quarries*

In the previous paragraph, we have seen that different sandstones are widespread in many part of the world, from the Americas to Asia, from Europe to Australia and Africa.

In Europe there are sandstone quarries in most countries, both the northern and the southern parts of the Continent, such as England, Scotland, Sweden, Spain, France, Belgium, Germany, Switzerland, Italy, Albania, Turkey, and others.

In the case of Italian sandstones many works are reported in literature, in particular sandstones from Lombardia, Liguria, Emilia Romagna and Toscana regions have been studied for their mineralogical, chemical and mechanical characteristics and for their conservative conditions due to their natural petrographic composition.

Since the antiquity, in our Country these stones have been used for buildings and to make architectonical elements both for the great abundance of quarries in different places and for ease of extraction and working.

Quarries can be found in many places, in particular along Alpine and Apennine chains. Often, each of them show a specific type of sandstone with different composition and genesis, for instance Grödener sandstone from South Tyrol [Franzen *et al.* 2000], Sarnico and Molera sandstones in Lombardia region [Caro *et al.* 2002; Carlessi 2012], Lunigiana sandstone in Lunigiana and Parma lands [Di Battistini *et al.* 2003], Pietra Serena in Tuscan-Emilian Apennine (in particular from Firenzuola quarries) and Macigno sandstone in Tuscan Region (from Fiesole city) [Gurrieri 2002, Massi 2002]. Other sandstone types are known in quarries from Emilia Romagna, Marche, Umbria and Sardegna (near Alghero) Regiones.

In the case of Lombardian sandstones, the use of Sarnico, Pavia, Flysh of Bergamo or Molera sandstone has characterized the building trade in this land for many centuries [Carlessi 2012].

In Emilia Romagna, sandstone quarries are present in the lands at south of Bologna (such as “alle Grotte”, Santa Margherita al Colle and Barbiano areas), but these stones do not exhibit good characteristics: they have yellowish color, low cement and show easy granular disaggregation. Instead, good materials are extracted in quarries near Via Emilia and in Apennine, like Varignana, Reno Valley, Sasso Marconi, Monte Mario, Mont’Ovolo, and Monte Vigese [Del Monte 2005].

Pietra Serena is extracted in many places along Apennine chain of Emilia-Romagna, such as Porretta (Madonna del Ponte, Costa, Puzzola, San Rocco) and Sarsina quarries [Del Monte 2005].

Other sandstone quarries are present in Lunigiana (Liguria Region) and in Parma district (in Magra Valley) and they are characterized mainly by Macigno sandstones (upper Val Magra), or

similar sandstones (Monte Gottero), and turbidite sandstones characterized by quartz and feldspars composition with medium-fine grains (Monte Molino and Monte Cervarola) [Di Battistini *et al.* 2003].

Little and local sandstone quarries are present in Emilia Romagna, mainly near the Apennine layer or across the rivers, were small pieces of sandstones are transported and taken out to the mountain formations by natural erosion action. For instance, sandstones employed in Montegibbio archaeological site (Modena) showed local provenance, and they consisted of two different stone types: biocalcareous sandstones from Pantano formation (emerged near the site), and peat sandstones with fossil traces from Termina formation (which emerged under the Montegibbio Castle, ca. 2 km after the archaeological site) [Lugli *et al.* 2010].

In Toscana region, two sandstone types are mainly diffuse, Macigno sandstone and Pietra Serena, extracted from the Apennine chain.

These stones have been employed in the past ages to build many historic monuments and buildings in Florence, Arezzo, Siena, and other cities. Also, these types of stones were employed in some cities in Emilia Romagna, Marche and Umbria Regions, placed near Apennine's layer where the sandstone quarries are diffuse.

Macigno sandstones are extracted in quarries on Fiesole hills, in the Mesola Valley, and near Maiano and Settignano, while, in the past Pietra Serena was extracted from Gonfalina quarries near Signa, and from Montebuoni, between Greve and San Casciano. At the moment, only Firenzuola quarries are used for the extraction of this type of stone [Massi 2002].

The sandstone samples used for our research come from Firenzuola quarries in the Toscana Region and from local quarries present on the hills of the Modena district.

In the next paragraph, we present the situation of Pietra Serena of Firenzuola, discussing the genesis, characteristic and decay, while examples of architectonical application were reported in the last paragraph of preface (the case of Florence).

1.4. *Firenzuola quarries: genesis, petrography formation, physical-chemical and mechanic characteristics of Pietra Serena and its deterioration*

1.4.1 *Genesis and petrography formation*

Firenzuola sandstone is a coherent sedimentary rock made by consolidation of incoherent materials (such as fragments, clasts, grains) called “Sand” for their dimensions, from 2 mm to 0.0625 mm [Pettijohn *et al.* 1987]. These little materials were deposited in sedimentary basins by

tubidity current effects and in the time, through "lithification" processes (consolidation, compaction, cementation), they form a compact sedimentary rock. In the eves, the materials transported in the sedimentary basins in continuous mode, will give rise to new sedimentary sequences [Bargossi *et al.* 2002].

Northern Apennines is formed by sedimentary rocks, mainly turbidite sandstones with multi-layers structures that suggest a temporally sequence of deposition (lithostratigraphic unit or "Formation"). Firenzuola sandstone is part of Marnoso-Arenacea Formation. Its sediments were deposited since Langhiano (ca. 17 million years ago) in a sea basin depth, with length of 200 km in NO-SE direction and width of 50 km. This basin occupied the actual northern and central Apennine, in correspondence of the strip of land from Piacenza to Perugia. The layers of this formation are exposed from Santerno Valley (near Imola) till Perugia, while they are covered by other formations across the northern part [Bargossi *et al.* 2002].

In Marnoso-Arenacea Formation, the sedimentation was continuous until Tortoniano (ca. 7 million year ago) when it stopped due to the closing of the basin. The Formation became ca. 3000 m high and the sedimentation lasted ca. 10 million of years.

Each single turbidity event shows a layer that consists in a coarse part of sandstone and in a fine part of pelite, in different ratio between them, but always with pelite layer above sandstone one. Sometimes pelite is little or absent. Also, the pelite layer is formed by a fine carbonatic part and thus takes the name of "marna" [Bargossi *et al.* 2002].

The main layer of Marnoso-Arenacea Formation is the "Contessa layer", locally called "Alberese" o "Colombio". It is a layer of thick turbidite made by a sandstone part, with a thickness of 5 m below, a marnosa part of 8-10 m above, and Apennine debris.

Pieces of sandstone debris are composed by different minerals, such as quartz, feldspars (orthoclase and plagioclase), micas (muscovite and biotite), carbonates (calcite and dolomite), and fragments of metamorphic and magmatic rocks [Bargossi *et al.* 2002].

1.4.2. *Petrography, physico-chemical and mechanic characteristics of Pietra Serena*

The major parts of information on characteristics of Pietra Serena come by studies of ancient and modern authors, and by modern scientific analysis (such as chemical and mineralogical) and mechanical tests.

Firenzuola sandstone is a feldspathic greywacke with clay matrix and low calcite content. It shows a medium and fine grain-sizes, and cerulean color that appears more dark in the case of Colombino sandstone.

Benvenuto Cellini in his book "*Della Scultura*", remembers the cerulean color of this stone, its working ease, and use to produce architectural elements [Massi 2002]. Giovanni Battista Tozzetti, in the "*Relazioni*" books, describes the color of the just-extracted stones. He says that the original block of stone exhibits a central part with cerulean color, identified as Pietra Serena, and an outside part with different grades of tobacco color, identified as Pietra Bigia [Massi 2002].

Also Leon Battista Alberti in the "*De Architectura*" observes the characteristics of sandstones employed in ancient buildings, such as color, compactness, hardness and resistance in situ under weathering agents. For instance, he remembers that if the stone shows a small number of veins, it will be a healthy and durable stone, while if the stone exhibits a large number of veins, it will be weakly compact with little durability [Massi 2002].

The mineralogical composition of Pietra Serena shows mainly quartz and feldspars, low rock fragments and low-medium amount of carbonates. An exception is Colombino sandstone that shows high value of carbonates (about 70%), thus it is identified as calcarenaceous sandstone [Bargossi et al. 2002].

In Pietra Serena an impurity made by a little white layer of limestone is often present, which makes the stone less durable and may cause its rupture.

Firenzuola sandstones can be classified as medium-heavy stones, on the basis of the ratio between volumetric bulk and absorption coefficient. Colombino sandstone, on the other hand, is heavier and exhibits lower absorption than other types, which are lighter and show higher absorption or present intermediate mechanical properties [Bargossi *et al.* 2002].

The study on mechanical properties of Firenzuola sandstones made by Bargossi, Gamberini and Paganelli for the book *"Pietra Serena. materiali della città"* [Bargossi *et al.* 2002] shows the agreement between the results of compressive strength, flexion and abrasion tests, and compactness and degree of cementation of the sandstone matrix.

Colombino exhibits the best mechanical properties than the other sandstones studied, but it has low microhardness due to the presence of carbonate in its mineralogical composition. Also, this type of stone shows a low value of the linear thermal expansion coefficient, as all sandstones with carbonate matrix. Instead, sandstones formed by quartz and feldspar exhibit high values of microhardness [Bargossi et al. 2002].

1.4.3. *Degradation*

Already the ancient peoples individuated in the water action the main cause of deterioration of Sandstone.

In the introduction of the *"Vite"*, Vasari speaks about the deterioration of Pietra Serena in outdoor environments under weathering agents (such as rain, ice, humidity, etc.). Also, he says that this stone is more durable in indoor environments. Likewise, Del Riccio talks about the weak resistance of sandstones in outdoor environment, and remembers that this stone resists only if covered and not exposed to weathering water. Also Tozzetti, in the *"Relazioni"* books, traces a complete profile on deterioration of Pietra Serena due to water action [Massi 2002].

During winter, after water absorption due to rain and humidity during summer, Pietra Serena undergoes freezing-thawing cycles and consequently, the stone is subject to increase and decrease of the volume. In the time, in the surface layer, this phenomenon creates scaling, flaking, exfoliation, granular disaggregation, and cracks.

The sandstone degradation may be due to different factors such as weathering, environmental (wet-and-dry cycles, freezing-thawing cycles, humidity, temperature, biological activity, salts transport, etc.), and pollution actions. All of them produce different types of damages like scaling, flaking, exfoliation, granular disaggregation and cracks, formation of black-crusts, formation of efflorescences or inorganic salts made by weathering agents (such as water, wind, ice, etc.), vegetal actions (lichens, musk, bacteria), temperature and humidity changes or pollution agents (NO_x, SO_x and CO_2).

Firenzuola sandstones have a clay matrix with low cement (calcium carbonate) and a structure made by parallel laminations. Therefore, the decay of the clay minerals depends also on chemical phenomena due to acidity of the water absorbed. This water reacts with atmospheric CO_2, and consequently the carbonic acid solubilizes the small quantitative of calcite present in the rock that precipitates when water evaporates. The result of this reaction is the formation of a structural discontinuity and/or exfoliation on the stone.

The protective systems to prevent or reduce water deterioration actions consist in hydrorepellent solutions applied on the stone surface, aiming to limit the water absorption capacity [Massi 2002].

1.5. *Restoration: influence of the stone type on consolidation treatments*

Restoration actions on deteriorate sandstones are intimately connected with the mineralogical and chemical nature of the stone type. A consolidating agent may show different results on the basis of composition of stone types on which it is applied. For instance, calcite and quartz powders consolidated with neat methyltrimethoxysilane (MTMOS) show fully consolidation of the fine quartz powder, while calcite powder remains unconsolidated [Charola *et al.*1984].

In the same way, purely calcite limestone and quartz-rich sandstone treated with MTMOS show a rapid evaporation of reagent in limestone after the treatment, while sandstone retains a small amount of alkoxysilane (about 24%) during gelation. Thus, in limestone traces of consolidation are not found because calcite slows the condensation or silicate-bond forming reactions more than the hydrolysis or silanol-forming reactions.

Quartz and calcite stones are considered to possess "acid" and "basic" surfaces, which, could produce more or less condensed gels in contact with alkoxysilane solutions that in turn may have different consolidating abilities [Wheeler 2005].

Laurie was the first to observe the influence of stone mineralogy on the nature of alkoxysilane-derived gels; he understood that acid and base catalysis produces gels of different structures. Indeed, he have found that if the silicic ester is slightly acid before it begins to hydrolyze, the hydrate silica which was deposited from a hard glassy layer is an excellent preservative or cement layer within the pores and on the surface of the stone. While, if the silicic ester is slightly alcaline, the hydrate silica is deposited as a soft gelatinous precipitate, useless as a cement or preservative. Limestone and calcareous sandstone are generally sufficiently alkaline to render the silicic ester alkaline and so make precipitate soft and useless [Laurie 1926, Wheeler 2005].

Many years later, Goins has made similar observations for uncatalyzed MTMOS reacting in the presence of sandstone, marble and limestone. She observes that the gels formed on the silicate mineral substrates appeared more suitable as consolidants than those gels formed on calcium carbonate substrates. [Goins 1995, Goins et al. 1996, Wheeler 2005].

The stone conservation literature shows linkages between alkoxysilane-derived gels and silicate minerals such as quartz. For instance, correlation between some alkoxysilanes and different mineral surfaces (such as quartz, feldspars, micas, calcite, and gypsum) from granite, sandstone, limestone, and marble have been studied [Elfving and Jäglid 1992].

The reaction of the alkoxysilane takes place in the presence of each mineral in form of powder. After the reaction, excess liquid is removed by filtration and the powders evacuated. The evacuation further removes excess starting materials and reaction products not attached to mineral surfaces. In the case of silicate minerals, the alkoxysilane is attached to mineral surface, such as quartz and albite; while on muscovite the higher number of OH groups condenses with alkoxysilane [Elfving *at al.* 1992].

The results of the studies on interactions of alkoxysilanes with sandstones and their main mineral constituents, for example quartz, are summarized by Wheeler [Wheeler 2005]. He says that for quartz and other silicate minerals commonly found in sandstones, different solutions reagents create conformal and relatively smooth gel coatings (for instance MTMOS, water, methanol or

catalyzed, partially polymerized TEOS formulations). In some instances bridges are formed among mineral grains and the surrounding matrices; alkoxysilane (such as trimethylmethoxysilane or TEOS) and silicate mineral substrate such as quartz, feldspars and, to lesser degree, micas. The consolidation reactions of uncatalyzed MTMOS solution in water and methanol are slightly reductive in the case of quartz, and with neat MTMOS evaporation do not show any effects. Gel formed from these solutions in the presence of quartz powder and sandstone are initially stronger and more coherent.

In sandstone restoration, another problem is represented by hydraulic swelling and shrinkage of the surface layers in clay-rich rocks [NORMAL 1/88; Wendler 2000]. For instance, after a brief rain the wet surface of clay stones swells while its interior remains dry. These effects are found in corners of the stones [Doehne *et al*. 2005]. Important studies on clay swelling of Portland brownstone have discovered that shear forces can cause buckling of wetted stone surfaces and that intracrystalline swelling of clay is the primary mode of swelling, despite the proportion of swellable clay is only 1 percent of the stone. Thus, the clay is present as cement at sand grain boundaries, permitting the clay sufficient leverage in brownstone [Duffus *et al.* 2008; Wangler-Scherer 2008; Jiménez Gonzalez *et al.* 2008; Doehne-Price 2010]. Also, soluble salts have a role in the decay of this stone type because, in some cases, they increase the swelling of clay minerals [Doehne-Price 2010].

Consequently, often clay-rich sandstones have need of consolidation treatment.

Clays with their abundant OH groups offer receptive surfaces for alkoxysilane, where this last is deposed on mineral rich in Si-OH bond, such as muscovite. In the case of ethyl-silicate, such as Wacker OH, it provide only a little consolidation to fine powders of illite clay or other phyllosilicates (which chlorite, muscovite, biotite). Many studies were made on different types of alkoxysilane employed in the consolidation of clay-rich sandstones, such as Wacker OH, Wacker H, Brethane and many others [Wheeler 2005]. They give different results, but it can be said that clays appear to reduce that performance on sandstones. Some clay-bearing sandstones are exposed to a higher risk to wetting and drying deterioration after treatment. The different structures of clay minerals may have an influence, which cannot be determined from the current stone conservation literature [Wheeler 2005].

Other two important factors in consolidation are darkening and color change of treated stones. These phenomena occur in all porous materials when they imbibe liquids because air/mineral interfaces are replaced by liquid/mineral ones. Under these conditions the refractive index of the liquid is higher than that of air. This phenomenon is visible when stone becomes wet with rain and appears darker. When liquid consolidant is applied, the process of darkening appears as

described above, where the liquid eventually turns to solid, and even if pores are filled or coated the darkening remains [Wheeler 2005].

The degree of color change and darkening depends on the degree of minerals present in a stone. Light colored minerals (such as quartz, albite and calcite) are much less affected than dark minerals (which red iron oxides, biotite, illite, clinochlore) [Wheeler 2005].

Alkoxysilane gels preferentially deposit in fine pores and can fill and coat them, resulting in darkening. The fine matrix of some sandstones, often composed of clays and iron oxides, will also darken with treatment [Wheeler 2005].

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Chapter 2

SANDSTONES CONSERVATION: AN ANALYTICAL APPROACH

2.1. *Sandstones conservation issue*

Generally, sandstones are deteriorated by weathering agents, but there are many other decay causes which may occur separately or at the same time. Some of these are sudden and rapid in their effects (i.e. earthquake, fire, vandalism, flood, and terrorism), while others are slow and more insidious (such as frost, temperature fluctuations, chemical attack, salt growth, pollution, biodeterioration, and so on) [Doehne-Price 2010].

Sandstone deterioration is due to physical-chemical and biological factors (like weathering agents, vegetal actions, temperature, humidity changes, or pollution agents), that produce many different kinds of alteration on the stone such as scaling, flaking, exfoliation, granular disaggregation, cracks, and formation of black-crusts, efflorescences, and inorganic salt [NORMAL 1/88, Martuscelli 2007].

The physical alterations derive to weathering and environmental agents (such as rain, wind action, and temperature fluctuations), that produce different disaggregation phenomena of stone surface.

In normal environmental conditions, water due to rain and humidity enters into the pores and interstices of the stones and fills the free spaces. During the freezing and thawing cycles, this liquid water solidifies in ice crystals when the temperature decrease below 0 °C with a consequent increase of the volume. At the same time, the pressure on the internal walls rises and this may lead to rock disaggregation [Martuscelli 2007]. Conversely, when temperature increases, the water contained into the stone changes its physical state (from solid to liquid to gas), with concomitant volume decrease. In this condition, water evaporates with deposition of soluble salts inside the pores of the stone, and consequently the crystallization and growth of these salts induce mechanical stress into the stone, and thus its degradation [Torraca 2002].

Also, disaggregation phenomena on stone surface may be due to biological activity (i.e. lichens and roots of plants) and pollution action (such as acid rain).

Other phenomena of mechanical decay are hydraulic swelling and shrinkage of the surface layers in rocks rich of clay, such as sandstones [NORMAL 1/88; Wendler 2000]. These effects are particularly evident on corners of architectonical clay-rich stones placed in outdoor

environments, when after a brief rain the wet surface of a stones swells while their interior remains dry [Doehne *et al.* 2005]. For instance, important studies on sandstones with clay-swelling have been made by Scherer, who found that the primary mode of swelling operates at the intracrystalline level into Portland brownstone [Duffus *et al.* 2008; Wangler-Scherer 2008; Jiménez Gonzalez *et al.* 2008; Doehne-Price 2010]. Moreover, the presence of soluble salts increases the swelling of clay minerals in a sandstone [on these studies: Doehne-Price 2010].

Water is the main source of chemical decay, as most chemical reactions require its presence for take place in environment conditions. For instance, acid rain formed in polluted environments are due to chemical-air pollutants (such as sulfur oxides, nitrogen oxides, and carbon dioxide), that react with weathering water to create acid solutions. This phenomenon produces chemical damages on stones containing calcium carbonate (like calcareous stones, marble, and sandstones with great amount of carbonate matrix), and leads to their slowly dissolution.

In the case of Pietra Serena, the acid rain can develop chemical interactions with low carbonate cement found in matrix. This acid water reacts with atmospheric CO_2, and produces carbonic acid that solubilizes the small quantitative of calcium carbonate found into the rock. The result of this reaction is the formation of calcium bicarbonate that produces a structural discontinuity and exfoliation into the stone [Massi 2002, Torraca 2002]. Moreover, when water evaporates, calcium bicarbonate may precipitate with formation of crusts on stone surface. This alteration is typical of calcareous stones.

Wind action shows a double effect on stone surface: an increase of evaporation rate and water flow from inside to outside of the rocks, that produces the erosion of the stone, and the increase of the rate of damage and pattern of soluble salts distribution due to wind speed influences [Martuscelli 2007, Balaawi 2008].

Another type of mechanical damage is due to daily and seasonal temperature fluctuations, that produce continuous thermal expansion and contraction phenomena into the stone structure, especially in objects exposed to sunlight in outdoor environment. Stones composed by mineral with big and disordered crystals show a variable thermal expansion in function of the direction of the crystals (anisotropic properties). By time, this variation may give origin to decohesive processes of the crystalline structure, in the presence of water and acid substances [Torraca 2002].

We have previously mentioned the deterioration caused by soluble salts. This kind of alteration consists in the formation of inorganic salts (nitrates, sulfates, chlorides, etc.) and efflorescences [NORMAL 1/88; Charola 2000] into the pores of the stones, after evaporation or cooling of salt solutions and consequently after the crystallization of the solutions. Water placed on surface or

inside the stone induces salts solution reactions and thus, the easy transport of ions and molecules into the stone. These phenomena change the chemical equilibrium of the rock and may show their effects on the stone surface. In serious cases, these effects cause fragmentation, lamination, and pulverization of the stone. In the last case, the transformation in a powder is due to the growth of salts into the stone, which can generate stresses that are sufficient to overcome the tensile strength of the stone.

Sodium sulfate is one of the most dangerous soluble salts. It exists in both anhydrous (Na_2SO_4) and decahydrate ($Na_2SO_4 \cdot 10H_2O$) forms, and the passage from one to the other produces an increase of volume that may cause hydration damage, i.e., a special case of crystallization deterioration [Doehne-Price 2010].

Salt damage can occurs in outdoor and indoor environments (such as open air museum, building walls, indoor rooms of a museum, etc.).

Vegetal and animal actions produce both mechanical and chemical damages into the stone. Mechanical damage may be caused by roots of plants and lichens. The roots of climbing plants have the ability to penetrate into the cracks of the stone, and their expansion leads to enlargement of the cracks and, consequently, makes easy the penetration of water and pollutants into the stone [Martuscelli 2007].

Instead, lichens action is due to hyphae penetration and expansion and contraction of the thallus into the stone, under humidity changes. They produce chemical damages to the stone since they secrete oxalic acid, or by the development of carbonic acid made by chelating ions [Doehne-Price 2010].

Other forms of chemical damage are caused by some bacteria, mosses, fungi and algae that produce acidic substances, which may react on carbonate and silicate surfaces giving rise to degradation processes.

Both autotrophic and heterotrophic bacteria degrade the stones. The first are able to oxidizing air pollutants in acid compounds. For instance, sulfur and nitrogen compounds are oxidized to sulfuric and nitric acids that cause stone decay. In the case of heterotrophic bacteria, they produce chelating agents and organic acids that are weaker than the inorganic acids produced by the sulfur oxidizing and nitrifying bacteria [Martuscelli 2007; Doehne-Price 2010].

An example of chemical reaction between bacteria and polluted agents (like NO_x, SO_x, and CO_2) is the formation of black-crusts on stone surface. The same type of damage can be obtained by chemical interaction of lichens, fungi, and mosses with sandstone surfaces.

Generally, animal action produces a chemical damage due to deposition of excrements on stone surfaces that induces an acid attack into the stone.

The resistance to degradation of sandstone depends on the physical-chemical structure, porosity, pores size, and water absorption capacity of the stone. For instance, the resistance to frost damage decreases when porosity increases. The resistance of a stone is evaluated from the saturation coefficient, which indicates the ratio between water retention and the empty pores present in the rock.

The resistance to salt damage is directly proportional to the sizes of the pores, inasmuch as resistance increases when increase the pores with big size while it decreases when increase the pores that show small size.

Sandstones employed in cultural heritage with deep degradation in their structure show the complete alteration of the artifacts.

2.2. *Overview of chemical treatments for sandstones preservation*

The history of chemical treatments employed for stones conservation was made in the preface of this work. Now, we discuss the main treatments used in sandstones preservation with a focus on the studies, techniques, and products developed in the last years.

During the first decades of XX century, A.P. Laurie did the first studies on sandstones conservation through experimentation of different ethyl silicate formulations employed on degraded stone surfaces. His work was very important for understanding the relationship between stone mineralogy and tetraethoxysilane catalysis. This research contributed to the development of modern studies and the creation of new consolidant products (such as Wacker OH, Tegovakon V, and many other ethyl silicates), which started to be commercially available only in the second part of XX century [Wheeler 2005, 2008].

In the last fifteen years, new consolidation and protection treatments were tried for sandstones conservation other than traditional treatments based on ethyl silicate. On these treatments and their application a very large literature exists, and a summary of these studies was proposed by E. Doehne and C.A. Price in the book "*Stone conservation. An overview of current research*" [Doehne-Price 2010], G. Wheeler in the book "*Alkoxysilanes and the consolidation of stone*" [Wheeler 2005] and in the article "*Alkoxysilanes and the consolidation of stone: where we are now*" [Wheeler 2008], but also in the proceedings of international congresses, like the *International Congress "The silicate in conservative treatments"* held in Italy in 2002 [Various Authors 2002], or in some Editions of the *International Congress on Deterioration and Conservation of Stone* (which the 9th Edition was held in Venice [Fassina 2000] and the 12th Edition in New York [in print]), and in many other national and international congresses on

monitoring, conservation and preservation of stones and buildings (for instance, the *International Symposium Stone Consolidation in Cultural Heritage* [Delgado Rodrigues *et al.* 2008], and in different Editions of the Italian Congress of *Scienza e Beni Culturali* [Biscontin *et al.* 2007, 2012]).

A first group of new sandstones conservation products belongs to the molecular composites category, made by inorganic products (such as nano-silica or nano-calcium) or inorganic and organic compounds, that are developed with the aim to improve the performance of silica gel obtained by TEOS. In the first case, calcium hydroxide or silica nano-particles are suspended in different alcohol solutions and applied on sandstones decay. After evaporation of the alcohol, the formation of a binder between calcium hydroxide or silica and the stone matrix can be noted.

These materials show the advantages of a rapid deep penetration into a deteriorated stone, high reactivity and fast reaction in the treated zones, and high purity and defined composition.

For instance, an evaluation on consolidant effects of calcium nano-particles applied on Italian sandstones from Emilia Romagna land (i.e. Campolo and Grelio sandstones) has shown reasonable results. This research has noted that calcium nano-particles show a deep penetration into the stone samples (between 100-200 micron), besides a filling of superficial pores, without their full occlusion. Also, a good reduction of the materials removed was indicated by surface abrasion test, and another test shows that this treatment does not change the water absorption properties of the stones [on this study: Daniele *et al.* 2007].

In the second case, the composite materials are made with sol-gel processes, through the synthesis and polycondensation reactions of metal-alkoxides, modified with organic compound at high temperature. After that, the cross linking occurs between polymerized organic groups and inorganic network (i.e. Si-O-Si, Al-O, Ti-O, and Zr-O) created in the last step. Composite materials show properties both from the inorganic network (such as transparency, hardness, chemical and thermal stability), and from the organic part (i.e. resistance and easy synthesis process). On the other hand, silicone compounds give more elasticity and gas permeability at the hybrid product [on this topic: Murcia Mascaros *et al.* 2002].

One of the most promising hybrid stone consolidants was prepared from TEOS and oligomeric polydimethylsiloxane (PDMS-OH) [Mosquera et al. 2008, Zárraga *et al.* 2010]. An evolution of this product provides a mixture of TEOS, colloidal silica, and PDMS-OH developed for improving the gel properties like porosity and elasticity, leading to the formation of an elastic silica network and, consequently, to the formation of non-fractured and permeable gel [Salazar Hernández *et al.* 2010].

Moreover, recently particular attention has given to composites materials obtained from inorganic oxides nanoparticles introduced into hybrid siloxane or silicone polymers, the case of TEOS and colloidal fumed silica during a sol-gel process. The incorporation of oxide into the matrix increases the elastic modulus of the stone and decreases its thermal expansion, thus reducing the cracking seen in conventional treatments, and resulting in improved consolidation [Miliani *et al.* 2007, Zendri *et al.* 2007, Doehne-Price 2010].

An important study employed stone consolidants made by a commercial ethyl silicate (Convervare OH-100 by Prosoco) that was filled with a dispersion of colloidal oxide particles (such as titania, alumina, and silica). These products are demonstrated to be very promising inasmuch they reduce drying shrinkage of the gel network, and the viscosity of the solution is not too much increased by the loading with titania and silica particles. Also, the type of filler employed in the composites depends on the specific requirements given by the stone that needs to be consolidated. Finally, these particle-modified consolidants were tested on Ohio Massilian sandstones [on this research: Miliani *et al.* 2007].

Also, a water repellent product was obtained from the same process and its effectiveness was tested on Italian sandstones belonging to Macigno Formation, with interesting results. This product was made from two siloxanic compounds charged with different amounts of silica nano-particles functionalized with 1,1,1-trimethyl-N-(trimethylsilyl)silanamine [De Ferri *et al.* 2011].

Other studies take into consideration consolidants based on epoxy resin in organic solvents, as water emulsion or in mixture with low molecular epoxy resin (called reactive solvent) for the treatment of artificial sandstone [Kotlík *et al.* 2008].

Also, water repellents made with fluorinated resins are employed on degraded sandstones and other porous stones with good results. For instance, the better effects of this treatment can be noted on Lecce Stone, where it increases water repellency and permeability of the stone, and consequently the resistance of the stone to water deterioration is increased [Borgioli 2006].

Currently, a line of research on water repellent employed on sandstones includes the study of polymers obtained from renewable and biodegradable raw materials. In this context, polymers derived from lactic acid are employed and can be modified through the use of perfluoropolyethers with the aim of improving water repellency and giving stability to the stone in the passage of time. For instance, some of these products tested on sandstones are homopolymer called PLLA and two copolymer knowing as PLDA-FLK and PLLA-FLKA [on these research Salvini *et al.* 2012].

Other stone consolidants are based on the application on stone surface of inorganic salts employed by themselves or combined with organic polymers such as TEOS products, with the

aim to replace lost binding materials and increase the strength of mechanical properties of the stone. These compounds are often used on limestone and marble [Doehne-Price 2010], but rarely on sandstones. On this last kind of surface treatments based on lithium hydroxide [Buj *et al.* 2006, Thorn 2011, Thorn 2012], potassium hydroxide [Buj *et al.* 2006], and barium hydroxide [the topics of this thesis work, an preview of the results are reported in Botticelli *et al.* 2012, and Lugli *et al*. 2013] have been tested, and each formulation has shown interesting results, but also some limits. Inorganic hydroxides react with ethyl silicate to give a new chemical formulation (such as lithium silicate, barium silicate or titanium silicate) that once applied on a stone show equal or better consolidative benefits with respect to traditional consolidants based on TEOS.

Lithium silicate shows higher absorption rate of the solvent in a short time, and it forms lithium carbonate and calcium silicate into the matrix, in addition to silica formation common to ethyl silicate [Thorn 2011]. However, some studies on lithium silicate have reported modest penetration into the stone [Buj *et al.* 2006], but other studies have asserted that this compound can penetrate as well as or better than ethyl silicate [Thorn 2011, Thorn 2012]. Also lithium silicate provides a more cohesive matrix compared to TEOS, achieves similar consolidative strength to 100% of ethyl silicate at 20% dilution of supplied product (5% solids), and can be applied into wet surface, where TEOS would react too quickly [Thorn 2011, Thorn 2012]. Some limits of these treatments regard the darkening and staining of the surface [Thorn 2012].

Consolidants based on potassium silicate have been tested on Spanish sandstone from the Ebro basin [Buj *et al.* 2006], while barium silicate treatments have been applied on Italian sandstones [Preliminary results are reported in some congress papers: Botticelli *et al.* 2012, and Lugli *et al.* 2013].

The employ of barium silicate consolidants for the preservation of sandstones have been studied in this thesis work for the first time. In the next paragraph I will show the idea of this work.

In the preface it was recalled that barium silicate was employed as consolidant on calcareous stones because of its similar chemical composition to calcium compounds, and it also shows insolubility as sulfate, conversely to calcium sulfate, sparingly soluble. Thus barium sulfate was employed on calcareous surface to reduce damages due to dissolution and recrystallization of calcium sulfate [Lewin-Baer 1974]. In the preservation field, application of barium compounds (such as hydroxide and oxalate formulations) was proposed on limestone and marble [Schnabel 1992; Toniolo *et al.* 2001; Hansen *et al.* 2003, Bracci *et al.* 2008], on wall paintings [Matteini 1991; Ambrosi *et al.* 2000], and on calcareous stones and paintings [Messori et al. 2000, Matteini-Zannini 2004].

2.3. New approaches for the strengthening of silica stones

Silica stones result very difficult to be preserved by the actions of weathering, biological, and polluted agents, mainly due to their composition (silica, clays, low calcite and some rock fragments) and their structure, that show parallel lamination. In the last paragraphs we have seen different methods for the conservation of deteriorated sandstones. The aim of this thesis is to study new products and procedures for the conservation of this stone.

The idea behind the project is to find a consolidant that penetrates into the stone, binding together and securing the fragments detached (such as scales, flakes or grains) from the matrix. Also, these treatments have to be easy to be applied on surfaces with different extensions, placed in indoor and outdoor environments, and then remaining effective during time.

Consequently, after the treatment, the strengthened stone has to be able to resist at decay agent actions (water damage, erosion by wind, and many others), and its detached surface has to be connected to the internal matrix. Moreover, the treated stone has to show the same characteristics of untreated stone in order to avoid internal stresses and assure compatibility, such as moisture and thermal expansion, and elastic modulus.

After the application and drying of the consolidant, the treatment must be completely invisible on the sandstone surface and this has to remain unchanged in the course of time.

In this thesis eight commercial ethyl silicates employed for the conservation of sandstones in many part of the world have been studied.. The binder action of TEOS is given by hydrolysis and condensation reactions that produce new silica bonding into the stone with its consequent strengthening. Composition and properties of each ethyl silicate examined and its chemical behavior into the sandstone samples will be discussed in the next chapter.

After reviewing recent researches on sandstones conservation [Wheeler 2005, Wheeler 2008, Doehne-Price 2010], we have chosen to try to improve the binder properties of ethyl silicate with the addition of inorganic salts, which increase strengthening of the binding between the stone fragments and the healthy stone.

Actually, different inorganic salts were employed for sandstones conservation like lithium hydroxide [Buj *et al.* 2006, Thorn 2011, Thorn 2012] and potassium hydroxide [Buj *et al.* 2006], but in this research we have chosen barium hydroxide for its interesting behavior on silicate matrix.

After the penetration into the stone, it has been supposed that barium reacts with silica matrix and gives rise to the formation of barium sulfate, that strengthen the chemical bonding into the stone and lead to the consolidation of the stone, and water, eliminated during the drying process.

The behavior of sandstones samples treated with barium hydroxide, employed only or added to ethyl silicate, has been studied. The objective is the knowledge of the chemical bonding that takes place between the consolidant and the substrate of the sandstones varying the consolidation methods, with the aim of finding an effective treatments that block the deterioration.

The sandstones used in this study came from Italian quarries placed in Toscana and Emilia Romagna Regions and belonging to different ages. The Toscana samples were taken to Firenzuola quarries (near Firenze) that is the last industrial zone where these stones are extracted. They are divided into three groups: modern stones that recently have been extracted, natural aging stone which have been exposed to weathering agents for over thirty years, and historical stones belonging to architectonical fragments of churches and civil monuments of the XVI century A.D. that have been replaced due to their degraded state.

The Emilia Romagna sandstones are preserved in archeological site of Montegibbio (near Modena), and belong to a building of II century B.C., and they came from local quarries.

The natural aging and historical stones show a detachment of the external surface layers due to the action of different deterioration agents with the formation of scale, flake, granular disaggregation and many other decays. The deterioration of these stones is related to their composition, i.e. silica and clay matrix with low calcium carbonate cement, and their structure made by parallel laminations.

When external water penetrates into the stone, a disequilibrium within the same stone occurs that can lead to the development of different deterioration forms. For instance, water causes an increase and a decrease of the stone volume during freezing-thawing cycles, which in the course of time can create mechanical stress on the outer layer with consequent scaling, flaking, exfoliation, granular disaggregation, and cracks formation.

Also, the hydraulic swelling and shrinkage of the surface layers of sandstones is due to acidity of the water absorbed by the outdoor environments. This water reacts with atmospheric CO_2, and consequently the carbonic acid solubilizes the small quantitative of calcite present in the rock that precipitates when water evaporates. The result of this process is the formation of a structural discontinuity and/or exfoliation on the stone. Often this phenomenon results to be limited to the surface layers that are directly in contact to weathering agents. Thus, i.e. after a brief rain the wet surface of a clay stone swells while its interior remains dry.

Therefore, the use of a treatment capable of penetrating in depth into the stone, strengthening the bonds within the matrix and connecting the different layers of the stone is necessary for blocking the degradation of sandstones.

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Chapter 3

ETHYL SILICATE: CHEMICAL REACTIVITY

In the previous chapters the consolidation methods employed on sandstones were reported. In this context an important role is played by alkoxisilanes and in particular ethyl silicates, which are the most applied products on deteriorated silica surfaces.

These compounds easily penetrate into the stone due to their low viscosities that make liquid solutions as mobile phases. After different chemical reactions (like hydrolysis and condensation reactions), alkoxysilanes produce siloxane bonds into the silica matrix and they are said to strengthen the detached fragments from the stone surface. Siloxane bonds are relatively strong, possess thermal and oxidative stability, and gels formed after the reaction show a little tendency to discolor through breakdown and reconfiguration of the bond network.

Moreover, stones treated with ethyl silicate show light stability and does not change their appearance, therefore TEOS products are good candidates for the application in outdoor environments [Wheeler 2005].

In this chapter we will explain the chemical reactivity of organic silicates, and in particular of ethyl silicate, and their behavior on sandstone surfaces. Also, the results obtained from the combined use of TEOS and inorganic compounds, aiming to increase the silica bonding resistance, will be treated. At last, silicates employed in this research and their characteristics will be introduced.

3.1. *Organic silicates: an overview of their use*

The history, the composition and the behavior of organic silicates employed in restoration field have been very well explained by George Wheeler in the book "*Alkoxysilanes and the consolidation of stone"* [Wheeler 2005] and in the article "*Alkoxysilanes and the consolidation of stone: where we are now"* [Wheeler 2008].

Organic silicates belong to alkoxysilanes, that are synthetic polymeric compounds where two Si-O bonds react with ester groups to form new Si-O bonds, strengthening the stone matrix. These compounds derive from silane (SiH_4) in which one silicon atom is bound with four hydrogen

atoms. These can be replaced by other reactive elements or groups, and this determines the functionality of the compound.

During hydrolysis, the functional parts (Si-OR) can be removed by water and replaced by hydroxyl groups, giving rise to the formation of alcohol compounds and silanol (based on Si-OH bond) [1].

In the case of condensation reaction, the silanol groups can react with each other [2] or with alkoxy groups [3], and produce siloxane bonds (Si-O-Si).

Hydrolysis Reaction

$$\underset{\textit{Silane}}{R'\text{-}Si(OR)_2\text{-}OR} + \underset{\textit{Water}}{H_2O} \Longrightarrow \underset{\textit{Silanol}}{R'\text{-}Si(OR)_2\text{-}OH} + \underset{\textit{Alcohol}}{ROH} \quad [1]$$

Condensation Reaction

$$\underset{\textit{Silanol}}{R'\text{-}Si(OR)_2\text{-}OH} + \underset{\textit{Silanol}}{OH\text{-}Si(OR)_2\text{-}R'} \Longrightarrow \underset{\textit{Siloxane}}{R'\text{-}Si(OR)_2\text{-}O\text{-}Si(OR)_2\text{-}R'} + \underset{\textit{Water}}{H_2O} \quad [2]$$

Condensation Reaction

$$\underset{\textit{Silanol}}{R'\text{-}Si(OR)_2\text{-}OH} + \underset{\textit{Alkoxide}}{CH_3OSi} \Longrightarrow \underset{\textit{Siloxane}}{R'\text{-}Si(OR)_2\text{-}O\text{-}Si} + \underset{\textit{Alcohol}}{CH_3OH} \quad [3]$$

The functional groups are made by reactive elements such as hydrogen, fluorine, chlorine, and alkyl groups (i.e. methyl, ethyl, and so on). For instance, tetramethoxysilane (also called TMOS, $Si(OCH_3)_4$) and tetraethoxysilane (known as TEOS, $Si(OCH_2CH_3)_4$) are obtained when the four hydrogen atoms are completely replaced with alkoxy groups.

In the presence of organic groups R' (that do not show oxygen atoms interposed between silicon and carbon bonds), the pendants groups remain unreactive or stable during hydrolysis reactions.

Many siloxane compounds have been synthesized by mixing and matching reactive and unreactive groups, but only a limited number of these have been employed in restoration field, like tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), and methyltrimethoxysilane (MTMOS). These formulations have to be able to form a three-dimensional network with a minimum of three reactive groups. Also, some tri- and tetra-functionalized alkoxysilane compounds show properties that disqualify them as stone consolidants or conservation materials. During hydrolysis these compounds can for example develop volatile hydracids (i.e. HCl and HF) due to their reactive functional groups, and this can damage stone surfaces (such as limestone, travertine, and marble).

Indeed, alkoxysilanes used in stone consolidation must show: low volatility, low or moderate reactivity in water solution, and no formation of corrosive byproducts (like acid compounds) [4] after hydrolysis reaction. Nevertheless only few alkoxysilanes give rise to the formation of silicon products employed in stone conservation, like TMOS, MTMOS, MTEOS, and TEOS.

$$\underset{\textit{Alkoxysilane}}{Si(OR)_{4\,(l)}} + 4H_2O_{\,(l)} \Longrightarrow \underset{\textit{Silicic acid}}{Si(OH)_{4\,(l)}} + \underset{\textit{Alcohol}}{4ROH_{\,(g)}} \qquad [4]$$

Many alkoxysilanes show a limited penetration into the stone. This phenomenon is mainly due to rapid hydrolysis reaction before gelation occurs, or high vapor pressure that leads to excessive evaporation of the consolidating material.

The reactivity of alkoxysilanes is also influenced to steric and inductive effects [Brinker *et al.* 1990]. Steric effects consist in the crowding or blocking of the central silicon atom by bulky alkyl or alkoxy groups. This effect reduces the rate of hydrolysis, and consequently interferes with condensation reaction and gel formation till block them [Wheeler 2005]. Inductive effects are due to the replacement of alkyl with alkoxy groups on silicon atom. These substitution increases the electron density on the silicon atom and, under acid condition, increases the rate of hydrolysis [Wheeler 2005].

Alkoxysilanes with alkyl group show a very slow reaction rate due to steric effect, with the only exception of methyl- and ethyltrimethoxysilane.

In normal condition, assistance is required to improve the time of formation of their products, because the formation of the gel is obtained very slowly and the consolidation does not occurs. The same aid is necessary to produce gels from tetramethoxysilane and ethoxysilanes. The way to solve these problems comes from the employment of environmental water (such as atmospheric moisture, weathering water, and so on) or water present inside the stone that is added to alkoxysilanes which increases the rate of reaction due to increase of collisions between water and alkoxysilane molecules take place than when atmospheric water is employed. Normally, these two reagents are immiscible, thus a solvent (such as ethanol) is necessary to obtain a homogeneous solution [Wheeler 2005].

Acid or basic catalysis is another important element that influences the hydrolysis reaction of alkoxysilanes. In fact, this leads to more rapid and complete hydrolysis compared to time required in neutral condition. The nature of the gel products comes from the type of acidic or basic catalyst chosen.

During acid catalysis, the hydrolysis occurs through nucleophilic attack by the oxygen atom of a water molecule on silicon. The acid protonates the oxygen atom of the alkoxide group which becomes a better leaving group [5], with a concomitant rapid hydrolysis. At the end of the reaction, silicic acid $Si(OH)_4$ is the main product, that can be further protonated by the acid catalyst [6].

The silicon atom of this protonated species $Si(OH)_3(OH_2)^+$ is more prone to nucleophilic attack by unprotonated $Si(OH)_4$ molecules, the only nucleophile present at this stage, creating a siloxane bond. Thus, the condensation reaction ends with the regeneration of the catalyst and water. This reaction is also called acid-catalyzed condensation [7].

The solution made to monomeric and condensed silanols show either species as candidates for protonation by acid catalyst, and normally the choice fall out on more basic silanol.

In acid catalyzed condensation, Monomers prefer to react with other monomeric species rather than with condensed silanols. When all monomers are consumed, the reaction involves oligomers where the most basic is protonated. Thus, acid catalysis involves the formation of siloxane bonds by reactions among monomers, monomer-oligomer, and oligomers. These conditions produce linear or branched structures.

Acid catalyzed hydrolysis:

$$\underset{H}{HOH}\ \ (OR)_3Si{-}\overset{+}{O}\underset{H}{R} \rightleftharpoons \overset{\delta+}{HO}\underset{H}{} \cdots (OR)_3Si \cdots \overset{\delta+}{OR}\underset{H}{} \rightleftharpoons HO - Si(OR)_3 \quad \underset{H^+}{ROH} \qquad [5]$$

Acid catalyzed condensation, first step:

$$Si(OH)_4 + \overset{+}{H} \longrightarrow \underset{H^+}{(OH)_3SiOH} \qquad [6]$$

Acid catalyzed condensation, second step:

$$(OH)_3SiOH + \underset{H^+}{(OH)_3SiOH} \longrightarrow (OH)_3Si{-}O{-}Si(OH)_3 + H_2O + \overset{+}{H} \qquad [7]$$

Silanol *Protonated silanol* *Siloxane bond*

In basic conditions, the hydrolysis occurs rapidly and involves the nucleophilic attack of the silicon atom by hydroxyl anion (OH^-) with the concomitant displacement of an alkoxide anion (RO^-) [8]. Condensation comes from deprotonation of a monomeric silanol by hydroxyl anion to create silanolate anion [9] that is a strong nucleophile and seeks to react with acid silanols. During the initial stage of the reaction, the most acidic silanols are $Si(OH)_4$. The reaction

between the silanolate anion and silicic acid produces a siloxane bond, and the catalyst is regenerated [10].

Condensed silanols (such as dimers and trimers) are more acidic than monomers, consequently they become the preferred target for deprotonation by hydroxyl ions.

In base-catalyzed condensation, the preferential activation of condensed silanols produces highly condensed structures in solution with respect to linear or weakly branched ones showed in acid catalysis. The degree of condensation is important for the kind of gels formed and for their consequent behaviors.

Base-catalyzed hydrolysis:

$$HO^- + (OR)_3Si–OR \rightleftharpoons \overset{\delta-}{HO} - - (OR)_3Si - - - \overset{\delta-}{OR} \rightleftharpoons HO – Si(OR)_3 + OR \quad [8]$$

Base-catalyzed condensation, first step:

$$Si(OR)_3—OH + OH^- \rightleftharpoons (OR)_3SiO^- + HOH \quad [9]$$

Base-catalyzed condensation, second step:

$$(OR)_3Si—O^- + (OH)_4Si \rightleftharpoons (OR)_3Si—O—Si(OH)_3 + OH^- \quad [10]$$

During condensation reactions, gels are produced continuously and these phases result in direct relationship between viscosity and the concentration of water. Indeed, solutions with molar ratio of water equal or greater than two show a rapid increase of viscosity during gelation, while solutions with lower values have very little change of viscosity and consequently the gelation occurs slowly.

Gelation does not represent the end of chemical activity, because condensation and hydrolysis reactions continue, causing the reduction of the volume of the gel. So, during the shrinkage the liquid is pushed out of the pores into the gel.

During the coarsening, the gel is also involved in dissolution and re-precipitation of some of its part with formation of strengthened and stiffer gel.

The ripening of the gel depends on pH and, therefore, is influenced by the original conditions of catalysis. For instance, silicates and siloxane bonds are more soluble in high pH values and their ripening is more active with base catalysis, which promote the creation of more condensed species.

Moreover, in environmental conditions, gel drying occurs after the evaporation of the liquid into the pores, and this leads to exposure of the solid network at the surface and causes liquid deeper inside the gel to cover the newly exposed solid. In attempting to cover this solid, the liquid stretches, or goes into tension. The tension in the liquid pulls the gel network inward, causing it to shrink further. If the liquid cannot flow easily through the solid network from inside to outside, the liquid placed in the extremities of the stone appears to be more in tension than the internal liquid. Consequently the outside gel shrinks along the surface and eventually may give rise to tears or fractures. The probability that the fracture occurs depends on tensile stresses, that are inversely proportional to the pore size (i.e., smaller pores create larger stresses), and on permeability of the gel, that influence the liquid flow through the gel (this permeability is proportional to the square of the pore size) [Wheeler 2005].

The alkoxysilanes employed on sandstone are influenced by clay matrix of this type of stone. In fact, their consolidant action depends on the type of clay minerals (like illite, smectite, kaoline and so on) that are present inside the stone, inasmuch different clay minerals belonging to different clay groups show different structures, and different amounts and distributions of water. These structures may have an influence on the consolidation ability of the alkoxysilanes but how those structure influence the consolidation process cannot be determined from the current stone conservation literature.

For instance, on fine power of some clay minerals (like illite, chlorite, muscovite, and biotite), a little consolidation effect is performed when products like MTMOS and Wacker OH are applied. Also, when clay-cemented sandstones are treated with TEOS, they exhibit only an increase of percent of the strengthening of silica cemented [Wheeler 2008].

After the treatment with an ethyl silicate, some clay-rich sandstones (like Molasses stones from Switzerland) show considerable shrinkage that may be due to the preferential deposit of TEOS between the plates of clay minerals. Thus, treatments based on alkoxysilanes are not recommended on clay-sandstones because they increase the hydric dilatation of the stones, and may lead to the opposite effect (*i.e.* their damage) [Snethlage1983, Snethlage *et al*.1991,Felix *et al*. 1995, Wheeler 2008].

In the next paragraph ethyl silicate composition and behavior on sandstone surfaces will be explained, both during and after the treatment (as chemical reactions, gel formation, and drying process), and the characteristics of commercial TEOS used in restoration field.

3.2. *TEOS. Characteristics and reactivity on silica surface*

The formulation, the characteristics and the chemical behavior of alkoxysilanes, and specifically of tetraethoxysilane, have been explained by the cited book "*Alkoxysilanes and the consolidation of stone"* [Wheeler 2005] and article "*Alkoxysilanes and the consolidation of stone: where we are now"* [Wheeler 2008]; many other authors show only the synthesis and focus their articles or books on this topic [like Biscontin *et al.* 2000, O'Connor 2000, Ioele et al. 2000, Lorusso *et al.* 2000, Snethlage 2000, Borgioli 2006, De Clercq *et al.* 2007, Martuscelli 2007, Sanmartín *et al.* 2007, De Moraes Rodrigues *et al.* 2008, Nardini *et al.* 2008, Salazar-Hernández *et al.* 2010, Zárraga *et al.* 2010, Thorn 2012, Ziegenbalg *et al.* 2012, etc.].

Ethyl silicate and alkoxysilanes show the same mechanism of reaction based on a series of hydrolysis and condensation reactions to obtain siloxane bonds, as explained in the previous paragraph. This mechanism appears very complex due to several factors, like temperature and environments moisture, presence of soluble salts, pH, amount and type of solvent employed, and typology of stone surface.

The course of reaction may be influenced by moisture that is found inside and onto the stone, and in atmospheric environment. For instance, TEOS reactions do not occur in the absence of water, however it is present in form of molecules on stone surface.

In environmental condition, the temperature affects the outcome of reactions, i.e. high temperature (over 25 °C) gives rise to rapid evaporation of the solvent that leads ethyl silicate to go towards the stone surface with formation of compact crusts. In the case of reduction of the external temperature below 10 °C, the condensation reaction is blocked.

Therefore, hydrolysis and condensation reactions occur in good environmental conditions, like moisture in the range 30-60% (RH) and temperature between 10 and 25 °C [Brogioli 2006].

Moreover, TEOS reacts slowly, hence the addition of a catalyst is required to initiate and accelerate the cross-linking reactions. The rate of reaction is increased by catalysts bases on tin compounds (such as dibutyltindilaurate), lead naphthenate, and titanium derivatives [Wheeler 2005, Brogioli 2006].

Hydrolysis and condensation reactions that employ dibutyltindilaurate as catalyst are described by Wheeler in his book.

During hydrolysis, an organotin molecule reacts with water to form a tin-hydroxyl compound and an organic acid [11]. After that condensation reaction between tin-hydroxyl compound and TEOS occurs, with formation of tin-siloxane and ethanol [12]. Tin-siloxane reacts in the presence of any silanols and promotes the condensation between the siloxyl part of the tin-siloxane and the silanol producing TEOS dimer (i.e. the compounds that strengthen the stone

matrix), and tin-hydroxy compound (i.e. the same byproduct of reaction obtained in the primary hydrolysis reaction) [13]. This last is the real catalyst of the reactions, because it is recycled back and continues to generate the siloxane bonds that lead to gelation.

Moreover, small amounts of silanol must be employed to complete the siloxane-forming reactions (like in Wacker OH formulation), and the use of TEOS oligomers rather than TEOS monomers helps the catalyst to work better because they react more readily with base catalysts (i.e. tin-hydroxy compound) to produce siloxane linkages.

Results of catalysis depend on pH (acid or basic). In basic pH, hydrolysis occurs rapid because TEOS molecules are more reactive and readily start to condense with silanols. In acid medium, instead, TEOS molecules are less reactive after hydrolysis, and the condensation reaction may occur on functional groups at the end of chain. Therefore, in acid pH the formation of extended and little-branched chains is favored, while in alkaline environment the chains are shorter and branched [Brogioli 2006].

The first researcher who understood that acid and base catalysis produces gels with different structures was Laurie. He observed the nature of the gels formed in relationship with the mineralogy of stone type. He found that after hydrolysis, the slightly acidic TEOS formed a hard glassy layer that strengthened the internal pores and the surface of the stone. In the case of slightly alkaline TEOS, silica is deposited like a soft gel precipitate, which is useless as consolidant [Laurie 1926].

Another property of catalyst is the decrease of the fractures into the gel due to the organic acid produced during the hydrolysis of organotin compound. This acid shows low vapor pressure and high viscosity, which allows a good penetration of solvent inside the stone. Also, the catalyst remains into the gel and reduces the tensile stress into the pores [Scherer *et al.* 1997].

In many ethyl silicate products (such as Wacker OH), the catalyst is activated by relative atmospheric humidity and water vapor found in the stone, and the time of gel forming depends on relative humidity and temperature [Wheeler 2005].

During transition from solution to gel, polymers with little resistance may be obtained due to quick time of reaction (i.e. under 10 hours) as a consequence of the application of high amount of catalyst [Borgioli 2006]. Normally, low time of gelification is necessary for a good penetration of silicate into the stone (between one and seven days) [Borgioli 2006, Wheeler 2005].

If soluble salts are found in water on stone surface, they may give rise to crystallization reactions, which interfered with gel formation. Also, hydrolysis and condensation reactions do

not occur in the absence of water such as in extremely dry environments that show very low reaction rates and the gel is not formed [Borgioli 2006].

After gel formation, hydrolysis and condensation reactions continue until OH groups belonging to water and solvent are completely removed through drying process, from inside to outside of the stone.

During this drying step, the gel may develop cracks caused by internal stress due to the reduction of empty spaces of the network, which are crossed by solvent molecules, and an increase of interconnection into the network. A good solution is given by application of TEOS diluted into the pores of the stone without their saturation [Brogioli 2006].

In good environmental conditions and after correct application of the solvent on the stone, all commercial TEOS compounds show a time of reaction evaluated between two to four weeks.

Hydrolysis Reaction

$R_2Sn(OOCR')_2 + H_2O \Rightarrow R_2Sn(OOCR')OH + R'COOH$ [11]

Organotin compound *Tin-hydroxy compound* *Organic acid*

Condensation Reaction

$R_2Sn(OOCR')OH + Si(OCH_2CH_3)_4 \Rightarrow R_2Sn(OOCR')\text{-}O\text{-}Si(OCH_2CH_3)_3 + CH_3CH_2OH$ [12]

Tin-hydroxy compound *TEOS* *Tin-siloxane* *Ethanol*

Condensation Reaction

$R_2Sn(OOCR')\text{-}O\text{-}Si(OCH_2CH_3)_3 + HO\text{-}Si(OCH_2CH_3)_4 \Rightarrow$ [13]

Tin-siloxane *Silanol*

$(CH_3CH_2O)_3Si\text{-}O\text{-}Si(OCH_2CH_3)_3 + R_2Sn(OOCR')OH$

TEOS dimer *Tin-hydroxy compound*

TEOS compounds are widely employed as consolidant products for different kind of stones [Wheeler 2005].

The first commercial ethyl silicate employed for the conservation of stone was made by Wacker industries in 1970s. Today, different Wacker products based on TEOS are applied as consolidants in many part of the world and the two main formulations used are Wacker OH and Wacker H. Today, new versions of OH and H products called Wacker OH100 and H100 are commercially available.

Wacker OH is an ethyl silicate without water repellent in its formulation. This product shows a main composition made with TEOS monomer and some dimer with smaller amounts of ketone solvents (like methylethylketone, MEK, and acetone that reduces the viscosity of the solution), and ethanol, which is the byproducts of the TEOS hydrolysis. Also, Wacker OH contains dibutyltindilaurate as catalyst.

The composition of Wacker OH is 75% in volume of alkoxysilane, and 25% of ketone solvents, with more MEK than acetone [Bosch *et al*. 1976]. These solvents show higher vapor pressures than any of the TEOS components and thus evaporate preferentially and lead to the elimination of a part or excess of TEOS through their evaporation. Modern products, Wacker OH100 and H100, do not show the addition of solvents.

Wacker OH is commercially available in liquid solution, which is immiscible in water due to the alkoxy groups, thus the gel remains hydrophobic for months after its application on the stone. This water repellency decreases when the residual alkoxysilanes contained into the pore of the gel hydrolyze and condense, alkoxy groups on the gel itself are hydrolyzed, and residue of MEK departs because of its low solubility in water [Riddick *et al.* 1986, Wheeler 2005].

The difference between Wacker OH and Wacker H is that H products remain permanently hydrophobic due to use of equal part of MTMOS, TEOS and their oligomers in the formulation. Wacker H contains the same solvents and catalyst of Wacker OH. Also it shows the same gel properties described for OH compound with the exception of repellency, but it undergoes less fractures than OH gel due to low functionality of MTEOS that helps this gels during drying phase.

In the case of Wacker OH100, the viscosity is nearly twice that of the early version, but the flash point increase from 2 to 40 °C, and make it safer to use. Also, this viscosity value does not significantly affects the performance as consolidant [Wheeler 2005].

Other commercially TEOS products similar to Wacker OH and H, and employed as stone consolidation, have been made by other industries, like ProSoCo (Conservare OH), Keim (Silex OH and Silex H), Goldschmidt (Tegovakon V and Tegovakon T), Remmers (Funcosil OH, Funcosil 100, Funcosil 300 and Funcosil 510), Rhone-Poulenc now known as Rhodia (RC70, RC80, and RC90), and Building Research Establishment (Brethane) [on following overview of their characteristics: Wheeler 2005].

Conservare OH is mainly used in restoration field in USA, and it shows similar behavior and characteristics of Wacker OH100 and H100. The only difference is the composition, i.e. Conservare OH show mineral spirits in addition to MEK and acetone like solvents. Mineral

spirits show very low viscosity, which does not change the viscosity of the final product, and also flash point shows very low value.

Silex OH and H show the same composition of Wacker products in their early formulation (i.e. mostly monomer and some dimer of TEOS and MTEOS), but the modern version contains only TEOS and MTEOS oligomers. In these products, the solvent is toluene and the catalyst dibutyltindilaurate. Gels formed result less fractured than the similar Wacker and Conservare versions, probably due to the lower vapor pressure of toluene that reduces the capillary tensile stress in the pores.

Tegovakon V (i.e. the OH equivalent) and T (i.e. the H equivalent) show the same composition of the products mentioned above, based on oligomeric TEOS and MTEOS though they are weighted more toward monomers and dimers. The catalyst is always a tin compound and the solvents are naphtha and ethanol that compose 34% of the formulation (17% for each component). The gels formed by Tegovakon V and T are much less fractured than other formulations based on catalyzed TEOS or MTEOS, and Tegovakon T is even less fractured then V.

Funcosil OH show similar composition of Wacker OH, it contains 75% in weight of oligomeric TEOS and the remaining amount is MEK and catalyst (dibutyltindilaurate). Conversely, Funcosil 300 show similar composition of Wacker OH, but it does not contain solvent and thus similar to Wacker OH100, while Funcosil 100 and 510 are also catalyzed and contain additional solvents. Funcosil products give rise to the deposit of different amount in weight of gel (i.e. 45% for Funcosil 510, 30% for the OH and 300 varieties, and 10% for the type 100).

RC70 of Rhone-Poulenc consists in a mixture of 70% of TEOS oligomers and the remaining 30% of solvent (i.e. white spirits), and a catalyst (i.e. an organoditinsiloxane, like ethyltinsiloxane). Conversely, RC80 and RC90 contain water-repellent components in addition to oligomeric TEOS, white spirits and the tin-siloxane catalyst.

RC80 shows slight reduced amount of oligomeric TEOS and little part of white spirits is replaced by xylenes (about 8% of the solvent), used to dissolve the methylsilicone resin employed as water-repellent. Indeed, RC90 contains the same amount of TEOS of RC80 and white spirits, but in this last formulation the solvent is replaced by toluene (about 6%), in order to dissolve the methylphenylsilicone employed as water-repellent.

The gel formed through RC80 and RC90 is less condensed and contains some silicone resin fragments. During gel formation, fewer cracks appear as in the case of RC90 that show an increase of the elasticity of the gel due to large phenyl groups present in the compound. In fact, RC90 gels are less fractured than RC80 gels and other TEOS-derived gels.

After gelation, the gels derived from RC80 show white colour, probably because methylsilicone resin produces a separate and insoluble phase in the TEOS matrix.

All these TEOS formulations are commercially available in liquid solution and ready for their use, with the exception of Brethane that is a mixture of MTMOS monomer, water, industrial methylated spirits (i.e. denatured alcohol), and Manosec Lead 36 (i.e. a solution with 36% of naphthenate in hydrocarbon solvent, and employed such as catalyst), that are mixed at the time of application on the stone.

The gel formed from Brethane is much less fractured than gels from other commercial products, due to MTMOS behavior. Also, water is added in order to complete hydrolysis and condensation reactions, and only 1.5 moles of water to 1 mole of MTMOS are necessary.

Ethanol is the solvent that makes water, MTMOS and catalyst miscible. The lead naphthenate catalyst is diluted in dried white spirits and only a little part of this solution (about 1%), is used to catalyze the reaction. After hydrolysis, this catalyst reacts with MTMOS to produce a lead-siloxane intermediate, which reacts rapidly with other MTMOS molecules or more condensed MTMOS oligomers and creates the siloxane bonds that lead to gelation.

The gel time of Brethane depends on the instability of the catalyst, normally it shows lower value than other alkoxysilane, 2-6 hours compared to 12 hours [Again *et al.* 1995].

Brethane can also form homogeneous solution with water that may be present in the pores of the stone. This product seems to show good results on limestone than sandstone. Conversely, as already mentioned, Wacker OH and similar products seem have better behavior on sandstone surfaces [Wheeler 2008].

3.3. *TEOS and inorganic salts. Combined use for stone consolidation*

In the last decade, consolidation treatments based on inorganic salts employed by themselves or combined with organic polymers such as TEOS products have been used to improve properties of ethyl silicate with the aim to strengthen the binding between the detached fragments and the healthy stone.

The behavior of different inorganic salts employed for sandstones consolidation, like lithium hydroxide [Buj *et al.* 2006, Thorn 2011, Thorn 2012] and potassium hydroxide [Buj *et al.* 2006], have been described in the last chapter (*Par.2.2*). After the penetration into the stone, all these salts react with silica matrix and give rise to the formation of new compounds that strengthen the chemical bonding into the stone and lead to the consolidation of the stone.

In this thesis, we have chosen to employ consolidants based on barium silicate for the preservation of sandstones for the first time [first results are available in Botticelli *et al.* 2012, Lugli *et al*. 2013]. We have supposed that barium hydroxide in water solution reacts with silica matrix of the stone to create barium silicate, based on Si–O–Si links with Ba through O, showing good physical-chemical affinity and compatibility with the internal structure of the sandstone [14], and do not change the physical appearance of the stone.

Moreover, barium silicate should lead to improvement of the hardness and abrasion resistance of treated sandstones. So, this behavior should be improved when barium hydroxide reacts with ethyl silicate and gives rise to new barium silicate bonds. This should lead to equal or better consolidative benefits than to traditional consolidants based on TEOS or barium hydroxide solution applied separately.

$$Ba(OH)_2 \cdot nH_2O + SiO_2 \longrightarrow BaSiO_3 + (n+1)\,H_2O \qquad [14]$$

Barium Hydroxyde *Barium Silicate*

In this research, barium hydroxide has been applied by itself or added to eight available commercial TEOS products with the aim to discover the better treatment for the strengthening of deteriorated matrix. These topics will be discussed in details in the next chapters (i.e. Cap.7).

In literature, barium silicate has been employed as consolidant on calcareous stones because it shows similar chemical composition and insolubility properties to calcium compounds, all these characteristics makes it suitable to reduce the detachment of calcareous matrix [Lewin-Baer 1974, Matteini 1991, Schnabel 1992, Ambrosi *et al.* 2000, Messori *et al.* 2000, Toniolo *et al.* 2001, Hansen *et al.* 2003, Matteini *et al.* 2004, Bracci *et al.* 2008].

Several previous studies on barium hydroxide have revealed the consolidant effect of this compound that reacts with carbon dioxide of the air and produces barium carbonate that is an effective inner structural ligand for the carbonate stones [Messori *et al.* 2000].

On sandstones, the formation of barium carbonate [15] should give important problems, like the development of white patinas that remain on surfaces treated and are not removable with other products or treatments. Therefore is essential to avoid this problem that causes a change in the superficial structure of the stone and does not allow the development of barium silicate on the surface.

$$Ba(OH)_2 \cdot nH_2O + CO_2 \longrightarrow BaCO_3 + nH_2O \qquad [15]$$

Barium Hydroxyde *Barium carbonate*

3.4. *Commercial formulation employed*

In this thesis eight commercial ethyl silicates commonly used in restoration field are studied like consolidants for the conservation of degraded sandstones.

All silicates declare the same formulation based on TEOS monomer, besides specific properties and compositions that lead to different consolidant effects on treated stones. Thus, these commercial products were evaluated through chemical and physical analysis to understand the formulations, the characteristics and behaviors before and after the application on sandstones. These results will be reported in the sixth chapter of this work.

Nevertheless, some information on the composition and behavior of these TEOS are available on the Product Data Sheets (obtained for many products) and in literature [Villegas Sánchez *et al.* 2000, Ioele et al. 2002, Wheeler 2005, Sanmartín *et al.*2008].

Ethyl silicates studied are commercially known as Tetraethyl Orthosilicate of Sigma-Aldrich S.r.l. (Italy); Silres BS OH 100, Silicate TES 40 WN, and Silicate TES 28 produced by of Wacker-Chemie and Tegovakon V100 of the Evonik (ex Degussa), belonging to Goldschmidt industries; ESTEL 1000 produced by C.T.S. S.r.l. (Italy); Ethyl Silicate WS of AN.T.A.RES S.r.l. (Italy); and DN-Considant of KERAKOLL S.p.a. (Italy).

These formulations differ for:

- type and concentration of ethyl silicate [Tab.1]. Indeed, can be found TEOS monomer or oligomer pre-polymerized;
- type and concentration of solvent, if found [Tab.1];
- presence of catalysts (such as tin-based products).

These products consist liquid solutions, colorless or slightly yellowish (*i.e.* BS OH 100), solventless and ready to use. Ignition temperature is around 230°C, while the boiling point shows a range between 145°C to 200°C (such as ESTEL 1000), but it corresponds to 168°C in many products (like TES 28). Some are solvent free, like TEOS of Aldrich, Tegovakon V100 or BS OH 100, while other are diluted in solvent such as white spirit: ESTEL 1000 and TEOS WS of AN.T.A.RES.

All TEOS show insolubility in water, while they are miscible in alcohol, they have low molecular weight (*i.e.* 208,33 g/mol) and low values of density (approximately 0.93 g/cm^3 to 1.06 g/cm^3) that lead to a good penetration into the stone, where acting as mineral binders , being resistant to weathering agents action (such as water).

Many of these products do not contain any hydrophobic additives such as silanes or siloxane, though the treated surface may show slight beading but this does not mean it is water repellents. All these liquid products can be applied on dry sandstone surfaces when the temperature are between 10° to 25°C to obtain a good gel-forming. They are put on the stone's surface through different methods like spraying, brushing or dipping in according to the nature of the object to be consolidated. In this research, we have chosen to apply the silicate by brushing (on this topic, see *par.7.1*). A good consolidant effect is said to be obtained after four weeks to the treatments, but after already two/three weeks the final hardness is reached, i.e. when most of the ethyl silicate has been converted to silica gel.

TEOS Commercial Name	**Acronym**	**Silica content (%W/W)**	**Solvent**
Tetraethyl Orthosilicate (Sigma- Aldrich)	RP	98	Free
Silres BS OH 100 (Wacker)	BSOH	100	Free
Silicate TES 40 WN (Wacker)	TES 40	41	Alcoholic Compounds
Silicate TES 28 (Wacker)	TES 28	28.5	Free
Tegovakon V100 (Degussa)	TV	12	Free
Estel 1000 (CTS)	Estel	75	White Spirit
DN-Consolidant (Kerakoll)	KDN	> 1 - < 20	No data available
Ethyl Silicate WS (Antares)	Antares	80	White Spirit

Tab.1. Value of silica content and type of solvent certified in the Product Data Sheet for each TEOS studied.

Ethyl silicate of Aldrich can be considered a neat TEOS due to high value of silica content (i.e. 98%) and absence of solvent in its composition. Also, it shows a density of 0.93g/cm^3 at 25°C. Indeed Silres BS OH 100 it is declared as a monomeric ethyl silicate with 100% of TEOS content and no solvent inside. This compound has a declared density of 1.00 g/cm^3 at 25°C, and requires of neutral catalyst for increasing the rate of reaction and consequently shorten the time of gelation. This product is an evolution of Wacker OH and OH100 described in previous paragraphs.

Wacker TES 28 is said to be a product with composition similar to BS OH, but with a silica content of 28.5% and purity greater than 99.00%, besides density of 0.93 g/cm^3 at 25°C, and slight acidity ($\leq$ 5%). Another Wacker product called TES 40 WN is declared as a mixture of monomeric and various oligomeric and cyclic condensates of ethyl silicate. The average chain length is approximately five Si-O units, and the reactive silicon dioxide (i.e. silica) is 41% of the formulation. This products is activated through partial hydrolysis with alcoholic solvent and acid (like sulfuric acid) or mixing with a catalyst (like ammine or titanates). At last TES 40 show a density of 1.06 g/cm^3 at 20°C.

Tegovakon V100 is an evolution of Tegovakon V. This product shows an active content of 98.5% and should be composed by tetraethyl ortosilicate as main component (concentration ranging between 1% to 20%) and stannane, dioctylbis[1-oxododecyloxy] as catalyst (concentration between 1% to 2%). Also it has a density of 1.06 g/cm^3 at 25°C that lead to liquid high penetration into decayed stones, and consequently a strength of the matrix through gel formation. The Data Sheet of Tegovakon V100 mentions that it is insoluble in water while it is miscible in methylethylketone (MEK) or white spirit.

ESTEL 1000 of C.T.S. is a product used by Italian restorers because it is said to be particularly suitable for the consolidant and pre-consolidant treatment of weathered silicate stone materials. Indeed, it shows an active materials content of 75% based on ethyl silicate diluted in white spirit solution (*i.e.* white spirit D40 of C.T.S.), and it does not contain water-repellent additive. Also, this product shows a density of 0.97 Kg/l at 20°C, and a boiling point in the range between 145°-200°C.

In the case of Ethyl Silicate WS of AN.T.A.RES., it is sold for the consolidation of building materials degraded with silica matrix and high porosity. Its formulation is composed to 80% ethyl silicate and 20% white spirit employed as solvent, and it does not contain water-repellent additive.

DN-consolidant has been obtained by Kerakoll Spa. It is used for the consolidation of stone buildings, and it is said to contain between 1% to 20% of ethyl silicate but other data on its formulation and behavior are available.

More information on this silicate will come from the chemical and physical characterization, whose results will be shown in the sixth chapter.

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Chapter 4

SANDSTONE SAMPLES: COMPOSITION AND CHARACTERISTICS

Several sandstones coming from the industrial area of Firenzuola (FI, Italy) have been studied in this thesis. Since the Middle Age, this place is famous for the extraction and processing of sandstones, and today these practices are still active.

Firenzuola samples show different origin. Some belong to natural quarries placed along the Tuscan-Emilian Apennine, such as Firenzuola and Sarsina areas, while others come from natural quarries placed in Europe and are commercialized by industries in Firenzuola (i.e., Albanese stone from Albania or Giallo Antico from Spain).

All these stones showed different degrees of deterioration and aging to weathering agents, thus they were classified in two groups, *i.e.* modern natural stones and naturally aged stones. Stones newly extracted and processed, which do not show deterioration, belong to the first group. Stones extracted and worked in the past, which have been subjected to natural aging due to the action of weathering agents, were placed in the second group.

In this chapter the samples selected, their composition and characteristics obtained from the literature will be reported, while chemical, mineralogical and petrographic composition will be treated in the sixth chapter.

4.1. *Modern Natural Stones*

The sandstones belonging to this group were recently extracted and they were exposed to environmental conditions only for a short time and thus they did not show any visible form of deterioration. Moreover they showed a compact matrix with, apparently, low porosity.

These stones were commercially available and distributed by some industries of Firenzuola like Toscana Pietre S.r.l., La Borghesiana S.r.l., and Pietre di Toscana S.r.l., which gave us sandstone samples and information on their technical and compositional behavior.

Firenzuola stones take their name from the quarries or extraction area, and show some different compositional characteristics due to the processes of deposition and formation of their sedimentary layers.

Modern natural sandstones employed in this studied were: Brento, Colombino, Castellina, Medicea, and Piancaldoli, truely from Firenzuola quarries; Sarsina from the quarries of the homonymous town in the Romagna Apennine; Albanese and Giallo Antico sandstones from quarries placed in Albania and Spain.

Firenzuola sandstone (or "Pietra Serena") is a feldspathic greywacke with clay matrix and low calcite cement. Normally it shows medium and fine grain sizes, and a cerulean color that appears darker in the case of Colombino sandstone.

The mineralogical composition of Pietra Serena includes mainly quartz and feldspars (with K-feldspar greater than plagioclase), low rock fragments (like acid and alkaline rocks, serpentine, flint, clay and so on), micas (such as biotite and muscovite), and low-medium amount of carbonates (under 30%). Moreover, this stone can be classified as medium-heavy stones, on the basis of the ratio between volumetric bulk and absorption coefficient. [On the study of chemical, mineralogical, and mechanical properties of Firenzuola sandstones: Bargossi *et al.* 2002].

Brento stone [Fig.3] is a grey type of Pietra Serena extracted from quarries placed in Brento area. This sandstone belongs to "Masso Grosso" layer, which is placed over the "Monte della Colonna-Casaglia" and "Contessa" layers, and shows a depth between 4.90 to 5.00 meters. This layer was formed through two different turbiditic events close in time, consequently its composition appears heterogeneous, and on the basis of "marna" content, it can be divided in two kinds . The first characterized by a high-level of marna, and the second by a low-level of marna [Bargossi *et al.* 2002].

Other two types of Pietra Serena are Castellina and Medicea sandstones that exhibit the same composition but different external appearance. Indeed, Castellina shows a uniform gray-cerulean color with a compact and fine matrix [Fig.1], while Medicea exhibits a grey color with yellow frame [Fig.2]. These stones have high hardness and strength, so the first is employed in the construction of buildings, while the second is used for outdoor floors.

Castellina stone takes the name from the place of extraction, while Medicea stone owes its name to the noble family of De' Medici who ruled Florence between 13^{th} and 17^{th} century, when Pietra Serena knew a great use in architectural and sculptural fields in Italy, and mostly in Florence. Consequently, many quarries were active in Firenzuola and near the city of Florence [Gurrieri 2002, Massi 2002].

Fig.1. Castellina sandstone.

Fig.2. Medicea sandstone.

Colombino stone (called also "Pietra Forte Colombino", Fig.4) is a dark gray calcareous sandstone found in “Contessa layer”, *i.e.* the main layer of Firenzuola quarries (on this topic: par. 1.4.1.). Consequently, Colombino stone is considered the most important type of Pietra Serena extracted from these quarries.

This stone shows the same composition of the other Firenzuola sandstone but differs for the high value of carbonates (about 70%) [Bargossi *et al.* 2002].

Moreover Colombino is a heavy sandstone that exhibits a lower absorption degree compared to other types, which are lighter and show higher absorption or present intermediate mechanical properties.

Colombino shows the best mechanical properties such as low value of the linear thermal expansion coefficient and low microhardness, due to the presence of carbonate in its mineralogical composition. Other sandstones formed by quartz and feldspar, exhibit high values of microhardness [Bargossi *et al.* 2002].

The last type of Pietra Serena extracted from Firenzuola quarries is Piancaldoli that shows the same composition and characteristics of the other sandstone types listed so far [Fig.5].

Fig.3. Brento sandstone.

Fig.4. Colombino sandstone.

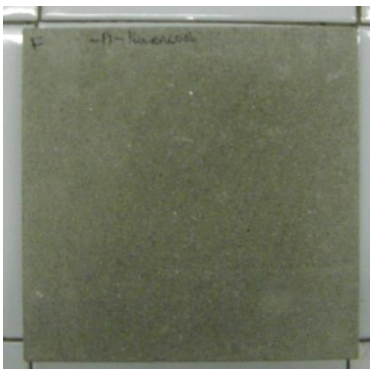


Fig.5. Piancaldoli sandstone.

Sarsina stone is another type of Pietra Serena belonging to Marnoso-Arenacea Formation, formed by sediments deposited since Burdigliano (ca. 20 million years ago) until Tortoniano (ca. 7 million year ago), when it stopped due to the closing of the basin. This formation is a flysh that consists of repeated sedimentary cycles with upward fining of the sediments, like sandstone, turbiditic pelite, pelagic marne that sometimes show turbiditic carbonates levels [Antoniazzi *et al.* 2011]. The main layer of this formation is the same of Firenzuola, *i.e.* "Contessa layer", locally called "Alberese" o "Colombio" (par. 1.4.1).

Sarsina sandstone is extracted from the area called "Para" situated in the basin of Para river, on the mountains near Cesena, between the city of Bagno di Romagna, Sarsina, and Verghereto [Antoniazzi *et al.* 2011]. This stone shows a yellowish color and the mineral composition is the same of the other samples studied.

Sandstones extracted from quarries placed in other countries were also examined, such as Albanese stones from Albania and Giallo Antico stone from Spain.

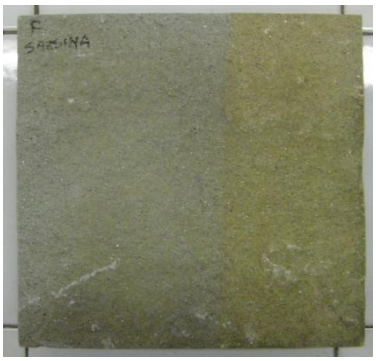


Fig.6. Sarsina sandstone.

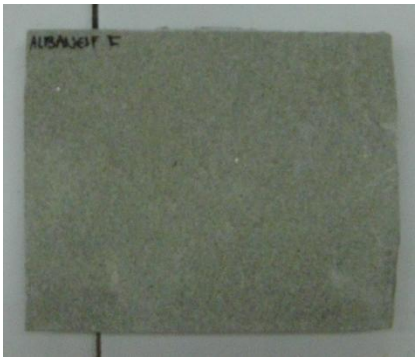


Fig.7. Albanese sandstone.

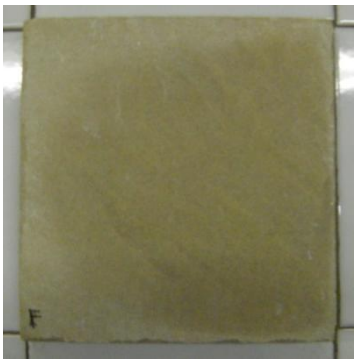


Fig.8. Giallo Antico sandstone.

Giallo Antico is a yellow sandstone that can be used for architectonical structures placed in indoor and outdoor environments. Albanese is a quartz-rich sandstone with a high natural resistance due to abundance of quartz grains (more than 90%) in its structure. So, this stone is employed in buildings and other architectonical objects.

During industrial processing, all modern sandstones were cut in small regular pieces with standard dimensions (ca. 15 × 15 × 1.5 cm). However some exceptions were found, like Medicea samples with rectangular shape or Sarsina pieces with its high thickness (ca. 3 cm).

On the composition, properties, and deterioration of each modern stone sample, little information were available. Therefore, physical-chemical, mineralogical and petrographic studies were required and their results are reported in the sixth chapter.

4.2. *Naturally Aged Stones*

These sandstones were extracted, worked, and deposited in an open space in the past (20-50 years). Stones were so exposed to the action of weathering and environmental agents for a long time, consequently they may have developed decay forms on their surface, like scaling, flaking, exfoliation, granular disaggregation, and cracks (preface par.1, and par.2.1).

Samples of Pietra Serena exposed to environmental conditions for more than thirty years were taken from the industrial deposit of La Pietra Serena di Firenzuola S.r.l., with the aim of studying their degree of deterioration and consequently proceed with their consolidation.

Fig.9. Mucchi 1 samples.

Fig.10. Mucchi 2 samples. .

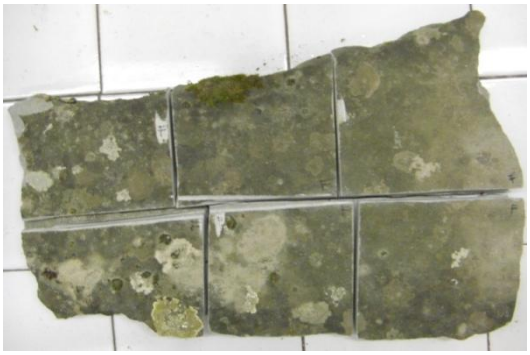


Fig.11. Mucchi 3 samples.

Fig.12. Mucchi 4 sample.

No information was available on these samples, thus physical-chemical, mineralogical and petrographic analyses were needed to understand their chemical and mineralogical composition. Also, the presence of decay elements was investigated. The results of these studies are available in the sixth chapter.

The naturally aged samples consisted in seven large and irregular plates of sandstone with different thickness between 1 cm to 5 cm. Some of these sandstones showed visible traces of biological attack due to lichens, mosses, bacteria, fungi and algae action. Consequently, we assumed the presence of chemical degradation into the stones, to be confirmed by the chemical and mineralogical analysis.

Conventionally, these plates of sandstone have been called "Mucchi" followed by a sequential number of identification for each samples (from 1 to 7). Moreover, each one has been cut in small pieces with different size due to irregular shape of the plates, on which the analyses were made.

Fig.13. Mucchi 5 samples.

Fig.14. Mucchi 6 sample.

Eight pieces of Piancaldoli stone exposed to the environmental conditions for ten years, were obtained from Toscana Pietre S.r.l.. These "Piancaldoli Aged" samples showed a regular shape and standard dimensions of 15 × 15 × 1.5 cm. No information was known about the composition and degradation of this stones, consequently further chemical and mineralogical analysis were required. These results are available in the sixth chapter.

Fig.15. Mucchi 7 samples.

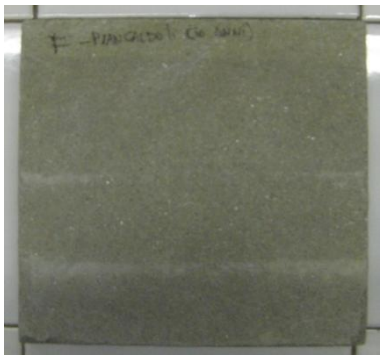


Fig.16. Samples of Piancaldoli Aged.

4.3. *Artificially Aged Stones*

After compositional and mechanical analyses (chapter 6), modern and aged natural stones showed a very compact and resistant structure without apparent loss of cohesion and with low decay elements. Consequently, these samples were not good candidates for experimental consolidation tests.

At the same time, few historical sandstones with high level of degradation were available in the laboratory, thus these samples cannot be employed for the screening of the better consolidant products. On historical stones, only the best consolidants coming out from this research had to be applied (the results are available in the chapters eight and nine).

Therefore, the compact matrix of modern and aged natural stones was degraded through thermal treatments with the aim to simulate an artificial aging. This methodology was developed by the research group of Dr. Ing. Elisa Franzoni at Engineering Department (DICAM) of Bologna University.

This action consists of thermal shocks where the stone sample is placed directly in preheated furnace at the temperature of 400 °C for two hours. After that it is removed and let cool down to environmental conditions. This process leads to a decrease of elastic modulus and an increase of porosity value, as demonstrated by the tests made on five samples of Colombino sandstone.

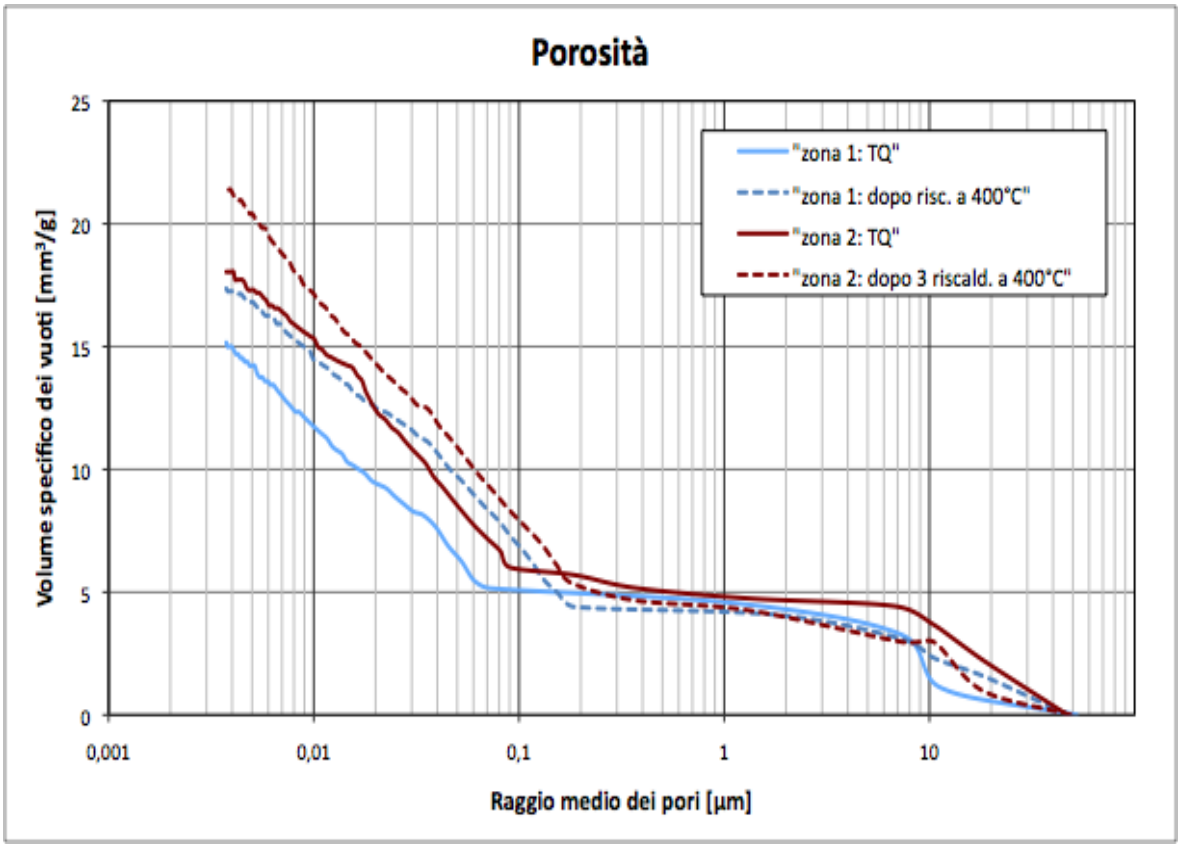
These treatments were repeated for two or three cycles, but the results do not show additional benefits. These tests showed a considerably variation of dynamic modulus [Tab.1]. Therefore, the comparisons between the data were made on the same points, both before and after the thermal treatments.

Porosity tests made after the first thermal cycle showed an appreciable increase of the porosity into the stone (ca. 22%), while the value of porosity do not increase further after two or three cycles.

Before and after the thermal treatments, porosity was measured in the same two points of the stone and it was also compared to untreated values (TQ). The results of these tests are available in Table n.1 and n.2.

Sample	Thermal treatment	Av. elastic dynamic module [GPa]	Variation [%]
COL1	TQ	48.8	-
	400 °C (2 h)	28.3	-42.0
	2 × 400 °C	26.2	-46.3
	3 × 400 °C	27.0	-44.7
COL2	TQ	45.4	-
	400 °C (2 h)	32.4	-28.6
COL3	TQ	10.9	-
	400 °C (2 h)	6.8	-37.6
COL4	TQ	42.2	-
	400 °C (2 h)	25.7	-39.1
COL 5	TQ	21.3	-
	400 °C (2 h)	13.8	-35.2

Tab.1. Results of thermal treatments of Colombino Sandstone (In cooperation with Dr. Ing. E. Franzoni *et al.*, UNIBO).



Tab.2. Results of porosity tests on Colombino Samples, reporting in abscissa the average radius in µm, and in ordinate the specific volume (In cooperation with Dr. Ing. E. Franzoni *et al.*, UNIBO).

On the surface of thermally-treated samples, some traces of decohesion were present, such as little cracks, scaling, and granular disaggregation [Fig.17-18]. Anyway, these treated stones are still more cohesive than historical samples.

Fig.17. Colombino untreated.

Fig.18. Colombino heat-treated with trace of disaggregation (on right and bottom side).

All natural sandstones (both modern and aged) showed a more compact matrix than historical sandstones. Thus thermal treatments were tested with the aim to obtain an acceptable disintegration of the matrix in order to test the consolidation treatments, aim of this thesis work.
The results of all these heat-treated samples show the same behavior of the Colombino stone, consequently the artificial aged stones are more cohesive and slightly degraded than historic samples. These cohesive properties are tested by surface abrasion and water absorption with sponge methods and reported in the sixth chapter.

4.4. *Artificial Test pieces*

The need of a sample that showed the same or very similar cohesion properties of historical sandstones, on which to perform the consolidation tests, brought us to realize artificial test pieces based on Firenzuola's sandstone powder.
Several specimens consisting in Firenzuola's sandstone powder (as main component, obtained by sandstone cutting), a cement (that simulates the natural binder of sandstones), and demineralized water, mixed together in different ratios, were tested.
Firenzuola's sandstone powder was provided by La Borghesiana S.r.l., and its chemical-mineralogical composition was characterized (Chap. 6).

The coarse part of sandstone powder was eliminated through a sieve of 500 μm, and the fine power so obtained was mixed with cement and water, with the aim to create the artificial test piece.

Two different types of binder (cement) were employed. The first binder was ABARIA CALCE RESISTENTE of BASF that is a hydraulic lime without cement, while the second was a special Portland cement (CEM I 42.5N SR0) with a low calcite content, created by ITALCEMENTI S.p.a.. Their composition was analyzed (chapter six).

Several artificial test pieces, with different compositional ratios between sandstone powder and binder, were tested, starting from 9 parts of sandstone and 1 part of binder and so on (i.e. 8:2, 7:3, 6:4 ratios), in which different quantities of water were added on the basis of total mass of the samples, in order to create new cementitious mixtures.

These artificial test pieces were allowed to stand for 28 days at 25°C and 50% RH, as usually reported by the standard cement practice. After that time, the surface layer was removed through dry abrasion with silicon carbide sandpaper (180), to bring out the surface layer, influenced by the contact with the plastic mold, and the characteristics of these samples were analyzed and compared.

The best specimen showing similar cohesive characteristics to the historical samples was IT20, made by 85 g of Firenzuola's sandstone powder (80% w/w) and 21 g of special Portland cement (20% w/w) for a total weight of 106 g. Moreover, 33 g of demineralized water were added to mix the two solid compounds (i.e. 31% of the total weight of the solid sample). These artificial test piece showed a circular shape with a diameter of 10 cm and thickness of ca. 1 cm.

Consequently, a substantial number of specimens IT20 was made for the experimentation of the different consolidating methods.

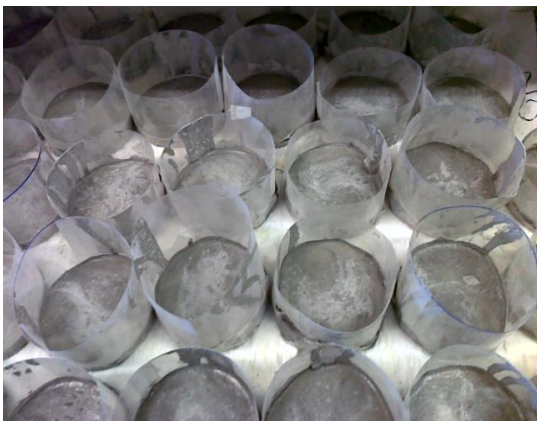


Fig.19. Creation of artificial test pieces.

Fig.20. Drying step of artificial test pieces.

Fig.20. IT20 sample with the surface layer not yet removed.

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Chapter 5

ANALITICAL TECHNIQUES

All sandstones samples, artificial test pieces, and ethyl silicates were preliminary studied by different analytical techniques with the aim to understand their composition, characteristics and properties.

Each stone sample (like Modern, aged, and historical that will be discussed in the eighth chapter), and Firenzuola's powder sandstone, were characterized through physical-chemical, mineralogical and petrographic analyses in order to know their chemical and mineralogical composition; the degree of cohesion of the matrix, and the presence of degradation elements were studied through XRF, XRDP, SEM-EDS, petrographic analysis on cross-section, pHmetry and conductimetry tests.

Stone properties like permeability and resistance were verified through water absorption capacity (NORMAL 7/1981) and the sponge contact method (UNI 11423/2011), and two mechanical resistance tests, which consist of superficial and deep abrasion (by ASTM D4060-95 and UNI EN ISO 10545.6/2000 methods).

FT-IR and NMR analysis were employed to investigate the formulations of eight commercial ethyl silicates; these products were then applied through different methods on artificial samples. The level of impregnation and distribution obtained and the possible chemical interaction were checked by SEM-EDS, FT-IR, XRF, XRDP techniques.

The characterization of the treated samples were made, again, by the sponge contact method (UNI and NORMAL tests) and two mechanical resistance tests to check the superficial and deep abrasion (by UNI EN ISO and ASTM methods).

Likewise treated and untreated samples with the different method (i.e. application of only TEOS products, only barium hydroxide, and barium hydroxide after ethyl silicate) were analyzed and the results were compared in order to understand which method showed good consolidation properties.

5.1. *Infrared Spectroscopy with Fourier Transform (FT-IR)*

Ethyl silicates have been investigated with the aim to know their chemical composition, so to understand their reactive behavior when applied on silica surface.

FT-IR transmittance spectra were obtained by Jasco FT-IR 4200 spectrometer, 32 scans, in the range 4200-450 cm^{-1}. Each ethyl silicate was analyzed in liquid state using two windows of NaCl.

5.2. *Nuclear Magnetic Resonance Spectroscopy (NMR)*

This analysis was made by FT-NMR AVANCE400 with ^{12}C proton, BBI 5mm multinuclear probe for liquid with Z gradients (intensity max. 53G/cm), acquisition to frequencies of the proton (400MHz) and of resonant nuclei between 161.9 MHz and 26.6MHz).

This technique was employed to try to identify unknown organic compounds in the commercial mixture of different ethyl silicate samples. It allows to obtain structural information and to characterize organic molecules, and synthetic and natural macromolecules found in liquid solution.

Ethyl silicate samples have been investigated using ^{29}Si isotope [On this method: Kelts *et al*. 1989, Cervantes *et al.* 1999, Zárraga *et al.* 2002, Zendri *et al.* 2007].

5.3. *X-Ray Powder Diffraction (XRDP)*

This technique was used to obtain information on the crystalline composition of sandstone samples, sandstone powder, cementitious binders, and artificial test pieces. It was also used to identify the nature of soluble salts extracted by some sandstone samples.

All samples treated with the different consolidation methods (i.e. artificial test pieces, artificial aged stones, and historical stones), were analyzed through this technique to identify, after the reaction, the possible new crystalline compound formed.

XRPD instrument was a Panalytical X'Pert Pro with Xcelerator detector, by Cu_{Kalfa} incident radiation, Ni filter, 40 KV as supply voltage, and current intensity of 40 mA in a range 5 to 65 2*theta*.

5.4. *X-Ray Fluorescence (XRF*)

XRF measures were performed with a Bruker spectrometer, type AXS Artax200, micro-EDXRF, with SDD detector and tube with Mo target (max 50 kV, 700μA, 30 W). The energy resolution is <155 eV at 10^3 Kcps, being the energy recording at 12 eV per detector channel,

while the collimation system consists of micro-collimators of X-rays with a spot of 650 μm in diameter. The instrument is equipped with a laser pointing system and a CCD camera.
This technique was employed to identify both the chemical elements that compose the stone matrix of each samples, and the level of impregnation and distribution of barium into the samples treated.

5.5. *Scanning Electron Microscopy (SEM*)

SEM analysis was used to study the morphology and microstructure of stone samples and the level of impregnation after the treatments, and to try to determinate the distribution-penetration of barium in the samples. The used scanning electron microscopy was a Philips XL-30 of FEI Company, with microanalysis system X-EDS (Oxford INCA-350).
All the stones and artificial test piece samples were analyzed by SEM technique gluing them on aluminum stabs by an Ag-conductive glue. After that, a superficial conductivity was obtained through ion sputtering of approx. 5nm of metallic gold on their surface.

5.6. *Petrographic Microscope*

The mineralogical compositions of natural and historical stones, and artificial test pieces, were studied through petrographic analysis on cross section. The purpose of this study was to identify the texture (i.e. grain-size, porosity, shape and distribution of the grain), and mineralogical composition of the matrix.
The stone samples have been incorporated in cross-sections and observed in transmittance through a petrographic microscope of Leitz Orthoplan, that works in polarized light, to identify the minerals present in the matrix.

5.7. *pHmetry and Conductimetry tests*

The determination of soluble salts present into the stone samples was made on water solutions and analyzed through conductimetry and pHmetry tests.
The solutions were obtained from 10 g of sandstone powder (removed from the stone and reduced in grain-sizes dimension by hand mortar), that was put in 100 ml of demineralized water and allowed to settle for a few minutes. Then the solution was subjected to cold magnetic agitation for one hour and consequently mechanically separated by centrifugation of the suspension, at 6000 rpm for 10 minutes. A clear liquid phase was obtained, that was used for conductimetry and pHmetry tests. The first analysis was made through conductometer Micro CM 2201 by Crison Instruments, 1 cm2 Pt cell electrode, that was previously checked for the cell

constant by immersion in KCl 0.1 M buffer solution. pHmetric analysis was made by pHmeter PH 510 of XS Instruments, with a glass electrode, previously calibrated by buffer solutions.
After these analyses the water solutions were put in an oven at 50 °C for 24 hours, to allow the evaporation of water with the precipitation of soluble salts, that were employed for other analyses (*i.e.* XRD and XRF).

5.8.*Granulometric Analysis*

This analysis determined the different coarse grain-size distribution that forms the Firenzuola's powder sandstone, used to prepare artificial samples. A set of sieves with different free net size (500 μm, 315 μm, 250 μm, 180 μm, 125 μm, 90 μm, and pan), placed one above the other in decreasing order was employed for the separation of the powder by mechanical vibration. In the first sieves a known amount of Fiorenzuola's powder (300 g) was placed and was then subjected to mechanical separation: after a given time the fractions remaining in each sieve were weighed, and the values were expressed as a percentage (% w/w) on initial weight of the sample.

5.9. *Water absorption*

Analysis of water absorption is a decisive aspect when monitoring deterioration of stone and the past conservation treatments, or when selecting a proper conservation treatment.
In sandstones, water absorption depends by structure and size distribution of the pores. This property is one of the main causes of accelerated deterioration. Consequently, the water absorbing behavior is a significant factor for the stones conservation, such as the determination of stone propensity to future deterioration. Moreover, changes in the capacity of water absorption can be an indication of the degree of deterioration or the effectiveness of past treatments.
The tests employed to measure water absorption were Capacity of water absorption for total immersion (Normal-7/1981) and Determination of water absorption by contact sponge (UNI 11432:2011).

5.9.1. Capacity of water absorption for total immersion (Normal-7/1981)

This test was employed to understand the capacity of water absorption of natural stones (which were modern and aged stones).
Stone samples were dried in an oven at 60 °C for 24 h, and weighed. After that, they were placed in a pot under total immersion in demineralized water and boiled for one hour. The stones were then swabbed with a damp cloth and weighed in ambient conditions. The difference between the weight of wet (w_2) and dry sample (w_1) divided dry sample weight expresses the capacity of

water absorption of the stone. The percentage of water absorption (Wa) is expressed by the following formula:

$$\text{Wa (\%)} = \frac{w2-w1}{w1} \cdot 100$$

5.9.2. *Determination of the water absorption by contact sponge* (UNI 11432:2011)

This technique gives a figure of the porosity of samples (porosity is proportional to the absorption) and hydrophobic/hydrophilic behavior of stone surface (i.e. high hydrophobic behavior leads to a lower absorption). On the bases of treatments this two conditions can coexist, thus it is wrong to assume that a stone with high porosity absorbs more than a stone with low porosity.

This method consist of a sponge (type Calypso-natural made by Spontex), enclosed in a 1034 Rodac contact plate composed by a base and a cover. The diameter of the sponge corresponds with the inner diameter of the base, while the height of the sponge exceeds the vertical borders of the bases. For the measurement the cover of the contact plate is removed, and 6 ml of demineralized water are added to the sponge: the sponge, again enclosed in the contact plate, is weighed (m_i). After weighing, the cover of the contact plate is removed and the sponge is pressed manually against the stone surface until the vertical borders of the base touch the stone surface. After a contact time (t) of 5 minutes, the sponge is removed and weighed inside the closed contact plate (m_f) [Recent studies on the application of this method on stone were made by Vandevoorde *et al.* 2012, Vandevoorde *et al.* 2013].

The water absorption (Wa) is calculated on the basis of the following formula:

$$\text{Wa (g /cm}^2 \cdot \text{min)} = \frac{(mi-mf)}{A \cdot t}$$

Where A is the surface of the sponge (i.e. A = 23.76 cm^2), m_i and m_f respectively the initial and final mass of the sponge enclosed in the contact plate, and t the time of contact on stone surface.

In this study this method was employed to determine the water absorption of all stone samples (natural, artificial aged, historical), artificial test piece, and treated samples with the different consolidating methods [Fig.1].

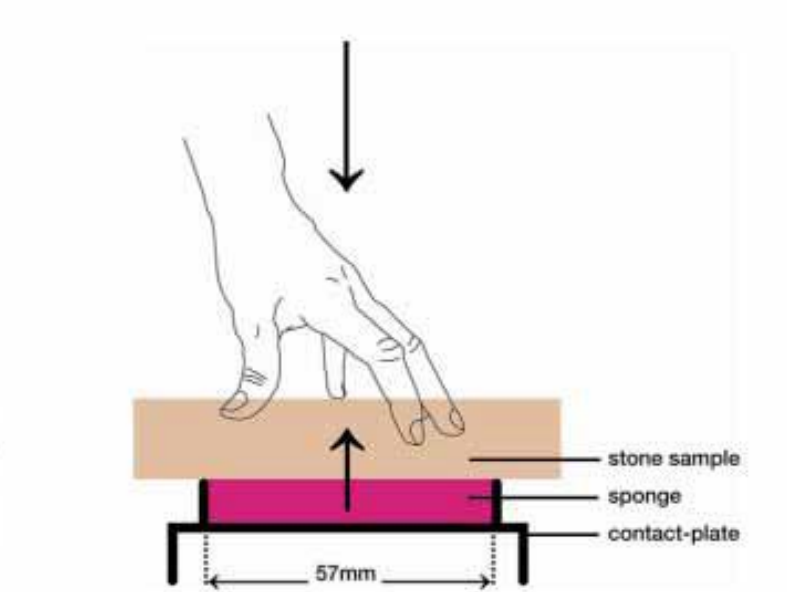

Fig. 6. Application of contact sponge method (Vandevoorde *et al.* 2013).

5.10. *Mechanical Resistance tests*

The abrasion, both superficial and deep, resistance properties of natural and historical sandstones, and treated and untreated samples were checked by two distinct mechanical resistance tests, to superficial and deep abrasion (named Taber and CAP methods). These tests should allow to determine the different resistance of a deteriorated stone (lower abrasion resistance means greater decay of the stone) before and after the consolidating treatment: the increase of the resistance of the treated stone could demonstrate the effectiveness of the treatment (low loss of weight due to abrasion means great strengthening effect of the consolidant).

The resistance tests were both executed at Kerakoll S.p.a. Labs, through the collaboration established during these years of research.

5.10.1 *Standard test method for abrasion resistance of organic coatings by the Taber abrader*

Surface abrasion resistance is evaluated using the Taber abrasion machine (model 5131, Fig.2) using the ASTM D4060-95 method.

The stone sample was mounted on a platform turning on a vertical axis against the sliding rotation of two abrading wheels, with one wheel rubbing the specimen toward the periphery, and the other rubbing inward toward the center [Fig.3].

The test specimen can be abraded using various loads (normally 500 or 1000g) for various cycles (normally 50 cycles at minute) using H-22 abrasion wheel. In this case, three cycles per minute

were made, corresponding to 50, 100 or 150 cycles of abrasion in order to measure the variation of the surface resistance of the sample when increasing the depth of abrasion. The stone sample was weighted before and after each cycle and the difference of weight corresponds to the volume removed.

Fig.7. TABER mod. 5131 (taberindustries.com)

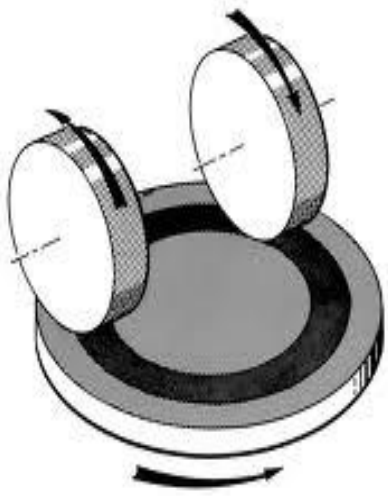

Fig.8. Action of abrasion wheel on stone surface (taberindustries.com)

5.10.2 *Determination of resistance to abrasion*

This instrument (called also CAP, Fig.4), was used to determine the resistance to deep abrasion (on the basis of the UNI EN ISO 10545.6/2000), by measuring the length of a groove produced on the specimen surface by a disk that turns at controlled angular speed and makes a constant pressure onto the specimen. A known amount of abrasive material, like Corundum (white fused aluminum oxide), falls down between the disk and the specimen and creates the furrow [Fig.5]. Its measurement of length leads to deduce the volume removed from the samples.

On each stone and artificial test piece samples, five measures were made in different point of the surface with the aim of acquiring information on the depth resistance of the sample within its structure. The cycles were made in the following order:

- n. 5 cycles with a fall of 10 g of Corundum
- n. 10 cycles with a fall of 20 g of Corundum
- n. 20 cycles with a fall of 40 g of Corundum
- n. 30 cycles with a fall of 60 g of Corundum

- n. 40 cycles with a fall of 40 g of Corundum
- n. 50 cycles with a fall of 100 g of Corundum

Theoretically, in a homogenous sample (i.e. untreated samples), the performance of abrasion depth is represented by an inclined line that increases towards positive values.

Fig.4. CAP Instrument (edit by abrasion gabbrielli.com).

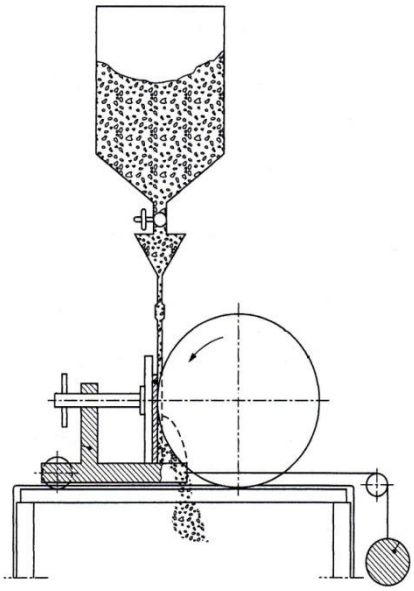

Fig.5. Diagram illustrates the CAP operation (edit by UNI EN 12808-2:2003).

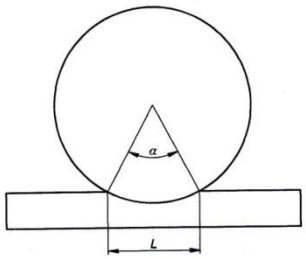

Fig.6. Definition of the length of (edit by UNI EN 12808-2:2003).

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http://www.taberindustries.com/taber-rotatory-abraser

Chapter 6

BEFORE THE TREATMENT: ANALYSIS OF THE MATERIALS

In this chapter we will report the results of the physical-chemical and mechanical characterization of the different TEOS, sandstones samples, and artificial test pieces employed in this research.

6.1. *TEOS Samples*

FT-IR and NMR analyses were employed to investigate the formulations of eight commercial ethyl silicates. After the trial of treatment, the level of impregnation and distribution into the samples obtained and the possible chemical interaction were checked by SEM-EDS, FT-IR, XRF, XRDP techniques.

6.1.1. *Infrared Spectroscopy with Fourier Transform (FT-IR)*

The FT-IR analysis did not provide, as expected, important information on the composition of the commercial products because they all showed very similar spectra with common bands assigned to various vibrations: 2975, 2925, 2890, 1895, 1485, 1440, 1390, 1365, 1295, 1170, 1100, 1080, 962, and 791 cm^{-1} [Some of these spectra are reported in Fig. 1-4].

The in-plane Si-O stretching vibrations of the silanol Si-OH groups appear at about 960 cm^{-1}. The intense silicon–oxygen vibrations appear mainly in the 1200–1000 cm^{-1} range, revealing the existence of a dense silica network, where oxygen atoms play the role of bridges between two silicon sites. The very intense and broad band appearing at 1095–1089 cm^{-1} and the shoulder at around 1200 cm^{-1} are assigned to the transversal and longitudinal optical modes of the Si-O-Si asymmetric stretching vibrations, respectively. On the other hand, the symmetric stretching vibrations of Si-O-Si appear at about 800 cm^{-1} [Al-Oweini *et al.* 2009].

Peaks corresponding to C-H vibrations appear in the 2975 to 2890 cm^{-1} range and between 1485-1365 cm^{-1}. These peaks were assigned to C-H symmetric deformation of CH_3 (2975 cm^{-1}) and CH_2 (2890 cm^{-1} and 1390 cm^{-1}) groups, C-H antisymmetric stretching vibration of CH_2 (2925 cm^{-1}), and C-H symmetric deformation vibration (i.e. bending) of CH_3 and CH_2 groups (1485, 1440, 1390, and 1365 cm^{-1}), the peak at 1295 cm^{-1} is due to C-O stretching [Rubio *et al.* 1998].

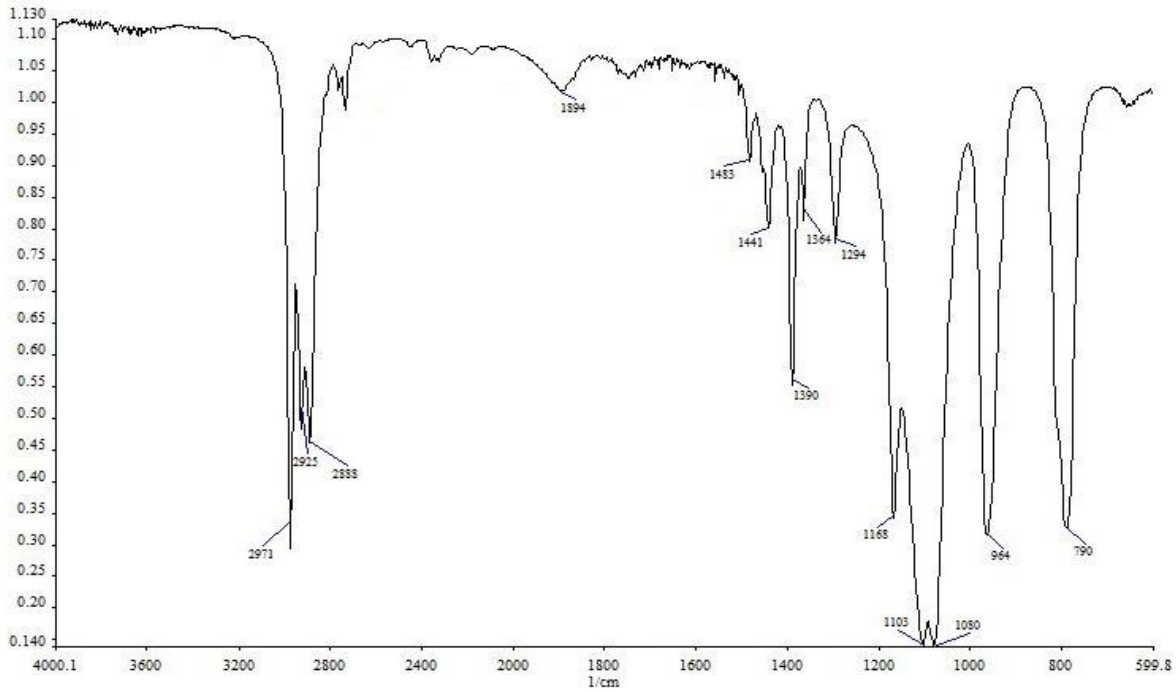

Fig.9. FTIR spectrum of RP TEOS from Sigma-Aldrich.

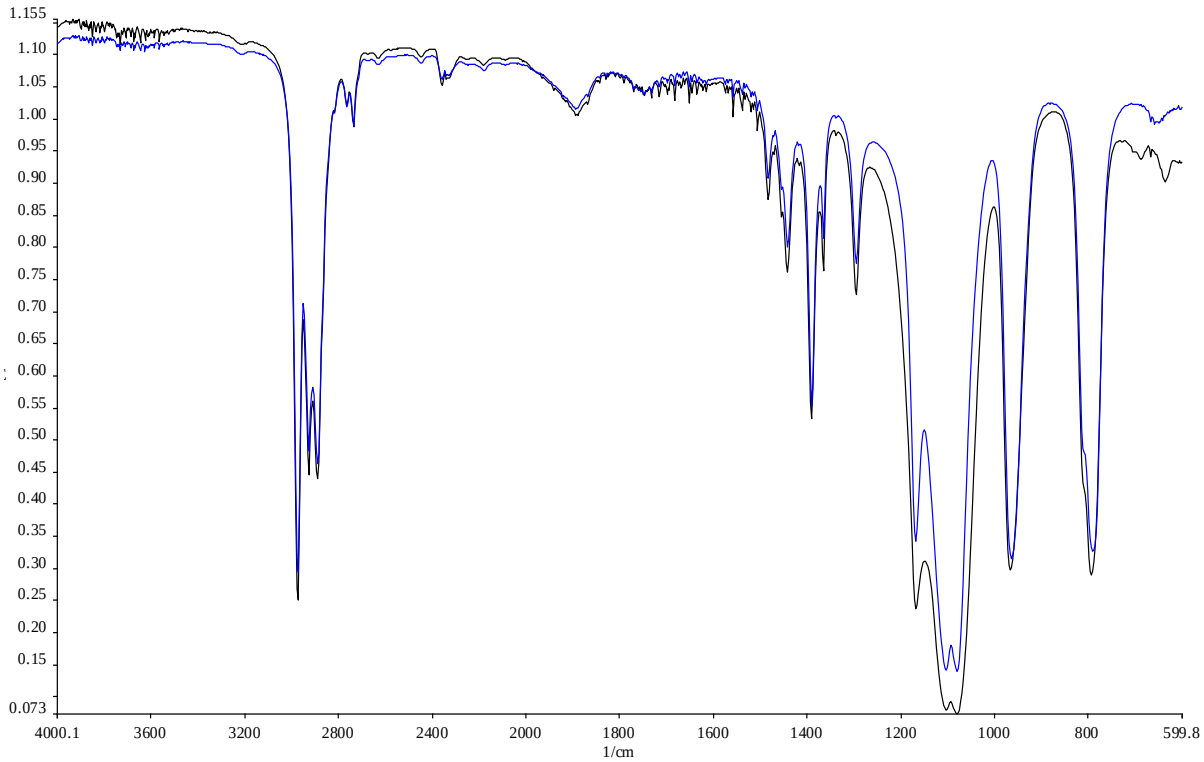

Fig.2. Comparison of FT-IR spectra of RP TEOS from Sigma-Aldrich (blue) and of BSOH100 (black).

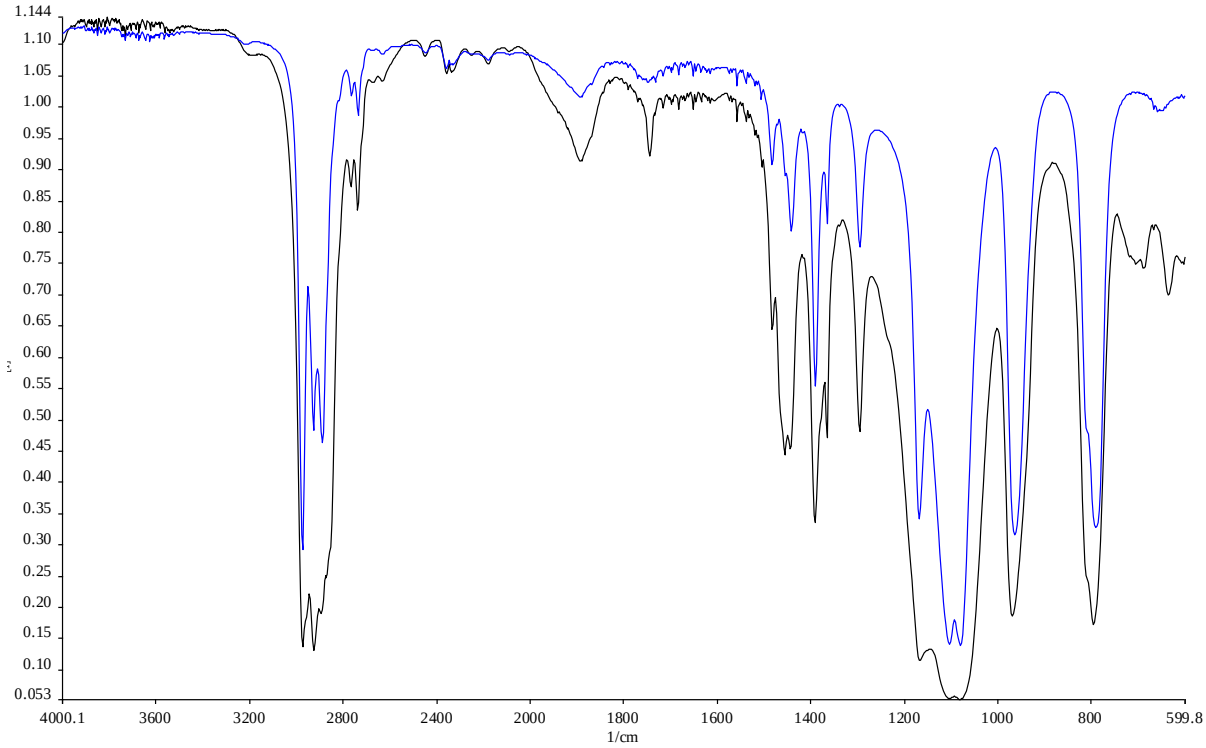

Fig.3. Comparison of FT-IR spectra of RP TEOS from Sigma-Aldrich (blue) and of ESTEL1000 (black).

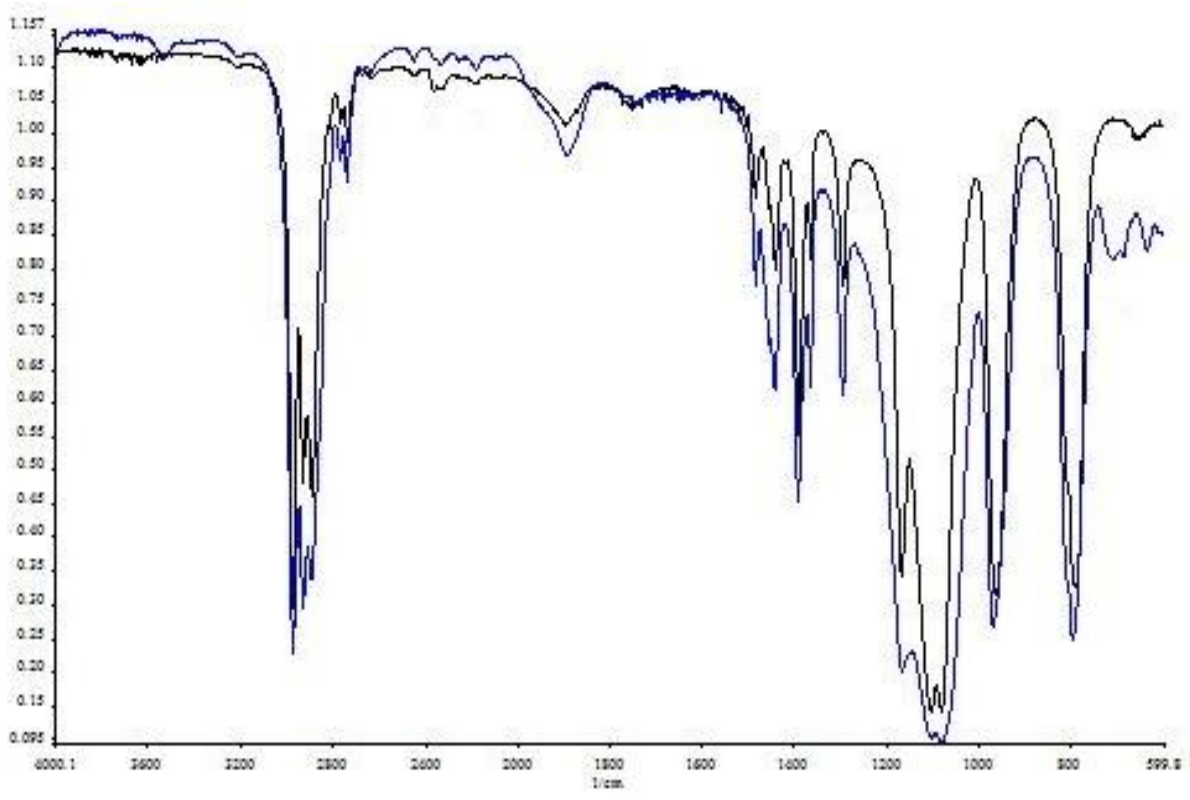

Fig.4. Comparison of FT-IR spectra of RP TEOS from Sigma-Aldrich (black) and of ANTARES (blue).

6.1.2 *Nuclear Magnetic Resonance Spectroscopy (NMR)*

NMR analysis of the commercial products gave some indications on the composition of the eight commercial ethyl silicates. Indeed, the interpretation of NMR spectra was not easy, due to the mixture of organic solvents and components in the commercial TEOS, but some common hints were found.

RP TEOS of Aldrich showed a clear and clean spectrum that is characteristic of the pure substance. Similar spectra were obtained from TES 28 and TES 40.

ESTEL 1000 and, mostly, ANTARES show small peaks at a chemical shift around -21 ppm, probably corresponding to silicone components present in low concentration.

BS OH 100 showed high signals at a chemical shift of -82 ppm, and a complex behavior around – 96 ppm: in this product, like in some other, the NMR spectra suggested the presence of pre-polymerization products based on ethyl silicate employed in the commercial formulations. This could be stated by the presence of typical spectra quartets, in the region – 86.2 -88.8 ppm, from the presence of condensation products (hydrolyzed monomers should give peaks in the region -79.02, -76.50 and -74.24) [Turner and Franklin 1986].

Moreover, solvents and dispersing agents with low molecular weight could be detected, probably belonging to the family of ethanol, white spirit (formed by a not pure mix. of aliphatic and acyclic hydrocarbides), dichloropropane, iso-propanol, methilethilchetone, toluene, and so on.

6.2. *Stone samples*

All stone samples and Firenzuola's powder sandstone were studied through XRF, XRDP, SEM-EDS, petrographic analyses on cross-section, together with pHmetry and conductimetry tests, with the aim of identifying their chemical-mineralogical composition, characteristics of the matrix (like cohesion, grain-size etc.), and degradation elements (like soluble salts).

Moreover, permeability properties were verified through water absorption capacity (NORMAL 7/1981) and sponge contact method (UNI 11423/2011), while resistance properties were checked by superficial and deep abrasion analyses.

6.2.1. *Granulometric Analysis*

The main granulometric fraction of Firenzuola's sandstone powder corresponds to grains with a dimension under 90 μm (35.60%), followed by grains with size over 500 μm (22.87%). The fractions between 90 and 250 μm shows approximately the same amount of grains (from 9.00 to

11.30%), while there are only few grains with dimension between 250 and 500 µm (i.e. 6.30% and 4.17% of the total sample) [see Tab.1 and Fig.5].

W1 Powder	W2 Powder	> 500 µm	500-315 µm	315-250 µm	250-180 µm	180-125 µm	125-90 µm	< 90 µm	H_20
300 g	296.4 g	68.6 g	18.9 g	12.5 g	27.1 g	28.7 g	33.8 g	106.8 g	3.6 g
100%		22.87%	6.3%	4.17%	9.03%	9.57%	11.27 %	35.6 %	1.2%

Tab.1. Values of the granulometric fractions (expressed both in grams and percentages) of the sandstone powder weighted before (W1) and after the analysis (W2).

After removing the coarser fraction (i.e. the fraction with grains over 500 µm), which is not present in the porous matrix of degraded stone samples, this sandstone powder was employed to create the artificial test pieces.

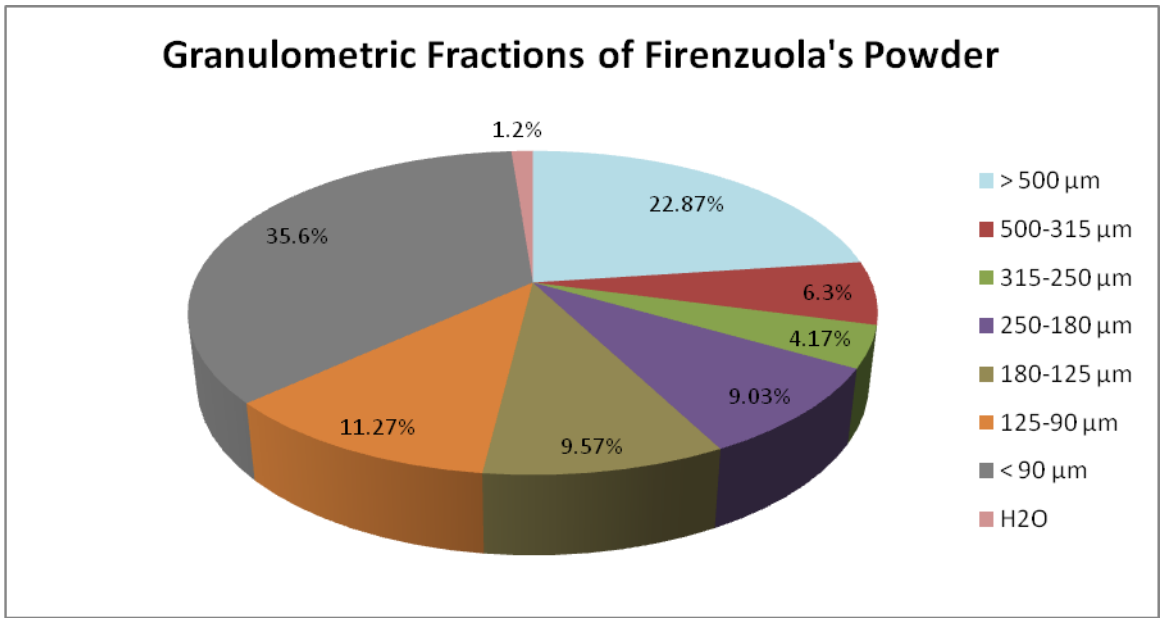

Fig.5. Percentages of granulometric fractions that form Firenzuola's powder.

6.2.2. *XRDP Analysis*

Modern and natural aged samples were studied through XRDP analysis.

All stones show a matrix based on Quartz, Feldspars (mainly Na-feldspars, like Albite found in all samples, and K-feldspars such as Microcline, Sanidine, and Orthoclase), Micas with Muscovite predominant on Biotite, and fragments from magmatic and metamorphic rocks (like Olivine in most samples of naturally aged stones, minerals of Chlorite group in all samples,etc.).

In some cases, traces of other clay minerals were found, like Illite and Montmorillonite (i.e. Albanese and Piancaldoli aged samples) [Fig. 6-9]. In all stones, the binder of the matrix was found to be calcite and dolomite.

Moreover, XRDP technique was used to identify the soluble salts extracted from modern and aged stone samples. Only few stones show the presence of this decay elements, being mainly calcium sulfate hydrate (i.e. gypsum) in Colombino, Albanese, and Castellina samples [Fig. 10-11].

This technique was employed to know the mineralogical composition of Firenzuola's powder and also the one of commercial cements (*i.e.* BASF and ITALCEMENTI) used to create artificial test pieces.

Firenzuola's sandstone powder shows, as expected, the same composition of all sandstones samples based on Quartz, Albite, Muscovite, Sanidine, Chlorite, Calcite and Dolomite. Cements exhibit, of course, calcium compounds as main components: BASF cement consists of calcium silicates (Alite, Belite, and so on), calcium hydroxide (Portlandite), calcium oxide/hydroxide (Lime), calcium carbonate (Calcite), and Quartz; ITALCEMENTI cement is composed by the same calcium silicates and calcium oxides, but with no carbonates [Fig. 12-14].

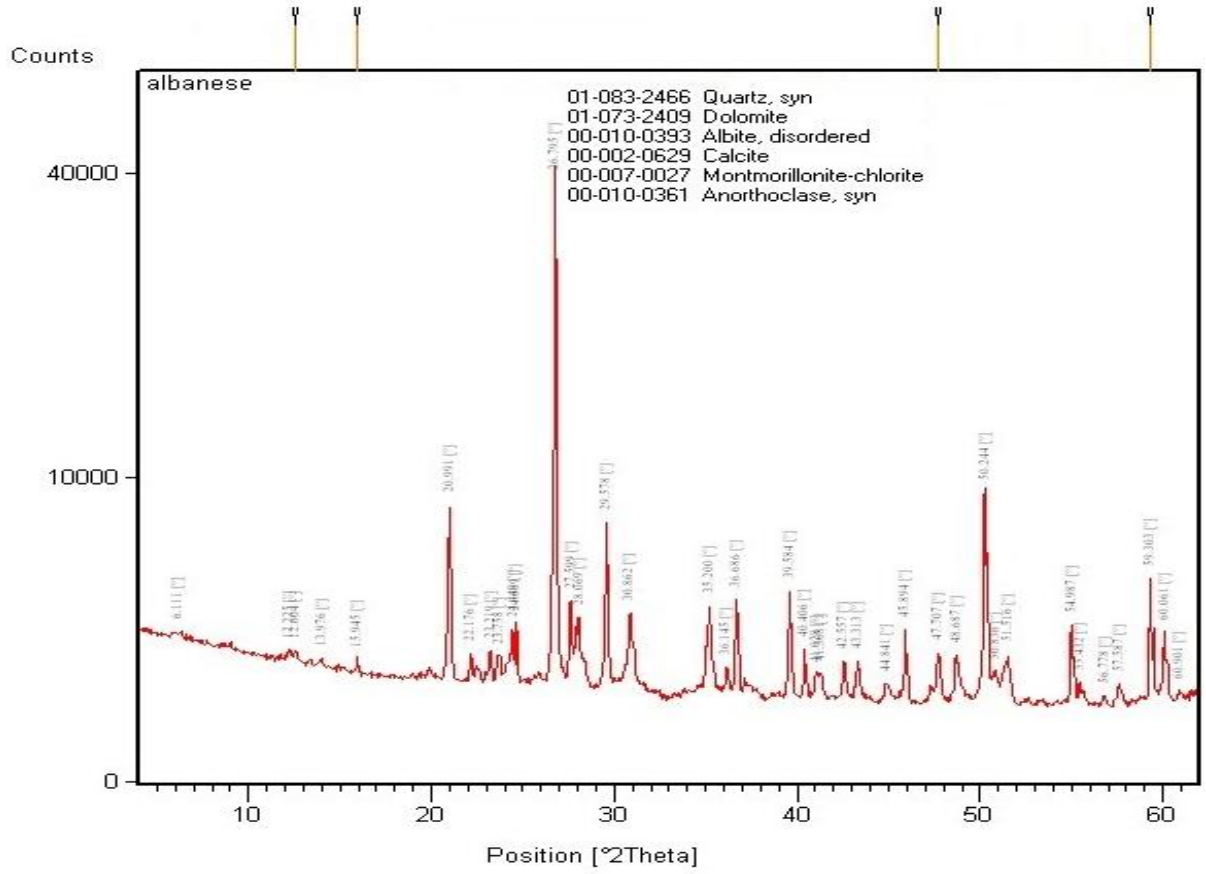

Fig.6. Mineralogical composition of Albanese stone, after XRDP analysis.

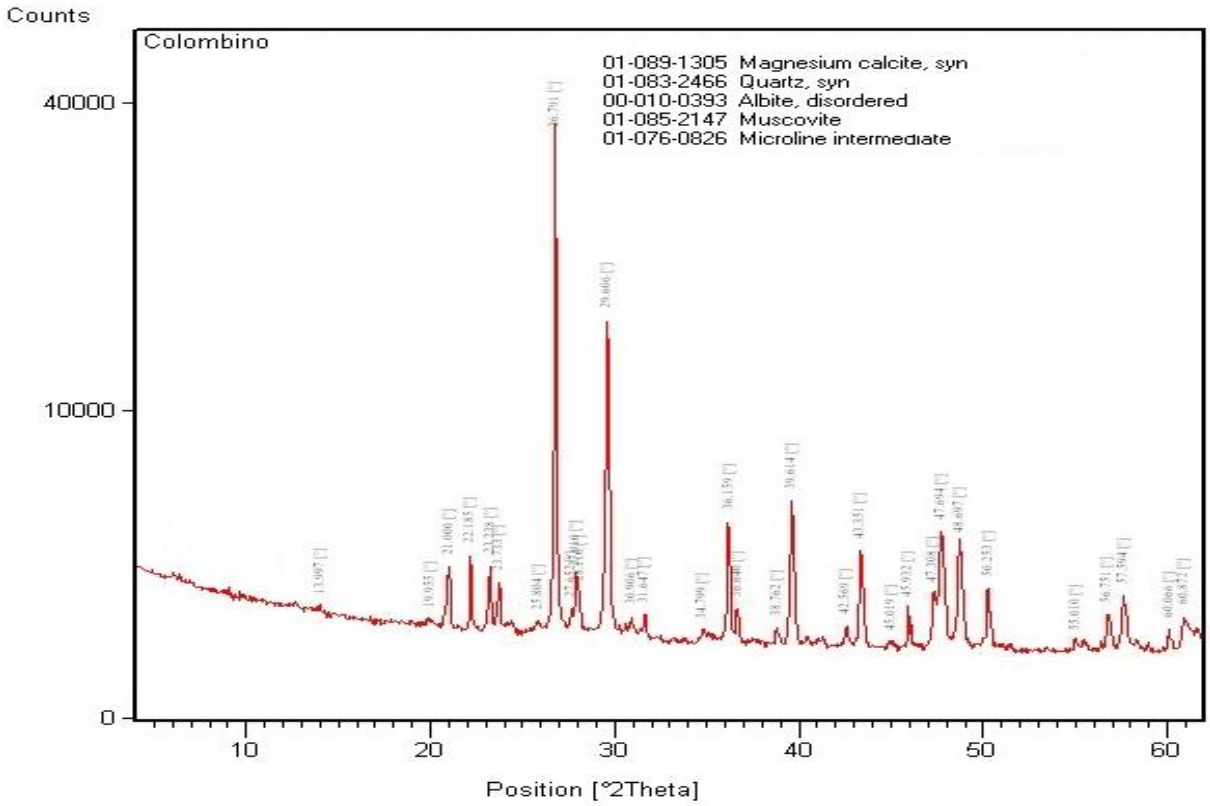

Fig.7. XRDP spectrum of the mineralogical composition of Colombino sample.

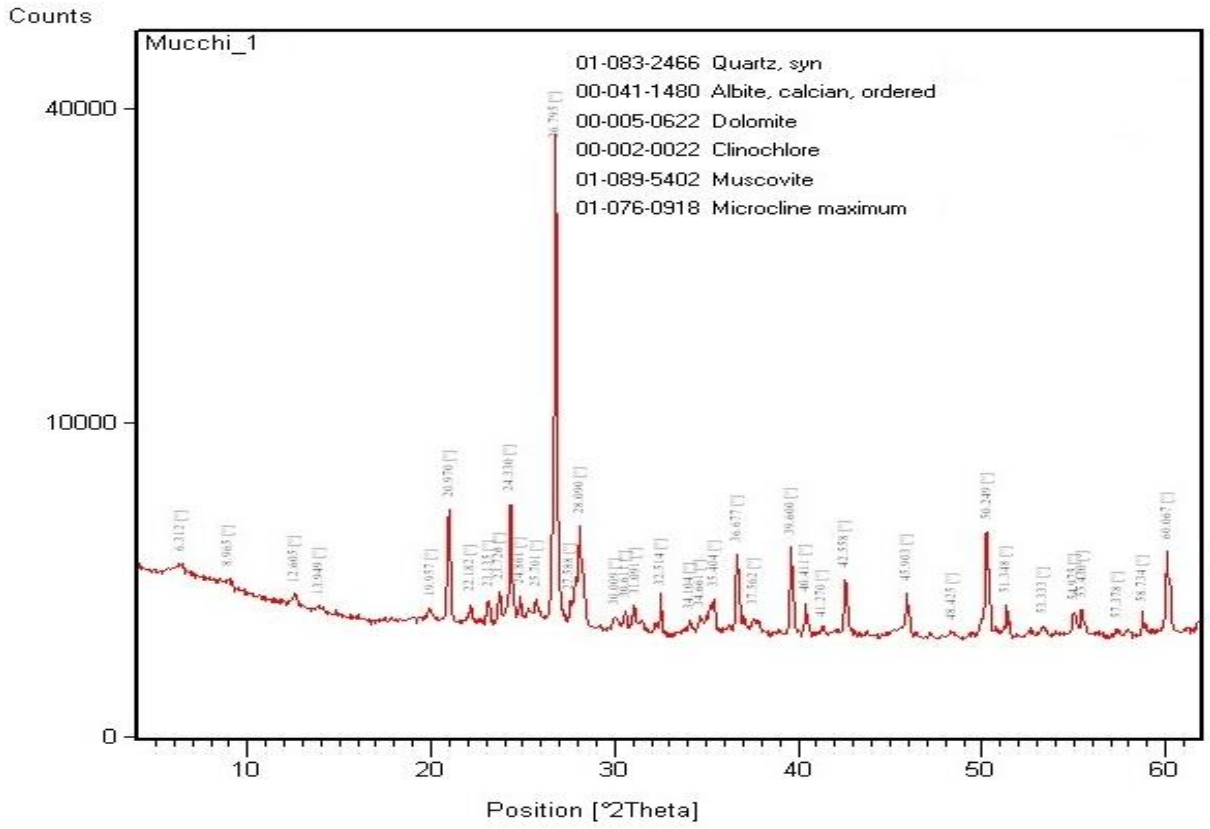

Fig.8. XRDP spectrum of the mineralogical composition of Mucchi_1 (natural aged stone sample).

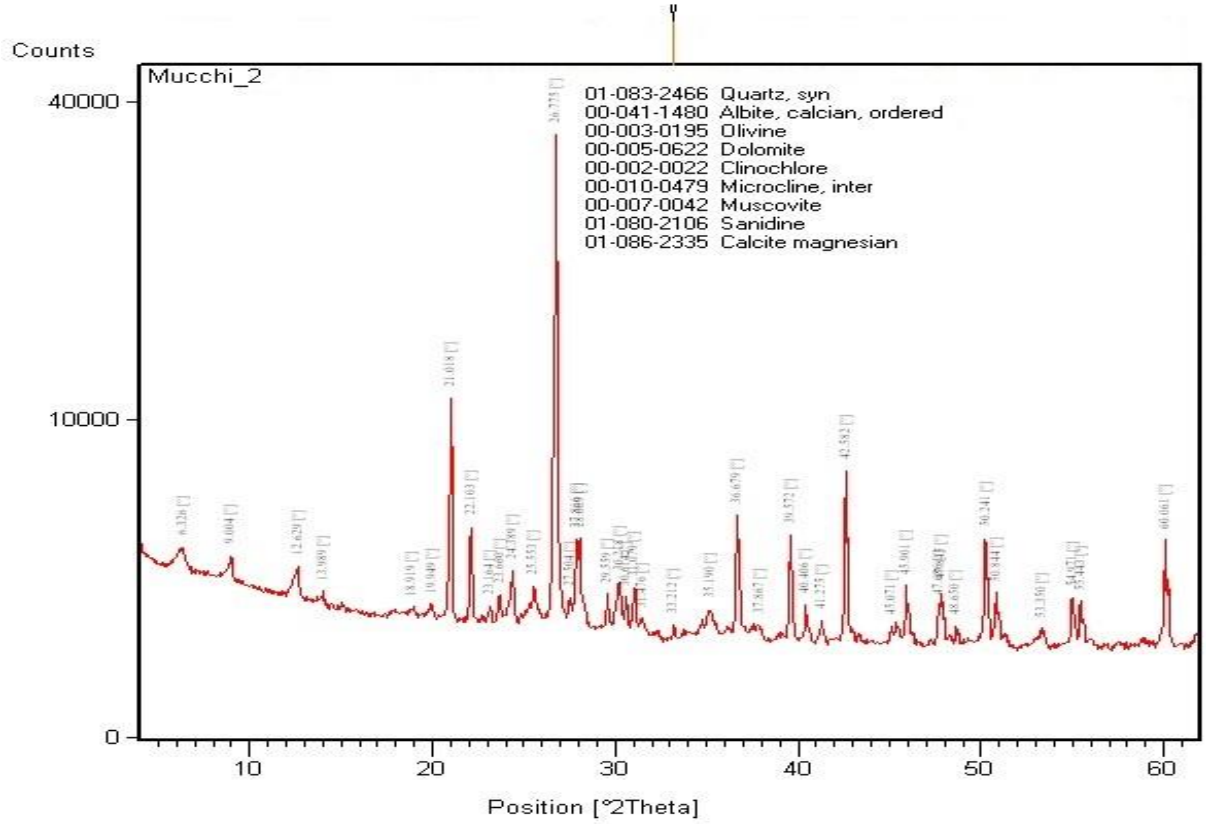

Fig.9. XRDP spectrum of the mineralogical composition of Mucchi_2 (natural aged stone).

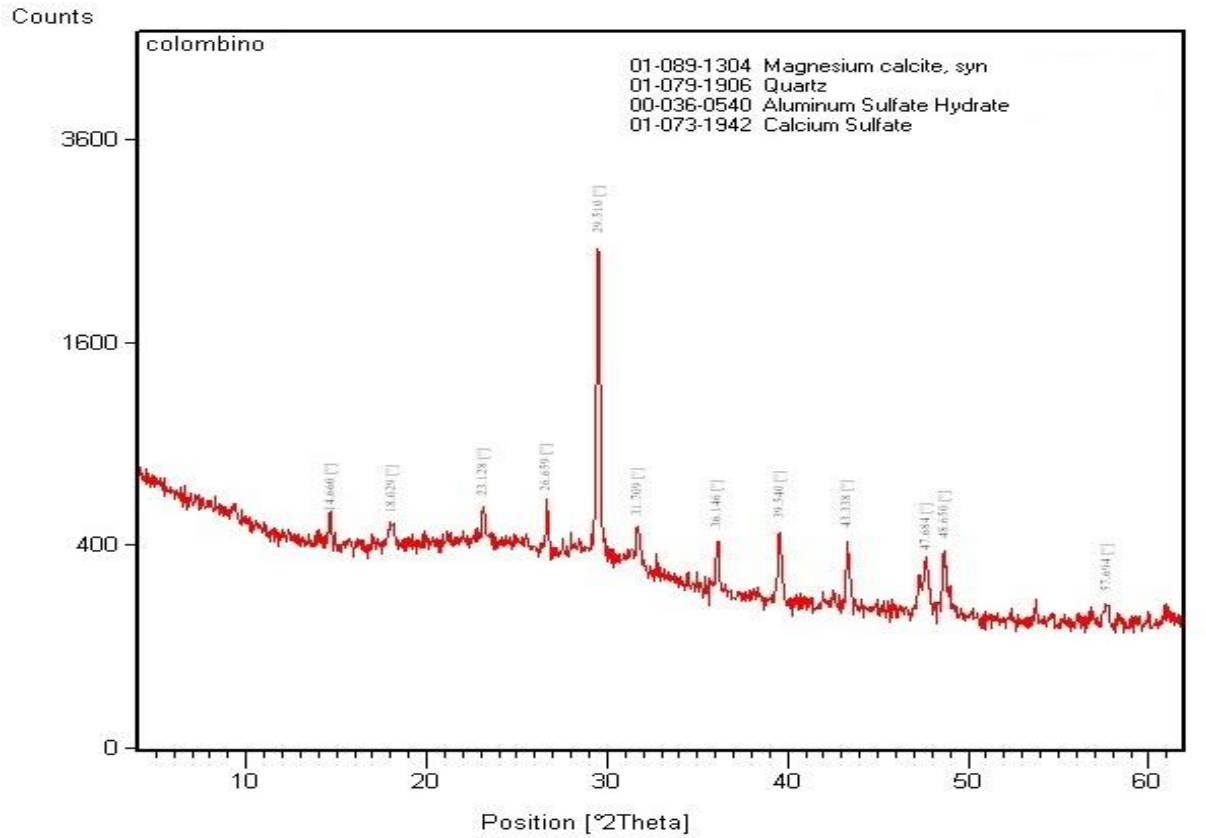

Fig.10. XRDP spectrum of soluble salts found in Colombino sample.

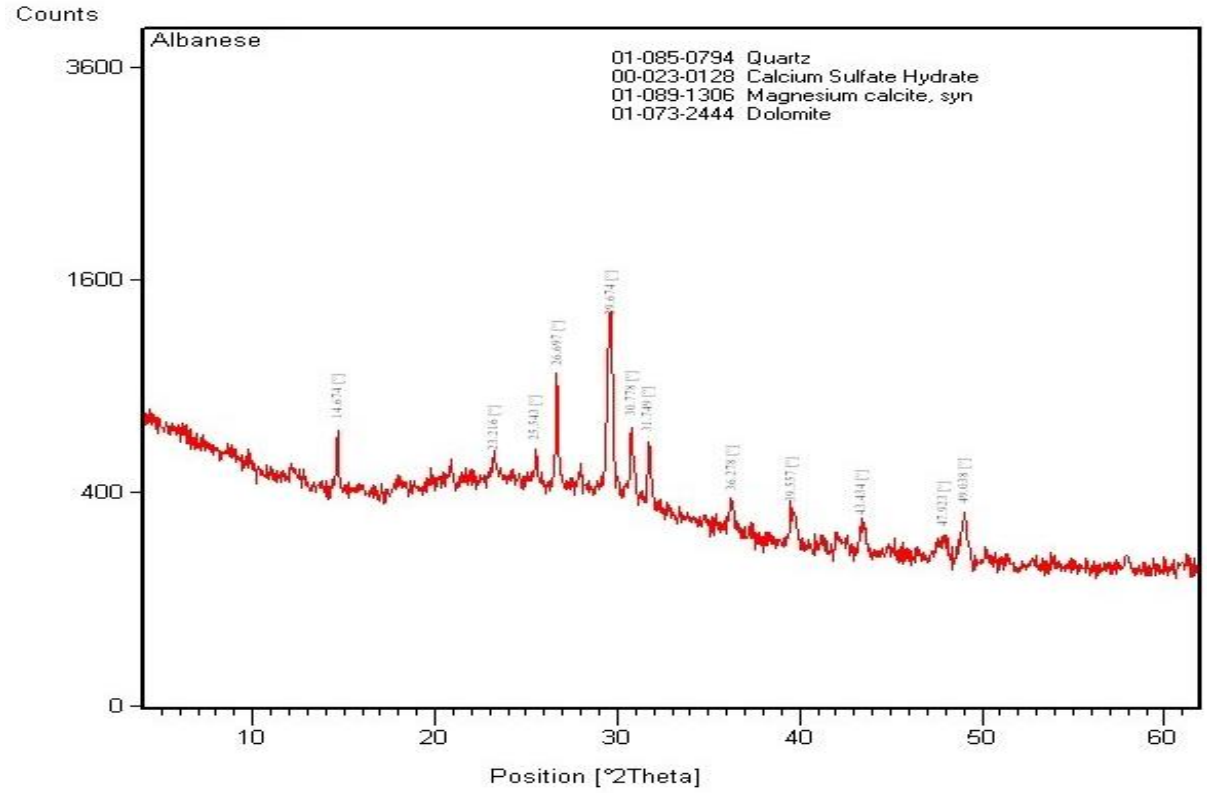

Fig.11. XRDP spectrum of a sulfate compound, found in Albanese stone.

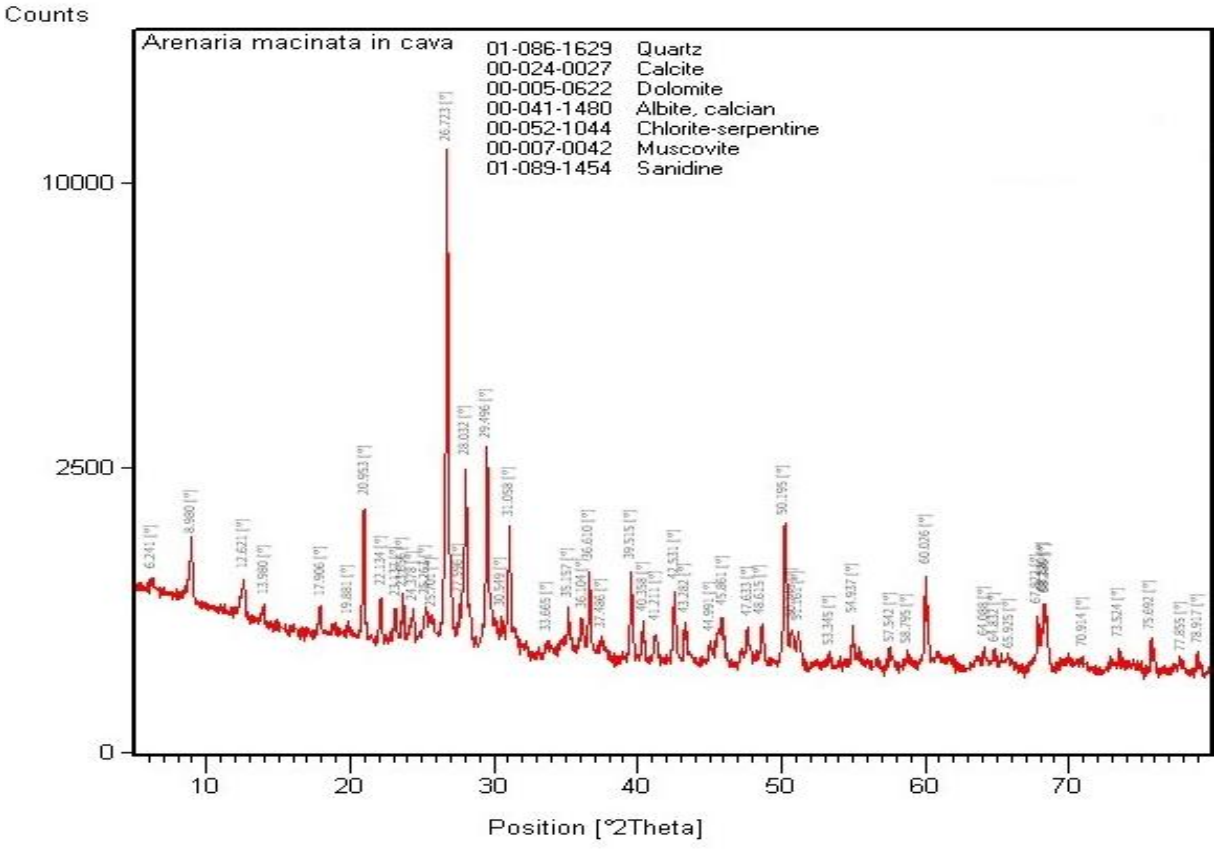

Fig.12. XRDP spectrum of the mineralogical composition of Firenzuola's sandstone powder.

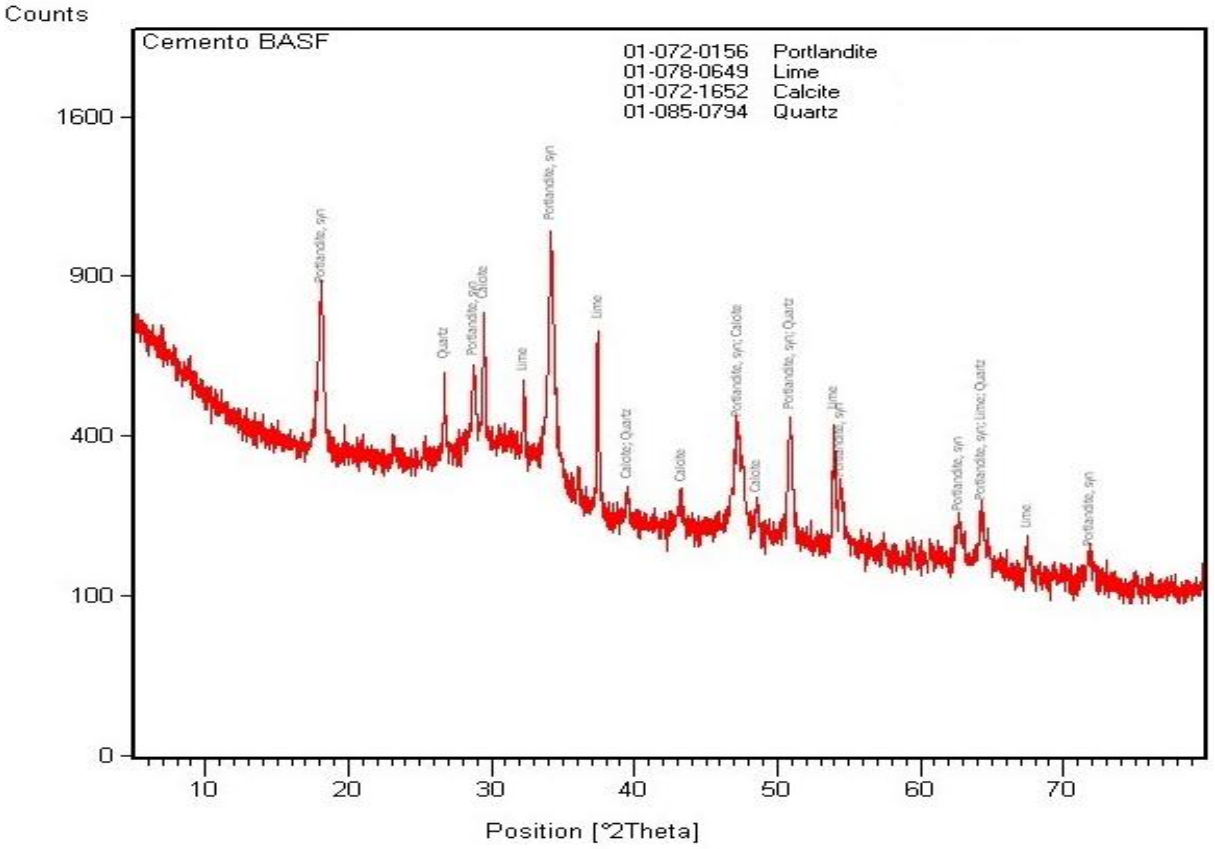

Fig.13. XRDP spectrum of the mineralogical composition of BASF cement.

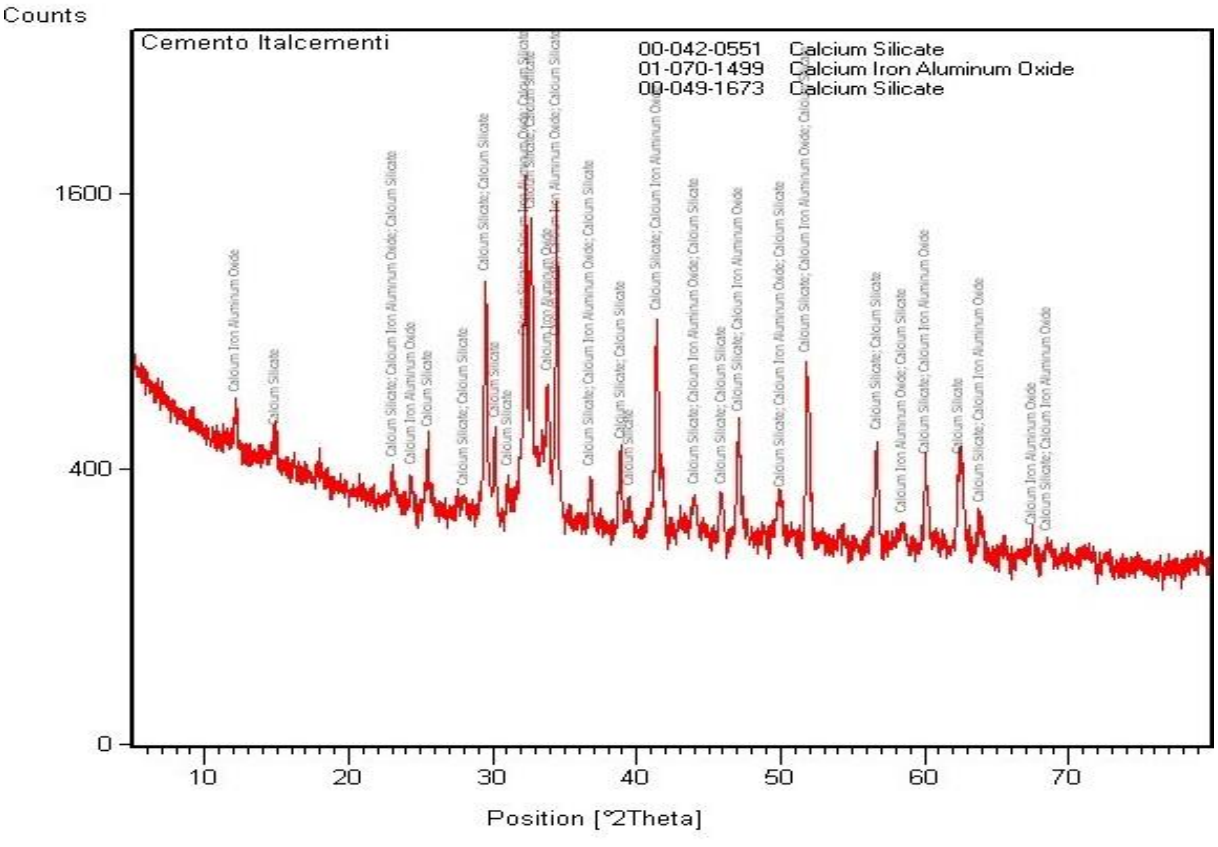

Fig.14. XRDP spectrum of the mineralogical composition of ITALCEMENTI cement.

6.2.3. *XRF Analysis*

The results of XRDP analyses are confirmed by XRF analysis, which shows an elemental composition based on Fe, Ca, and Si as main elements, followed by K, Na, Al, Mn, Mg, Ti, Sr, Cl, S, Ni, Rb, and Zn for all natural and natural aged stones [Fig. 15-18].

Silicon is, of course, the main element of sandstones, while Calcium forms the binder of the matrix. Fe, K, Na, Al, Mg, and Mn, added to compounds based on Oxygen and Silicon or Oxygen and Carbon, form different silicates (like Feldspars, Illite, Micas, Olivine,etc.) or carbonate minerals (*i.e.* Dolomite, Calcite, and Ankerite).

Chlorine can belong from Chlorite's group, which includes Clinochlore. Elements like Ti, Sr and Zn are often found in traces into the rocks. The natural aged stones show also traces of Phosphorus that can be due to residues of biological activity or animal excrements.

Results of XRF analysis made on some modern natural and natural aged stones are reported in Table 2.

SAMPLE	RESULTS OF XRF ANALYSIS
Albanese	**Ca, Fe, Si**, K, Sr (Mg, Al, S, Ti, Mn, Ni)
Piancaldoli	**Fe, Ca, Si**, K, Ti, Mn, Rb, Sr (Na, Mg, Al, S, Cl, Zn)
Colombino	**Ca, Fe, Si**, Sr (Al, S, K, Ti, Mn)
Medicea	**Fe, Ca, Si**, Sr, K, Ti, Mn (Al, S, Cl, Ni, Zn, Rb)
Giallo antico	**Ca, Fe, K, Si**, S, Sr, Ti, Mn (Na, Mg, Al, Cl, Zn, Rb)
Mucchi_1	**Fe, Si**, **Ca,** Ti, K, Sr, Mn, Zn, Rb, (Mg, Al, P, S, Cl, Ni)
Mucchi_2	**Fe, Si**, **Ca,** Ti, K, Sr, Mn, Rb, (Na, Mg, Al, P, S, Cl, Ni, Cu, Zn)
Mucchi_3	**Fe, Si**, **Ca,** Ti, K, Sr (Na, Mg, Al, P, S, Cl, Mn, Ni, Cu, Zn, Rb)
Mucchi_4	**Fe, Ca,** K, **Si**, Mn, Zn, Sr, Rb (Mg, Al, P, S, Cu)
Mucchi_5	**Fe, Ca,** K, **Si**, Mn, Ti, Zn, Sr, Rb (Na, Mg, Al, S, P)
Mucchi_6	**Fe, Ca,** K, **Si**, Mn, Ti, Sr (Na, Mg, Al, P, S, Cl, Ni, Cu, Zn, Rb)
Mucchi_7	**Fe, Ca, Si**, K, Mn, Ti, Zn, Rb, Sr (Na, Mg, Al, P, S, Cl, Ni, Cu)

Tab.2. Results of XRF analyses on different sandstone samples. Elements that show an intense signal are reported in bold, while elements with a weak signal are grouped in parentheses.

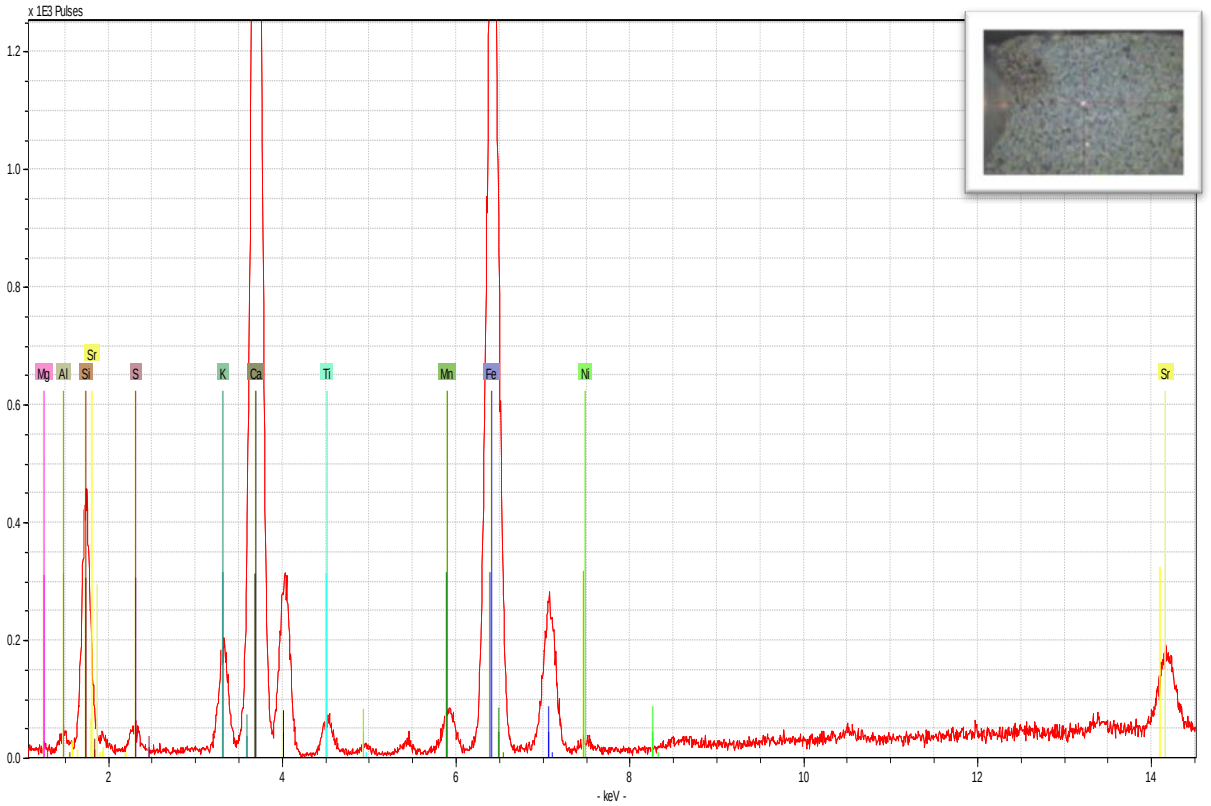

Fig.15. XRF spectrum of the elemental composition of Albanese stone.

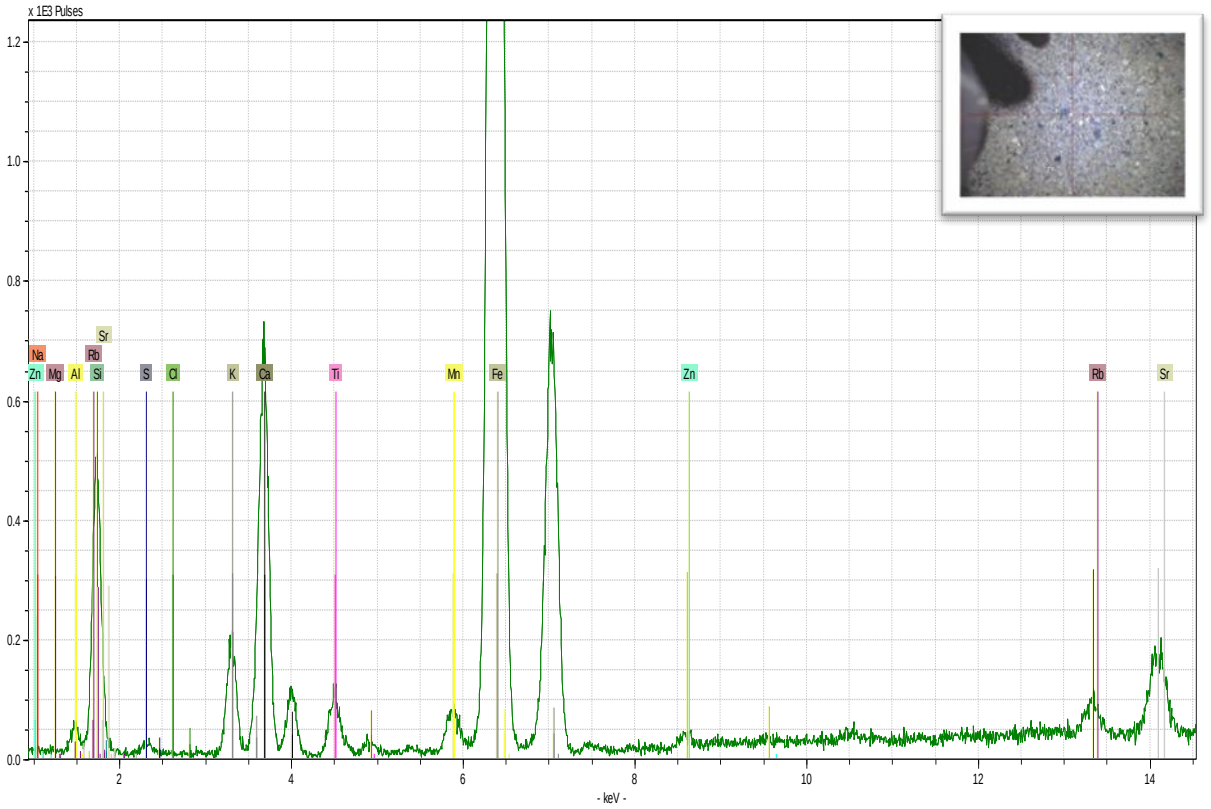

Fig.16. XRF spectrum of the elemental composition of Piancaldoli stone.

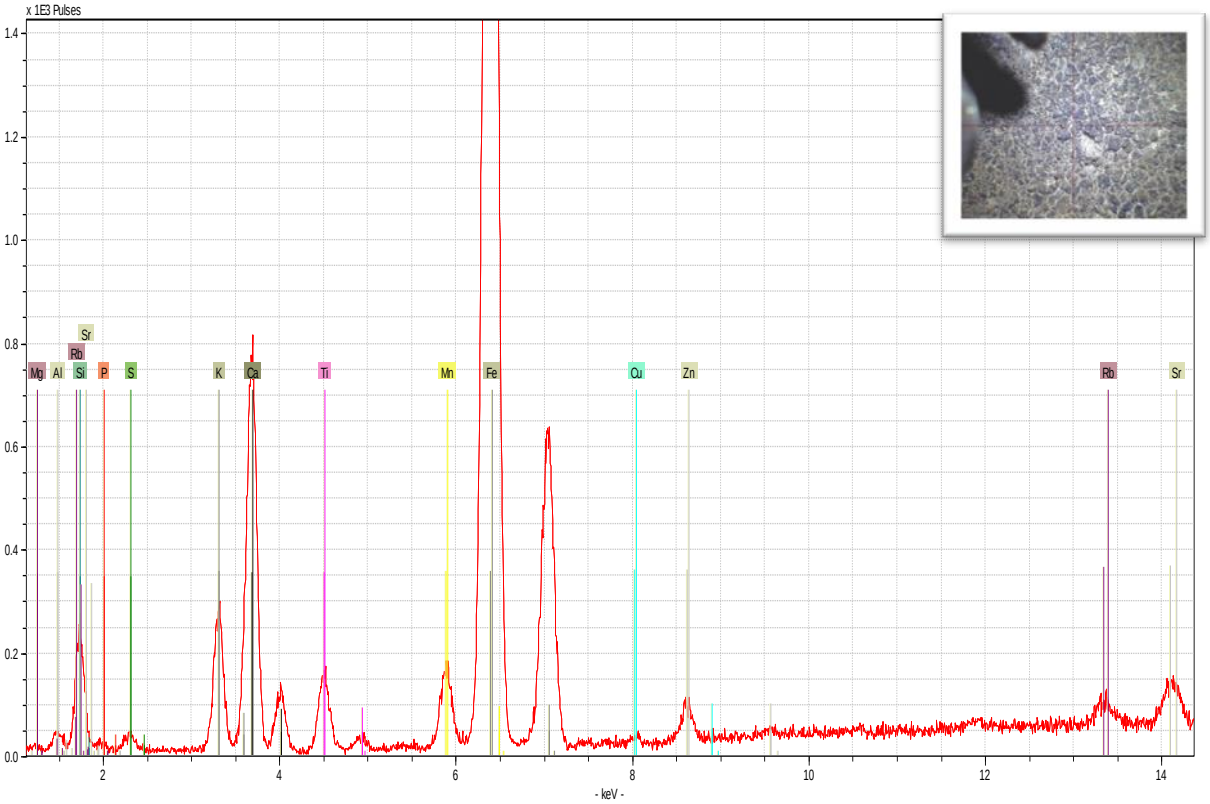

Fig.17. XRF spectrum of the elemental composition of a naturally aged stone (Mucchi_4).

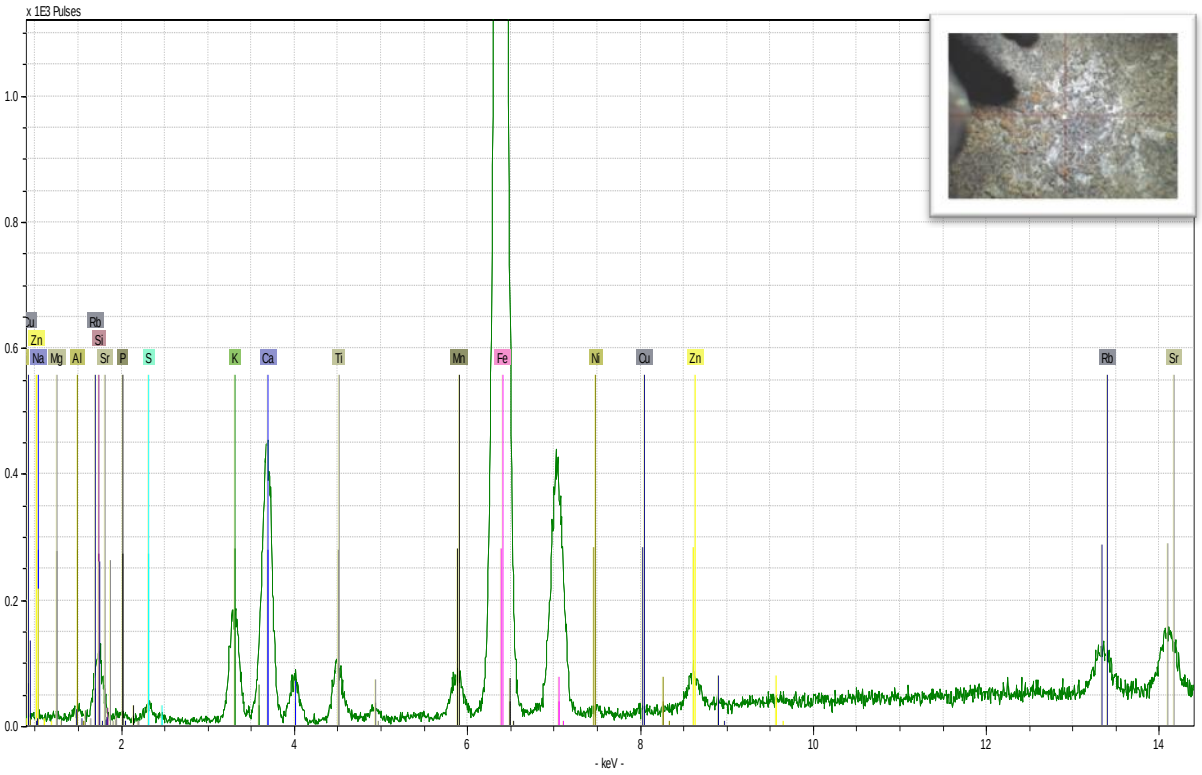

Fig.18. XRF spectrum of the elemental composition of Mucchi_7 (naturally aged stone).

6.2.4. *Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)*

SEM observations and EDS analysis, which is employed for the characterization of the chemical elements found in a sample, were carried out on some samples of natural stones. They confirmed an extremely compact matrix for modern natural stones based on Quartz and Silicate minerals (mainly Aluminosilicates compounds), and calcareous cements (Calcite and Dolomite), [Fig.19]. Natural aged samples showed the same composition of natural stones, but a less compact matrix that also appears covered with coatings of different origin, due to prolonged permanence in the external environment [Fig.20 and Tab.3].

Samples	Sandstone Matrix	Mineral composition (EDS Analysis)
Colombino	Extremely compact matrix based on aluminosilicate compounds with abundant calcareous cement.	K, Ca, C, Fe, O, Na, Mg, Al, Si
Albanese	Extremely compact and homogeneous sample, indeed it is difficult to distinguish the grains from the matrix. The binder of the matrix is formed by Calcite and Dolomite.	Al, Si, O, Fe, Ca, Mg
Medicea	Compact matrix with a predominance of aluminosilicate compounds, and calcareous cement.	Al, Si, O, Fe, Ca, Mg, Na, Ti
Mucchi _3	Fractured matrix with silica crystals covered by different compounds, many of which show organic origin, and due to prolonged storage in the external environment. Low calcareous cements.	Al, Si, O, Fe, Ca, Na
Mucchi _5	Compact matrix with silica crystals covered by a patina due to prolonged storage in the external environment. Calcite and Dolomite are the binders of the matrix.	Al, Si, O, Fe, Mg, Ca

Tab.3. SEM observations and EDS analysis on some natural sandstone samples.

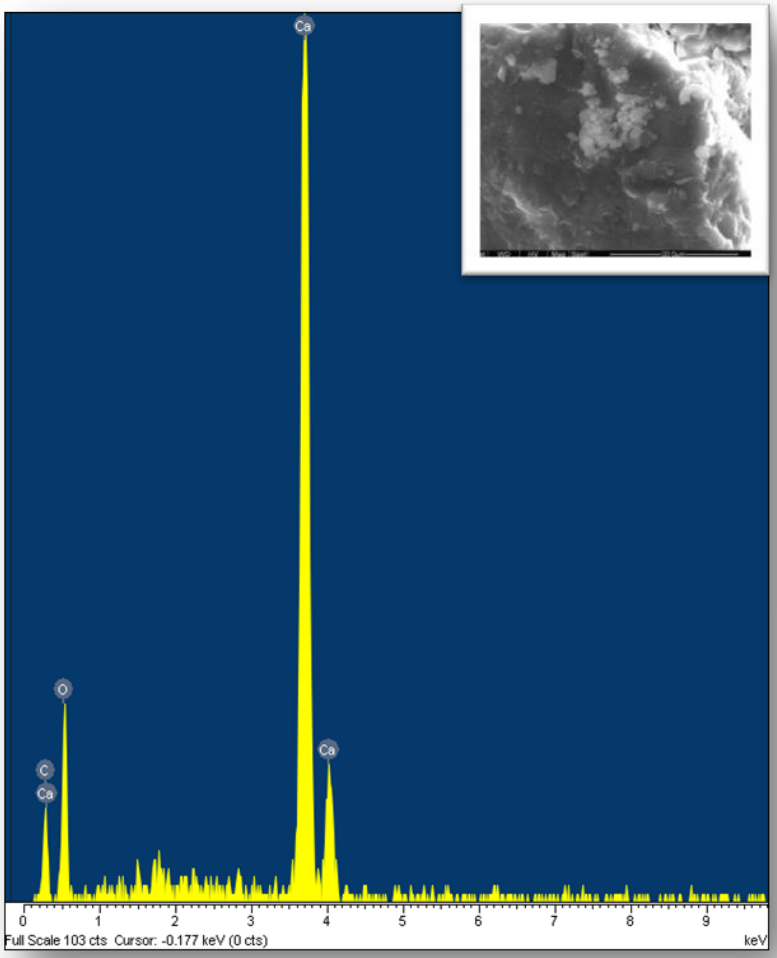

Fig.19. EDS spectrum of binder of the Colombino stone matrix.

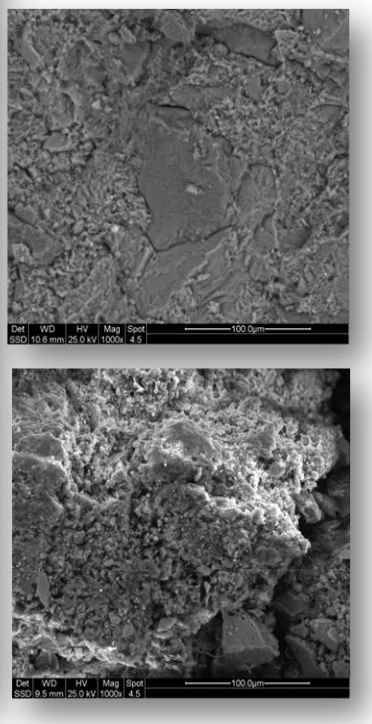

Fig.20. SEM images of Colombino matrix (over), and Mucchi_3 matrix (under).

6.2.5. *Chemical and mineralogical compositions of Firenzuola's sandstone powder.*

This analysis was made on a samples of Firenzuola's sandstone powder through quantitative XRF analysis (employed to determine the elements and compounds, even if in traces), with the aim to know its quantitative chemical composition of both major (expressed as % w/w) and minor (expressed in ppm) elements.

The results of this analysis are in line with those shown by the previous tests. Silica (55.9%), Aluminum Oxide (10.5%), and Calcium Oxide (10.2%), are the main compounds, followed by Iron, Magnesium, Sodium, and Potassium Oxides (with percentage between 2 and 4%). Few Titanium Oxide and Sulfite are found as well (< 0.5%). These values are similar to what is indicated in the literature [Bargossi *et al.* 2002]. Moreover, some anions were found in low concentrations (in the order of ppm) like Chloride, Fluoride, Nitrate, and Sulfate. Normally, these elements and compounds are connected to the presence of degradation elements. Thus, their low values confirm the good conditions of Firenzuola's powder [Tab.5].

At the same time, the quantitative mineralogical analysis confirms the dominant presence of Quartz (32% w/w), Plagioclase (12%), and Calcite (15%), followed by Feldspar, with Na type greater than K type (20 and 4%, respectively), Chlorite (8%), and Dolomite (7%). [Tab.4].
K type (20 and 4%, respectively), Chlorite (8%), and Dolomite (7%). [Tab.4].

	Unit	Rational analysis	Literature av. data
QUARTZ	%	32	38
K-FELDSPAR	%	4	14
PLAGIOCLASE	%	12	5
CHLORITE	%	8	9
CALCITE	%	15	8
DOLOMITE	%	7	-
Na-FELDSPAR	%	20	

Tab.4. Mineralogical composition of Firenzuola's sandstone powder.

	Unit	Firenzuola's sandstone powder	Literature (average on 10 references)
SiO_2	%	55.9	57.1
Al_2O_3	%	10.5	10.7
Fe_2O_3	%	2.90	
TiO_2	%	0.42	
CaO	%	10.2	10.1
MgO	%	3.66	
Na_2O	%	2.33	
K_2O	%	2.10	
SO_3	%	0.30	
P.F.	%	11.5	10.2
(*)			
F^-	mg/kg	12.6	
Cl^-	mg/kg	85.6	
NO_3^-	mg/kg	7.7	
$SO_4^=$	mg/kg	253	

Tab.5. Chemical composition of Firenzuola's sandstone powder. **(*)** 1 g in 10 mL of H_2O, 60 minutes, cold.

6.2.6. *pHmetry and Conductimetry tests*

These analyses were made to determine the presence of soluble salts into the modern and naturally aged stone samples.

Modern natural stones showed conductibility values slightly higher than naturally aged stones. The first exhibit values between 225 (Medicea) and 85.5 µS/cm (Brento), while the second show values between 178 (Mucchi_4) and 85.5 µS/cm (Mucchi_2). Anyway, the value of conductibility of the water solution is very low, meaning that the amount of ions due to soluble salts that are dispersed in the stone samples analyzed is very low.

In the case of pH analysis, the same behavior on both modern and aged stones was observed. Indeed, modern stones show pH values between 8.18 (Albanese) and 7.46 (Castellina) that correspond to weakly alkaline pH, with the only exception of Giallo Antico that show a stronger alkaline pH (8.60). Aged stones exhibit pH values between 8.09 (Mucchi_2) and 7.17 (Mucchi_4), closer to neutral pH. The results of pHmetry and conductimetry tests on natural stone samples are reported in Table n.6.

Moreover pHmetry and conductimetry tests were made on Firenzuola's sandstone powder, and they showed results similar to those of natural stones, like low conductibility value of 116.4 µS/cm at 25 °C and a weakly alkaline pH of 8.11.

6.2.7. *Water absorption tests*

The water absorption analyses were made on all natural stones using both the test for total immersion of the sample (Normal-7/1981) and the contact sponge method (UNI 11432:2011).

Naturally aged stones show values of water absorption for total immersion slightly higher than natural modern stones. Indeed the first show a range of values between 2.37 (Mucchi_5) and 1.13% (Mucchi_4), while the second exhibit values between 2.19 (Sarsina) and 0.33% (Colombino), with the exception of the Giallo Antico that show 4.58% of water absorption. This means that naturally aged stones are more porous than modern natural stones, due to the damages by weathering action, pollution, and animal and biological activities, during the prolonged storage in the external environment. Nevertheless, the values of water absorption of naturally aged stones are very low, lower than what we would expect for stones exposed to ambient conditions for thirty or more years.

The contact sponge method confirms the trend observed with the total immersion test, i.e. naturally aged stones show a slightly higher absorption than modern natural stones. The values of aged stones are between 0.29 (Mucchi_7) and 0.03 $g/cm^{2}\cdot min$ (Mucchi_2), while modern stones show values between 0.05 and 0.03 $g/cm^{2}\cdot min$, with the only exception of Colombino stone (0.90 $g/cm^{2}\cdot min$).

The contact sponge method could not be applied on rough surfaces, as the sponge did not adhere well to the stone surface and consequently, the water absorption by the stone is limited. This is the case of Sarsina stone, where the sponge did not adhere perfectly during the test, so its final value of water absorption is meaningless. The results of water absorption tests are reported in Table n.6.

Sample	pHmetry	Conductimetry (µS/cm 25 °C)	% H_2O abs (Normal-7/1981)	Wa ($g/cm^2 \cdot min$)
Albanese	8.18	143.9	1.40	0.04
Piancaldoli	8.17	90.1	1.80	0.05
Colombino	8.06	126.3	0.33	0.90
Medicea	7.54	225	0.66	0.04
Castellina	7.46	136.0	0.49	0.03
Sarsina	7.99	114.2	2.19	0.03 (*)
Brento	7.87	85.5	0.58	0.05
Giallo Antico	8.60	111	4.58	0.04
Piancaldoli Aged	7.96	88.1	2.26	0.08
Mucchi_1	7.78	75.8	2.28	0.04
Mucchi_2	8.09	70.5	2.16	0.03
Mucchi_3	7.94	89.8	1.57	0.11
Mucchi_4	7.17	178	2.41	0.13
Mucchi_5	7.26	167.5	2.37	0.14
Mucchi_6	7.79	112.2	1.13	0.08
Mucchi_7	7.76	145	1.53	0.29

Tab.6. Results of conductimetry, pHmetry, and water absorption tests on natural sandstone samples. (*) sample with incomplete adherence of the sponge to the surface.

6.2.8. *Mechanical Resistance tests*

Mechanical resistance tests, based on determination of the stone resistance to deep abrasion (UNI EN ISO 10545.6/2000), called also CAP, were made on natural stone samples. On each sample, five measures were made in different points of the surface with the aim of acquiring information on the abrasion resistance of the sample within its structure. The abrasions were made using different amount of abrasive powder of corundum.

All the samples investigated showed a small volume of material removed after each abrasive cycle, corresponding to a high abrasion resistance of the stones, and therefore an extremely compact matrix, that did not appear deteriorated. All naturally aged stones exhibit lower resistance to deep abrasion than modern natural stones [Fig.17 and Tab.7].

Some samples were not analyzed due to their large size (like Sarsina stone), which did not allow to place the stone inside the instrument.

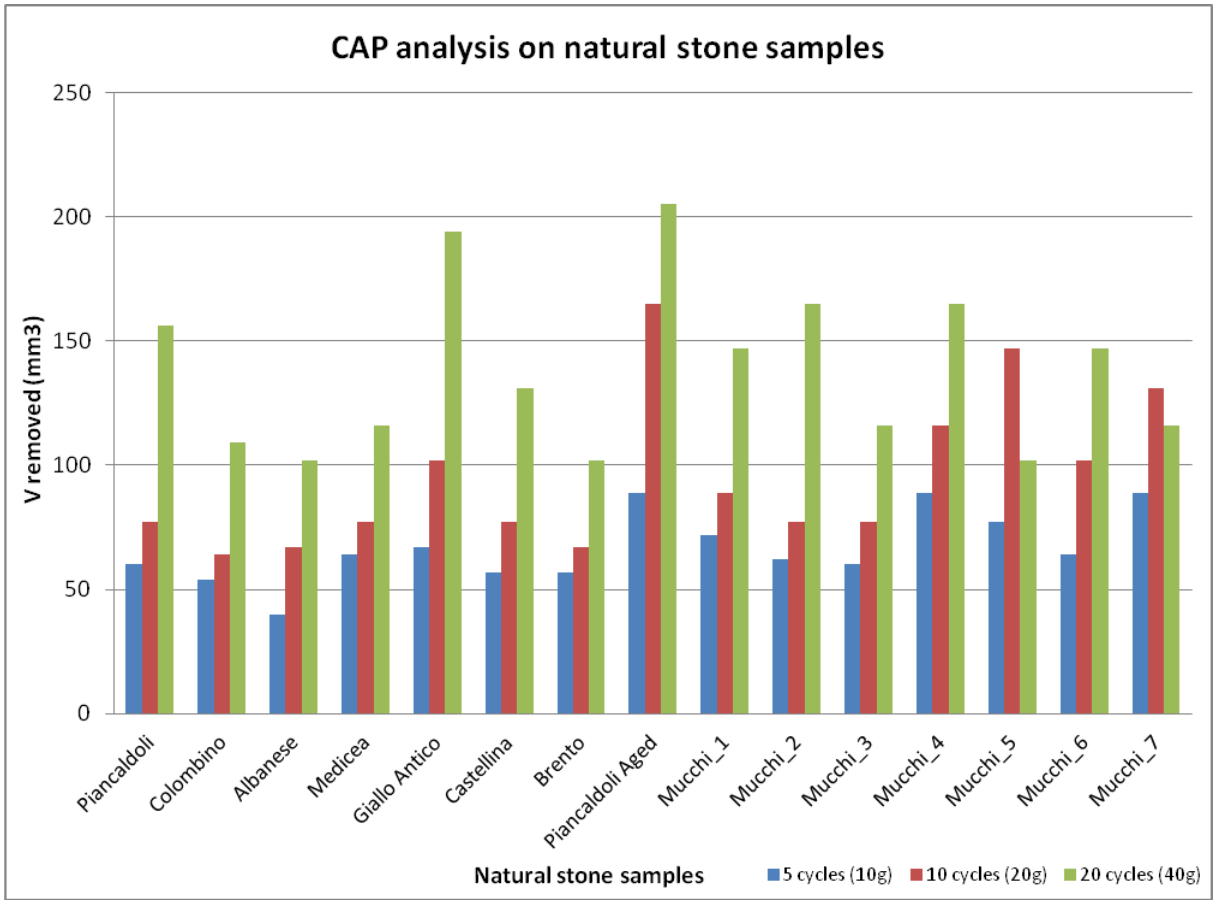

Fig.17. Comparison of the volume removed (expressed in mm^3) from natural sandstone samples, after the early cycles of abrasion

Samples	5 cycles (10g)	10 cycles (20g)	20 cycles (40g)	30 cycles (60g)	40 cycles (80g)	50 cycles (100g)
Piancaldoli	60	77	156	205	275	330
Colombino	54	64	109	131	174	194
Albanese	40	67	102	131	184	227
Medicea	64	77	116	147	184	227
Giallo Antico	67	102	194	275	316	361
Castellina	57	77	131	174	205	227
Brento	57	67	102	165	205	227
Piancaldoli Aged	89	165	205	330	427	540
Mucchi_1	72	89	147	262	302	361
Mucchi_2	62	77	165	205	227	275
Mucchi_3	60	77	116	165	227	275
Mucchi_4	89	116	165	227	288	444
Mucchi_5	77	147	102	302	275	409
Mucchi_6	64	102	147	205	205	227
Mucchi_7	89	131	116	165	205	227

Tab. 7. Volume removed (expressed in mm^3) from natural sandstone samples at different cycles of deep abrasion.

In this case, surface abrasion tests by Taber abrader (ASTM D4060-95) have not been performed due to the high thickness of the natural stone samples. Indeed, this test requires a thickness of the sample less or equal to 1 cm, in order to be executed.

6.2.9. *Conclusions*

All the tests showed the same composition for natural stones samples based on Quartz, Feldspars (i.e. Na-feldspars such as Albite, and K-feldspars like Microcline, Sanidine, and Orthoclase), Micas (Muscovite dominant on Biotite), and magmatic and metamorphic rocks fragments (like Olivine, Chlorites, etc.). Other clay minerals were found in traces (such as Illite and Montmorillonite), while the binder of the matrix is formed by calcite and dolomite.

Modern natural sandstones show a compact, slightly porous, and much more resistant matrix compared with historical sandstones (see cap.8). Indeed, modern stones have aldo slighty more resistant matrix than aged natural stones.

Natural aged stones reveal the same a compact matrix with some porosity, and low resistance to deterioration even if their long storage in the external environment under weathering, pollution, and biological actions.

6.3. *Artificially Aged Stones*

Modern and aged natural stones showed more compact and resistant structures without apparent loss of cohesion and with low decay elements. Consequently, these samples were not good candidates for experimental consolidation tests.

Therefore, to have propter samples for our experiments, the matrix disintegration of natural stones was tried through thermal treatments (TS) with the aim of simulating an artificial aging (par.4.3).

The efficacy of the thermal treatments was verified by water absorption through contact sponge method. The values obtained were compared with the water absorptions of the same stones before the thermal treatment (NT) and, in most cases, these data show a significant increase in water absorption of TS compared to NT [Tab.8]. However, artificial aged samples still exhibit a significantly lower water absorption than historical stones degraded, and still a good cohesion of the matrix (cap.8). Therefore, we had to prepare artificial samples based on Firenzuola's sandstone powder, showing the same or very similar cohesion properties of historical sandstones on which to perform the consolidation tests (Par.4.4).

Sample	TS	NT	% Wa increase [(TS – NT) /NT · 100]
Albanese	0.07	0.07	0
Brento	0.04	0.04	0
Castellina	0.03	0.03	0
Colombino	0.06	0.02	+ 200
Medicea	0.06	0.05	+ 20
Piancaldoli	0.11	0.08	+ 38
Sarsina	0.08	0.06	+ 33
Piancaldoli Aged	0.16	0.07	+ 129
Mucchi_1	0.16	0.1	+ 60
Mucchi_2	0.12	0.06	+ 100
Mucchi_3	0.08	0.06	+ 33
Mucchi_4	0.13	0.05	+ 160
Mucchi_5	0.22	0.12	+ 83
Mucchi_6	0.09	0.07	+ 29
Mucchi_7	0.11	0.08	+ 38

Tab.8. Results of water absorption tests with contact sponge method on artificially aged (TS) and natural sandstones (NT).

6.4. Artificial samples

Samples consisting in Firenzuola's sandstone powder added with an industrial cement (such as BASF or ITALCEMENTI) and demineralized water, mixed together in different ratios, were tested in order to create artificial test pieces.

The analyses on the composition of Firenzuola's sandstone powder and of cements have been reported previously in the paragraph on stone analysis (6.2).

Several artificial stones, with different compositional ratios between sandstone powder and binder, were prepared, starting from 9 parts of sandstone and 1 part of binder and so on (i.e. 8:2, 7:3, 6:4 ratios), in which different quantities of water were added on the basis of total mass of the samples, in order to create new cementitious mixtures.

All samples made by BASF cements showed the presence of white spots due to calcite on their surface, that were not found on pure sandstone surface. Consequently these artificial test samples were not employed in this research.

The best specimen showing similar cohesive characteristics to the historical samples was IT20, made by 85 g of Firenzuola's sandstone powder (80% w/w) and 21 g of special Portland cement (20% w/w) for a total weight of 106 g. Moreover, 33 g of demineralized water were added to mix the two solid components (i.e. 31% of the total weight of the final solid sample).

The mineralogical composition of IT20 sample was investigated by XRD analysis, showing Quartz, Chlorite, Feldspars (such as Albite, Muscovite, and Microcline), Calcite, and Dolomite [Fig.25]. Also, XRF analysis confirmed these results, with the peaks of Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, and Sr. The elements with the strongest signal are Silicon, Calcium, Aluminum, and Iron, i.e. the same elements at the base of the composition of silicate and carbonate minerals [Fig.26]. Therefore the cement, even if present at 20 %, does not seriously influence the composition of the mixture.

The SEM-EDS analysis of IT20 showed the presence of crystals with different grain size and composition (Si, Al, Na, K, Fe, Mg and Ca are the main elements that belonging to minerals like Quartz, Feldspars and Micas), and a dark matrix based on Ca, Si, Al, Fe, Mg, and K. Therefore, the binder of the artificial pieces consists in Calcium, Silica and Aluminum compounds [Fig. 21-22].

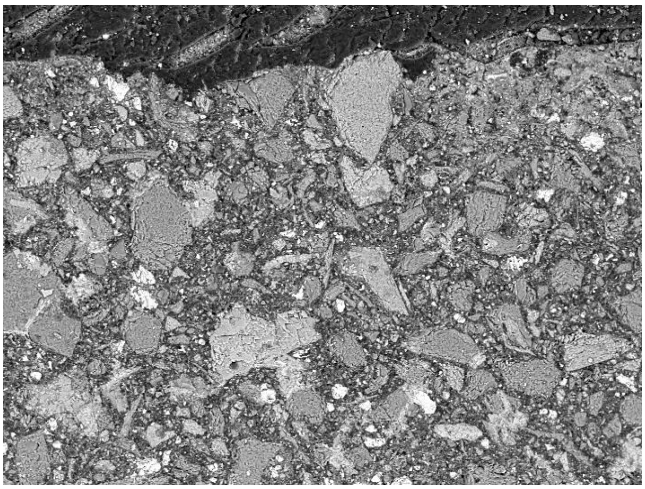

Fig.21. SEM images of the matrix of IT20 observed at 100x.

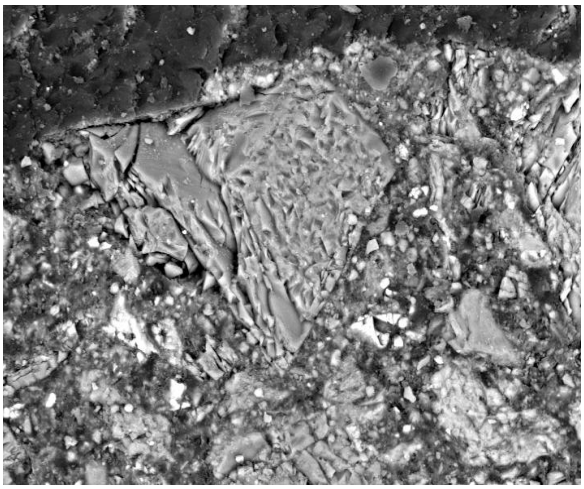

Fig.22. SEM images of a crystal made by Si, Al and Na observed at 500x.

In agreement with SEM-EDS analysis are the petrographic analysis that exhibits a mineral composition of Firenzuola's sand made by Quartz, Feldspars, Muscovite (prevalent micaceous component) and Biotite. The sample matrix shows a dark color based on Carbonate compounds, corresponding to special Portland cement used to bind the sand. Moreover, the sample matrix appears very porous with large grains [Fig.23-24], similar to the matrix of the historic sandstone.

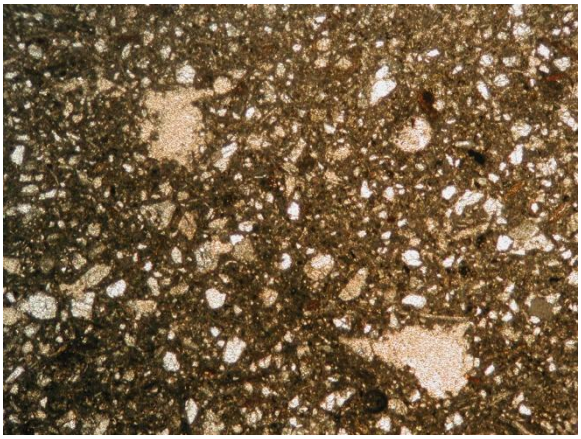

Fig.23. Matrix of IT20 observed at 2.5X at crossed Nicols.

Fig.24. Matrix of IT20 observed at 2.5X at parallel Nicols.

Permeability and resistance tests were made on these artificial samples using contact sponge method and TABER and CAP abrasions, in order to understand whether these samples showed a behavior, like it is assumed by a degraded sandstone under the same conditions.

The water absorption test showed high permeability (i.e. Wa = 1.44 g/cm^{2}·min), due to very porous structure of IT20. This result is in line with what would be expected by extremely porous sandstones.

The same behavior is highlighted by surface abrasion (TABER) and deep abrasion (CAP) tests. During the three cycles of surface abrasion, the samples showed almost a linear loss of weight, when increasing the depth of surface abrasion [Tab.9].

On the contrary, deep abrasion test showed data that are not easily interpretable, since the value of removed volume appears the same during the first and second step of abrasion (*i.e.* 5 and 10 cycles), and in the third and fourth step (*i.e.* 20 and 30 cycles). This incoherence of the results has been often found, and it could be due to the weak matrix of the sample itself, that tends to be easily abraded on this test. Moreover, the fact that the tests are performed on different parts of the specimen, which can show different strength of the matrix, can lead to incoherence of the data. However, even if deep abrasion tests were made on all samples during this research, it was decided to focus the attention on the results obtained from surface abrasion tests, also more significant to understand the effectiveness of treatments.

It is, of course, very important to note that these artificial test pieces show similar porosity and behavior of the historical sandstones. Consequently, a substantial number of specimens IT20 was made for the next application of the different consolidating methods (see the next chapter).

TABER TEST	50 cycles	100 cycles	150 cycles
IT20	5.37	11.34	17.26

CAP TEST V removed (mm^3)	5 cycles (10g)	10 cycles (20g)	20 cycles (40g)	30 cycles (60g)	40 cycles (80g)
IT20	462	462	696	696	1062

Tab.9. Results of Taber and CAP tests on IT20 samples.

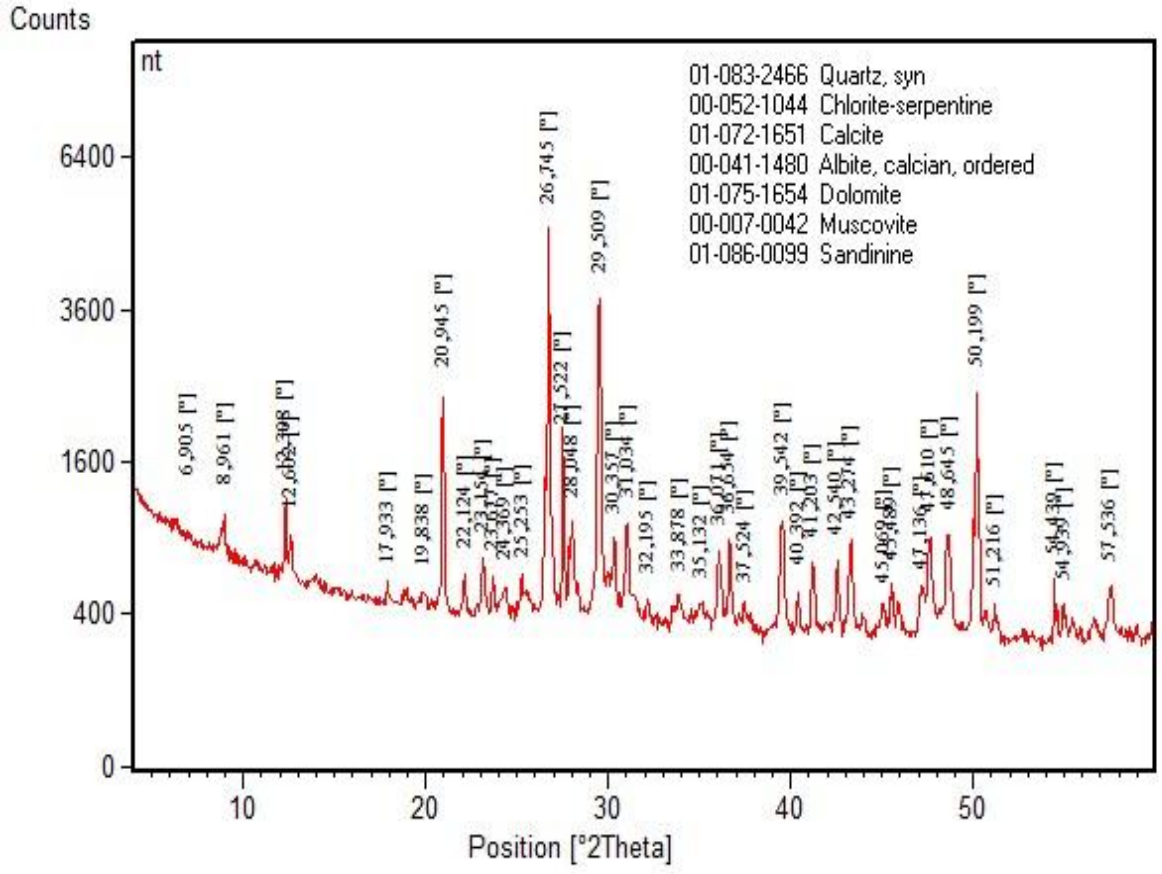

Fig.25. XRD spectrum of artificial test piece IT20.

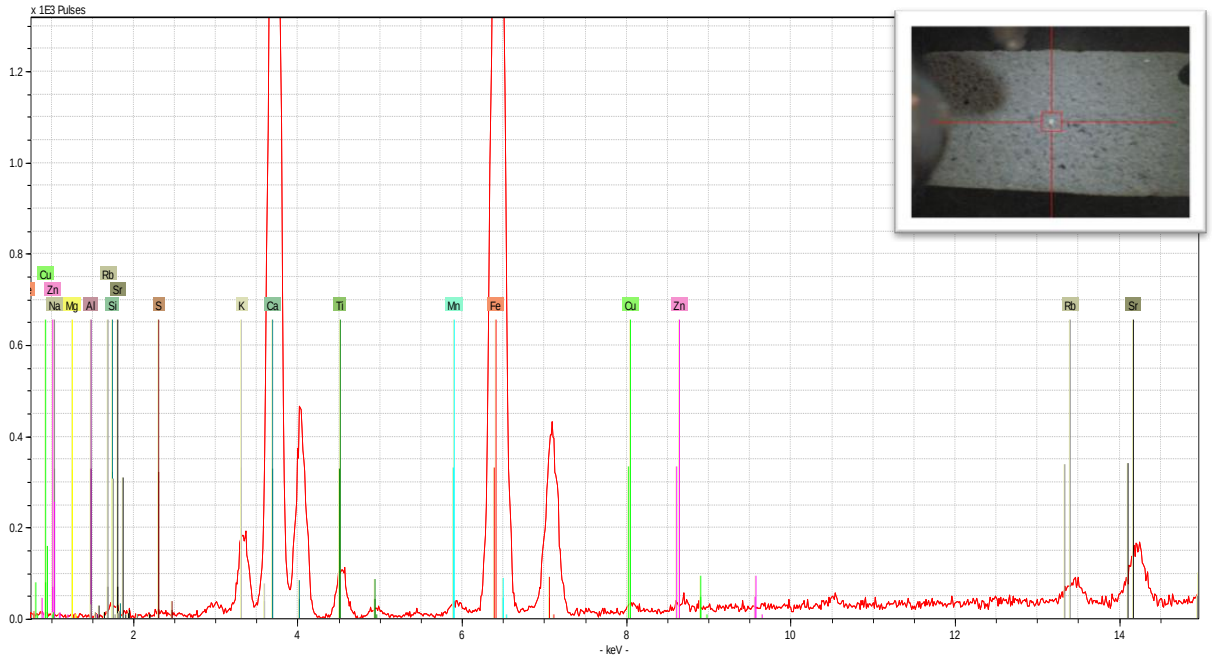

Fig.26. XRF spectrum of artificial test piece IT20.

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Chapter 7

CONSOLIDATING TREATMENTS: RESULTS AND DISCUSSION

The innovative elements of this research will be shown now, i.e. the attempt to let barium silicate to be formed inside the stones as consolidant, by the application of barium hydroxide solutions together with organic silicates. We have supposed that barium hydroxide in water solution reacts with silica matrix of the stone and organic silicates creating barium silicate, based on Si–O–Si linkages that show good physical-chemical affinity and compatibility with the internal structure of the sandstone, and do not change the physical appearance of the stone.

Therefore, barium silicate should lead to an improvement of the hardness and abrasion resistance of treated sandstones than to traditional consolidants based on either TEOS or barium hydroxide solution.

In this chapter we will evaluate consolidation treatments based on Ethyl Silicate, Barium Hydroxide, and Barium Silicate (obtained from the addition of Barium Hydroxide to TEOS), through physical-chemical analyses and mechanical characterization of both the test pieces treated and artificial aged samples.

The results will be discussed with the purpose to identify the better consolidation treatment that will be applied on deteriorated historic sandstones.

7.1. *Consolidation Treatments*

For each consolidant product, eleven artificial test samples were treated. All treated samples were dried in laboratory at environmental condition (i.e. 20 - 25 °C) for six days before being subjected to further analyses.

After this time, water absorption tests were made on all samples and the results were compared with the data obtained on the same untreated samples. One week after these tests, i.e. 14 days after the treatment, the mechanical abrasion tests (TABER and CAP) were executed on ten treated samples for each commercial product employed, and at the same time physical-chemical analyses (like XRD, SEM-EDS, and XRF) and petrographic characterization were made (on one sample for each products).

After completion of the analyses, the trials of consolidation were repeated to verify the reproducibility of the results. Thus, a total of n. 509 artificial test pieces were analyzed.

In this work, we report the data related to confirmation tests made on n. 220 artificial test samples: afterword the working method has been refined, and more samples were tested. The products with the better behavior were then tested on artificial aged samples and on historical sandstones.

7.1.1. *Ethyl Silicates*

Following the advice of experts in conservation field, we decided to firstly apply a known amount of ethyl silicate brushing it till saturation with complete absorption on the surface of the sample [Fig. 1]. In the case of artificial stone samples, the product enters through the surface until reaching the opposite side, due to their high water absorption, getting a complete wet sample. In most cases this phenomenon does not occur, instead, on artificial aged samples and natural stones, due to low water absorption and high thickness.

The silicate compounds were applied through four brushstrokes, corresponding to 2.10-2.70 g of product for specimen [Fig. 2].

Commercially available ethyl silicates used in this research were:

- ✓ Tetraethyl Orthosilicate of Sigma-Aldrich S.r.l. (acronym RP);
- ✓ Siler BS OH 100 of Wacker-Chemie (BSOH);
- ✓ Silicate TES 40 WN of Wacker-Chemie (TES 40);
- ✓ Silicate TES 28 of Wacker-Chemie (TES 28);
- ✓ Tegovakon V 100 of the Evonik (TV);
- ✓ ESTEL 1000 of C.T.S. S.r.l. (EST);
- ✓ DN-Consolidant of KERAKOLL S.p.a. (KDN);
- ✓ Ethyl Silicate WS of AN.T.A.RES S.r.l. (ANT or ANTARES).

Fig.1. Penetration of the silicate visible on the edge of the sample.

Fig.2. Weight of the TEOS just after the treatment.

7.1.2. *Barium Hydroxide*

The barium hydroxide employed in this research is commercially available with the name of Barium Hydroxide Octahydrate from Sigma Aldrich (pure at 97 %).

This compound was applied through poultice method (restoration technique), i.e. a mixture of 10 g of cellulose (like ARBOCELL BC 1000 of C.T.S. S.r.l.) in a saturated solution of 5 g of barium hydroxide dissolved in 40 g of demineralized water.

This poultice is not applied directly on stone surface, but separated from it by two layers of Japanese paper BIB TENGUJO of C.T.S. S.r.l. (11 g / mq, pH 7.1, 100 % Kozo) [Fig.3].

The poultice was applied in environmental conditions for a trial time of about 6 - 6.30 hours on each sample. After this time, the poultice was removed and the samples were dried at environmental conditions [Fig. 4].

Fig.3. Some poultice treatments.

Fig.4. Sample after the removal of the poultice.

7.1.3. *Barium Silicate*

This treatment is based on the combined use of Ethyl Silicate and Barium Hydroxide. It is applied through the same procedures described for the treatments based on TEOS and Barium hydroxide.

Initially, the samples were treated by brushing with TEOS-like products, then, when the surfaces appeared opaque and wet, Barium poultice was applied.

7.2. *Laboratory evaluations:*

7.2.1. *Water Absorption (Wa)*

The water absorption analyses were made on treated artificial test pieces using the contact sponge method (UNI 11432:2011). The results of these tests are related to the porosity and hydrophilic/hydrophobic behavior of the sample, inasmuch a sample that exhibits a high absorption has high porosity, i.e. less compact matrix and at the same time, a sample with hydrophilic character has higher absorption than a samples with hydrophobic behavior.

The results of treated samples were compared with untreated samples (Wa = 1.44 $g/cm^2 \cdot min$), showing a different behavior on the basis of the treatments employed (TEOS, Barium, or Barium Silicate).

In the case of TEOS treatments, three types of behavior were noted:

- ✓ no decrease in water absorption
- ✓ low decrease
- ✓ strong decrease, until no absorption

The strong decrease of water absorption was shown by the following products: ANTARES, DN-Consolidant, TES 40, ESTEL 1000, BS OH 100 and Tegovakon V 100. These products show a Wa near to zero, i.e. no absorption.

Although all tested products belong to the same chemical family, some of them show no decrease or low decrease of water absorption (i.e. RP and TES 28), while others show a strong decrease. Thus, it must be assumed that the latter products contain some water-repellent substances that cause no absorption of water, like silicone additives (probably this is the case of ANT, KDN, TES 40, and EST that contain partially unknown solvents).

In the conservation field, there are no valid reasons that justify the use of water-repellent products in consolidating treatment of stones, since they prevent the permeability of water and liquid solutions in the porous structure of the stone. Normally, protective treatments are used for this function, in order to defend the stone surface by the deterioration agents from outdoor environment that are water-soluble and tend to bind water on the stone. Nevertheless, on this topic there is a strong debate about the negative or positive effects that can result by an hydrophobic protective use when soluble salts, moisture, and very porous stones are present. Indeed, the salt solutions from inside the stone are hindered to come out due to water repellency, thus this can lead to more serious damages (like sub-fluorescence) than the ones visible on the hydrophobized stone surfaces (such as efflorescences).

Therefore, ethyl silicates that show strong decrease of water absorption have to be considered negatively for the purposes of our research, because their water repellency blocks access to water.

In the case of BS OH 100 and Tegovakon V100, low values of water absorption are shown, but none of them contains water-repellent products. After water absorption tests, RP and TES 28 gave the best treatments based on ethyl silicate. The results of these tests are reported in Table n.1 and Fig.5

TREATMENT	NT	ONLY BA	RP	BSOH	EST	ANT	TES28	TES 40	TV	KDN
TEOS	1.44		1.48	0.03	0.06	0.009	1.43	0.006	0.24	0.008
BARIUM		0.61								
BARIUM SILICATE			0.30	0.25	0.20	0.025	0.36	0.87	0.012	0.035

Tab.1. Results of water absorption tests with contact sponge method ($g/cm^2 \cdot min$).

After the treatment with Barium Hydroxide the situation changes again [Table n.1 and Fig.5].

The samples treated with TEOS, already showing strong decrease of water absorption due to probably water repellency, maintained these very low values after the addition of barium hydroxide: KDN and ANTARES recover a negligible increase of Wa, TES 40 and ESTEL1000 show a good increase of Wa.

BS OH 100 and Tegovakon V 100 are solvent-free silicates that show a little increase compared to the Wacker product, while TV undergoes a further decrease.

The products that showed good water absorption results after ethyl silicate treatment, now undergo a sharp decrease of Wa (i.e. RP and TES28), thus confirming the presence of an interaction between Ethyl Silicate and Barium.

In the case of the treatment based on the application of only barium hydroxide, the value of water absorption is less than half compared to the value of untreated samples, and therefore some interactions with the matrix of the stone occurred.

Now, a remark is necessary, because the treatments based on Barium Hydroxide (mineral substance) cannot lead to water repellency. So, it must be assumed that for those products with a further reduction of water absorption, the precipitation in the pores of some new material produced by the interaction between silicate and barium hydroxide (like barium silicate, i.e. a mineral and hydrophilic product) occurred.

This strong reduction of Wa can be caused as a consequence because the addition of barium hydroxide may lead to the closure of the pores of the sample. Although after barium application the water absorption decreases considerably, the system may remain hydrophilic, and the water might be absorbed slowly over time. In the trial time the water is found to be hardly absorbed.

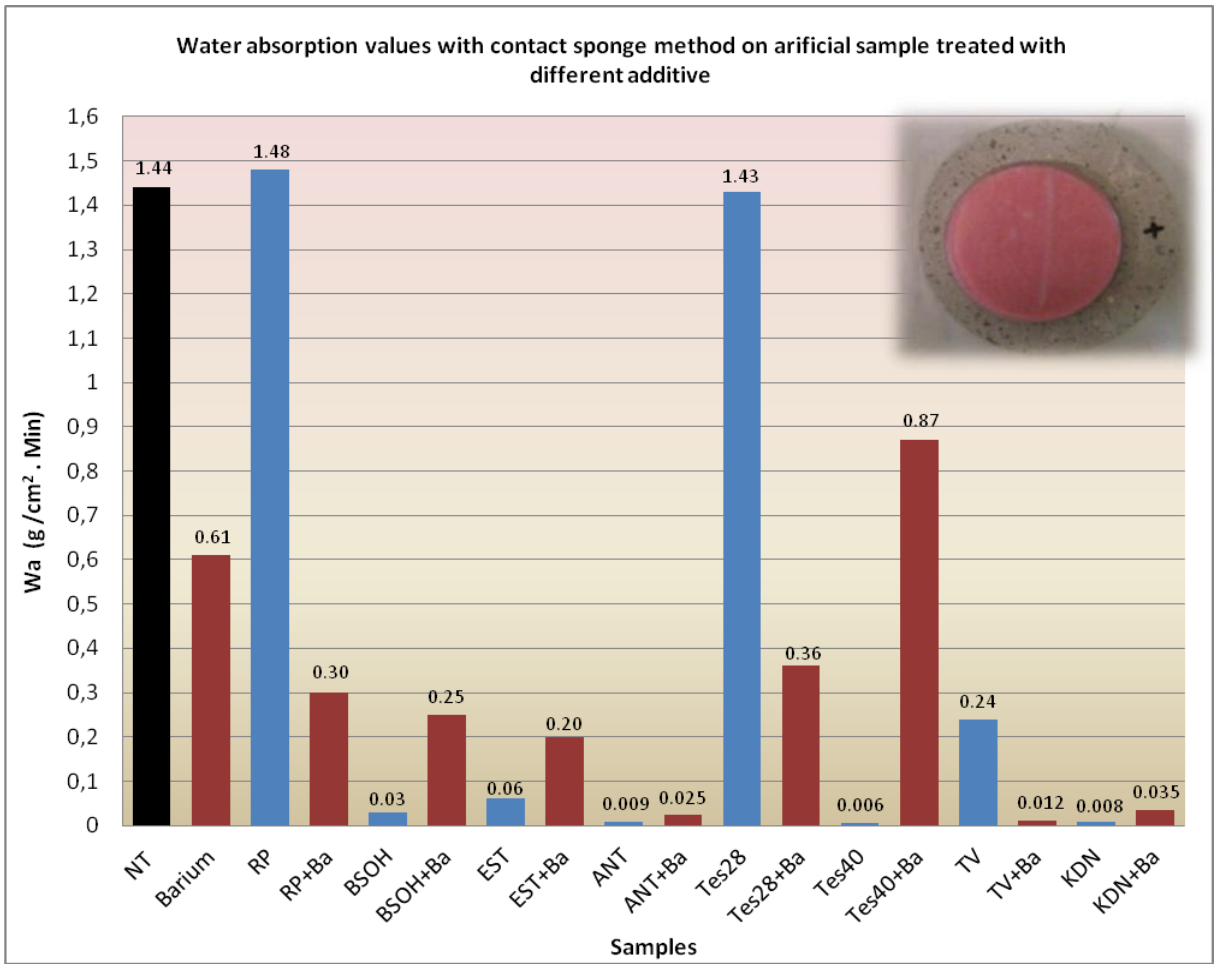

Fig.5. Results of water absorption tests with contact sponge method.

7.2.2. *Mechanical Resistance (RA)*: *Abrasion Test*s

The strengthening power of the treated samples was measured through the abrasion resistance (RA) tests. Indeed, the correlation between the abrasion resistance and the strengthening power is: RA is greater when the weight loss with abrasion is lower, thus the strengthening power is better.

RA was measured through deep abrasion test (CAP) and surface abrasion test (Taber).

In the case of Taber test, BSOH, EST, ANT, and TV show higher resistance to abrasion (i.e. they are more effective treatments) than untreated samples. In RP and TES 28 the weight loss during Taber analysis is higher than the products mentioned above, but lower than untreated samples. Thus these treatments show some resistance to surface abrasion.

Instead, other samples (like TES 40 and KDN) have unexpectedly a similar or lower resistance than untreated samples, as if the treatment with ethyl silicates lead to a weakening of the cohesion of the treated sample.

The behavior of the treatments based on ethyl silicate described above was observed at both 50, 100 and 150 surface abrasion cycles [Tab.2, Fig.6].

Samples	50 cycles	100 cycles	150 cycles
NT	5.37	11.34	17.26
BARIUM	2.93	6.68	10.53
RP	4.15	8.45	12.99
BSOH	3.29	6.5	10.42
EST	3.29	6.81	10.71
ANT	3.34	7.02	11.17
TES28	4.39	9.06	13.73
TES40	5.36	10.73	15.8
TV	3.66	7.3	11.29
KDN	5.82	11.45	17.08

Tab.2. Results of RA tests with Taber method (weight loss in grams).

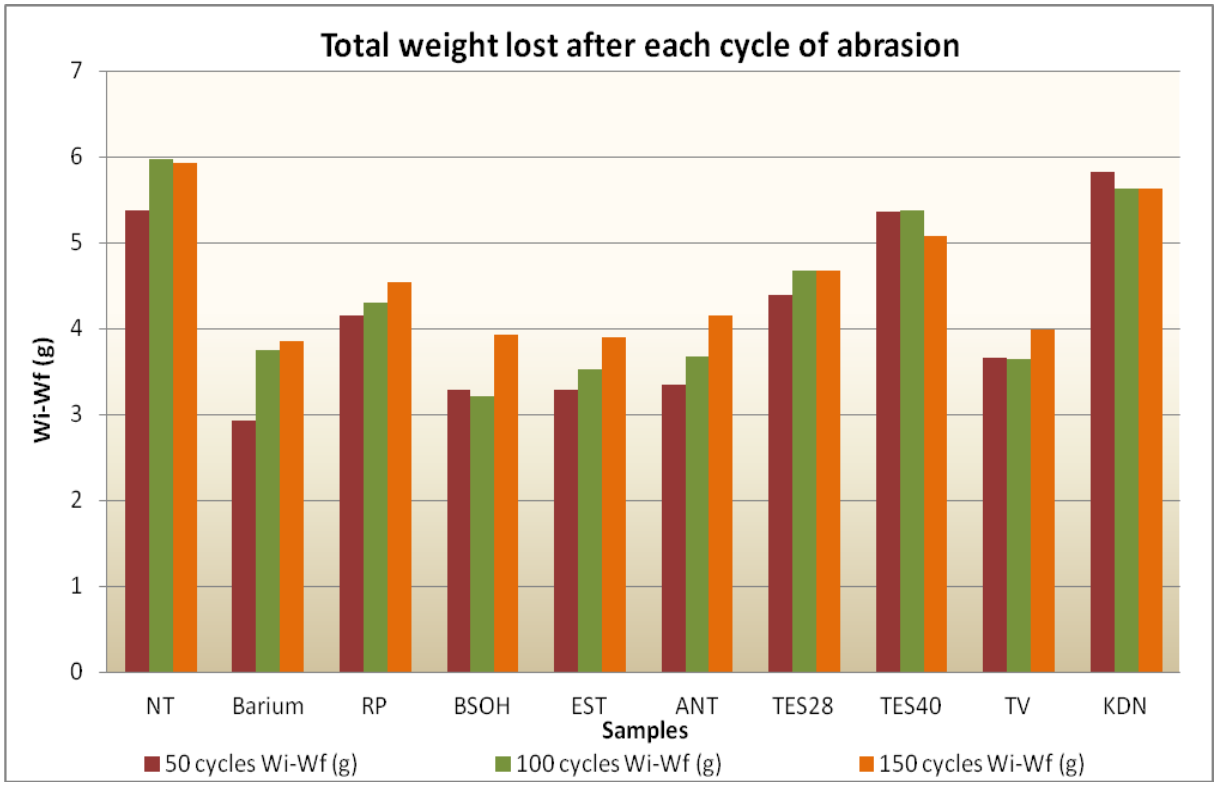

Fig.6.Total weight lost after 50, 100, and 150 cycles of surface abrasion on samples treated with different ethyl silicates.

The results of deep abrasion test (CAP) show lower value of volume removed for TV, RP, and ANT than untreated samples, therefore their strengthening effect is measurable.

Others samples, like BSOH, TES 28, TES 40, EST, and KDN have a little abrasion resistance and less cohesion than untreated samples. In these cases, the resistance values change at different cycles of deep abrasion, i.e. there is a good resistance till 20 cycles for BSOH and TES 28, afterwards their matrix show a loss of cohesion and the resistance of treated samples becomes lower than untreated. Instead, poor resistance to deep abrasion is shown by KDN, EST, and TES 40 (see Tab. 3 and Fig.7). DN-Consolidant shows a strengthening effect until the first 10 cycles of abrasion, while ESTEL 1000 and TES 40 resist only at the first cycle of abrasion (5 cycles).

	CAP (mm^3)					
Samples	**5 cycles (10g)**	**10 cycles (20g)**	**20 cycles (40g)**	**30 cycles (60g)**	**40 cycles (80g)**	**50 cycles (100g)**
NT	**462**	**462**	**696**	**696**	**1062**	*
RP	205	250	462	649	672	1196
BSOH	227	330	626	1026	1026	*
EST	409	500	520	824	1324	1305
ANT	288	393	500	649	999	1268
TES28	345	462	626	880	999	*
TES40	238	500	696	1062	2149	*
TV	275	275	393	582	880	*
KDN	316	444	746	999	2365	*

Tab.3. Volume removed (expressed in mm^3) from the artificial samples treated with different ethyl silicates at different cycles of deep abrasion. (*) No available values due to the rupture of the specimen during the analyses.

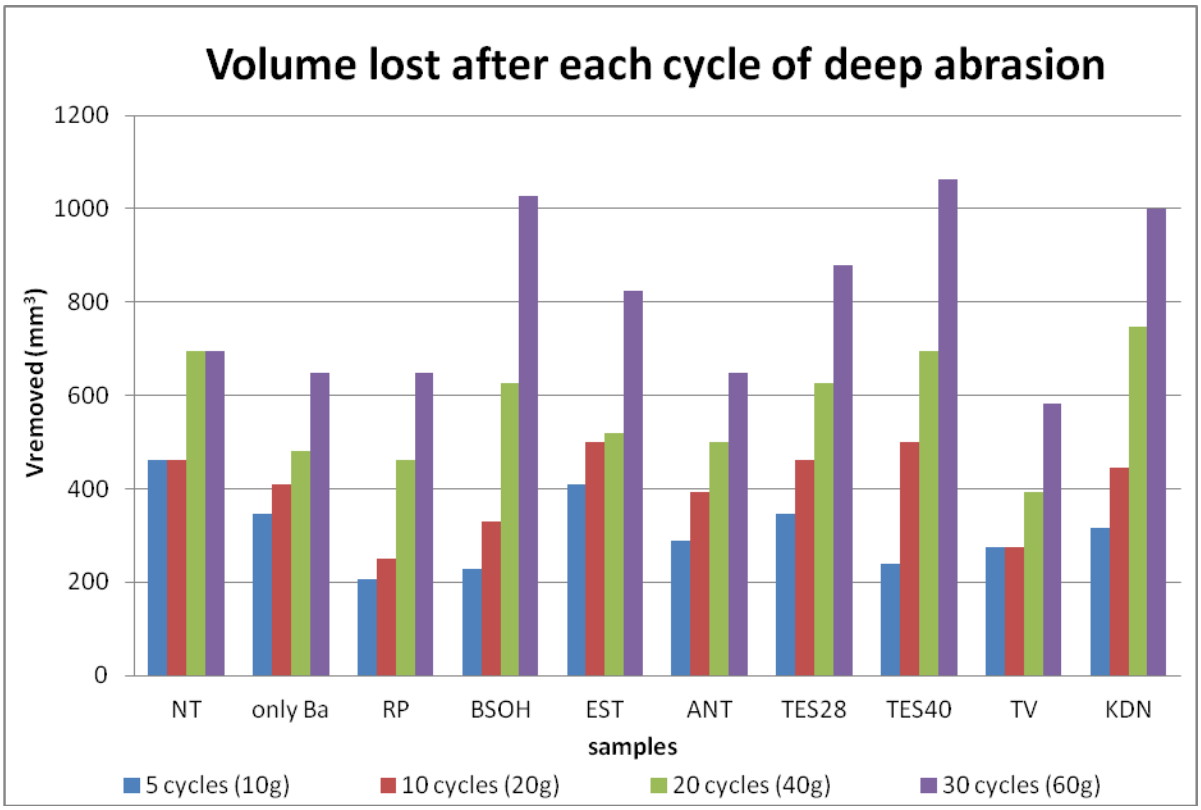

Fig.7. Comparison of the volume removed (expressed in mm^3) from artificial samples treated with different ethyl silicates, barium and untreated, after the early cycles of abrasion.

In the case of artificial samples treated with Barium Hydroxide and saturated solution of Barium added to TEOS treatment, an effective consolidation effect is detected for all samples, because their resistance to the loss of weight after surface abrasion and deep abrasion is increased.

This consolidation effect is supposed to be due to barium, that penetrates into the samples and reacts with the silica matrix of the artificial specimen and creates durable and strong Ba–Si–O–Si–Ba (barium silicate) bonds that show good physical-chemical affinity and compatibility with the internal structure of the samples, without changing their appearance.

In case of Taber test, ANT, EST, and TV show the best resistance to surface abrasion compared with untreated, treated with only barium poultice and treated with ethyl silicates.

BSOH, TES 40, and KDN have good consolidation effect. Conversely, TES 28 and RP show lower weight loss during Taber analysis than the untreated and treated with the same ethyl silicate product. Moreover, these products have lower resistance to surface abrasion than treatment with only Barium Hydroxide.

The behavior of the treatments based on saturated solution of barium hydroxide added to ethyl silicate described above was studied at 50, 100 and 150 abrasion cycles [Tab.4, Fig.8].

Samples	50 cycles	100 cycles	150 cycles
NT	5.37	11.34	17.26
BARIUM	2.93	6.68	10.53
RP+Ba	3.44	7.09	10.76
BSOH+Ba	1.42	3.19	5.33
EST+Ba	1.33	2.91	4.48
ANT+Ba	1.06	2.49	4.15
TES28+Ba	3.28	7.03	10.59
TES40+Ba	1.53	3.2	4.95
TV+Ba	1.26	2.79	4.53
KDN+Ba	1.69	3.54	5.98

Tab.4. Results of RA tests with Taber method (weight loss in grams).

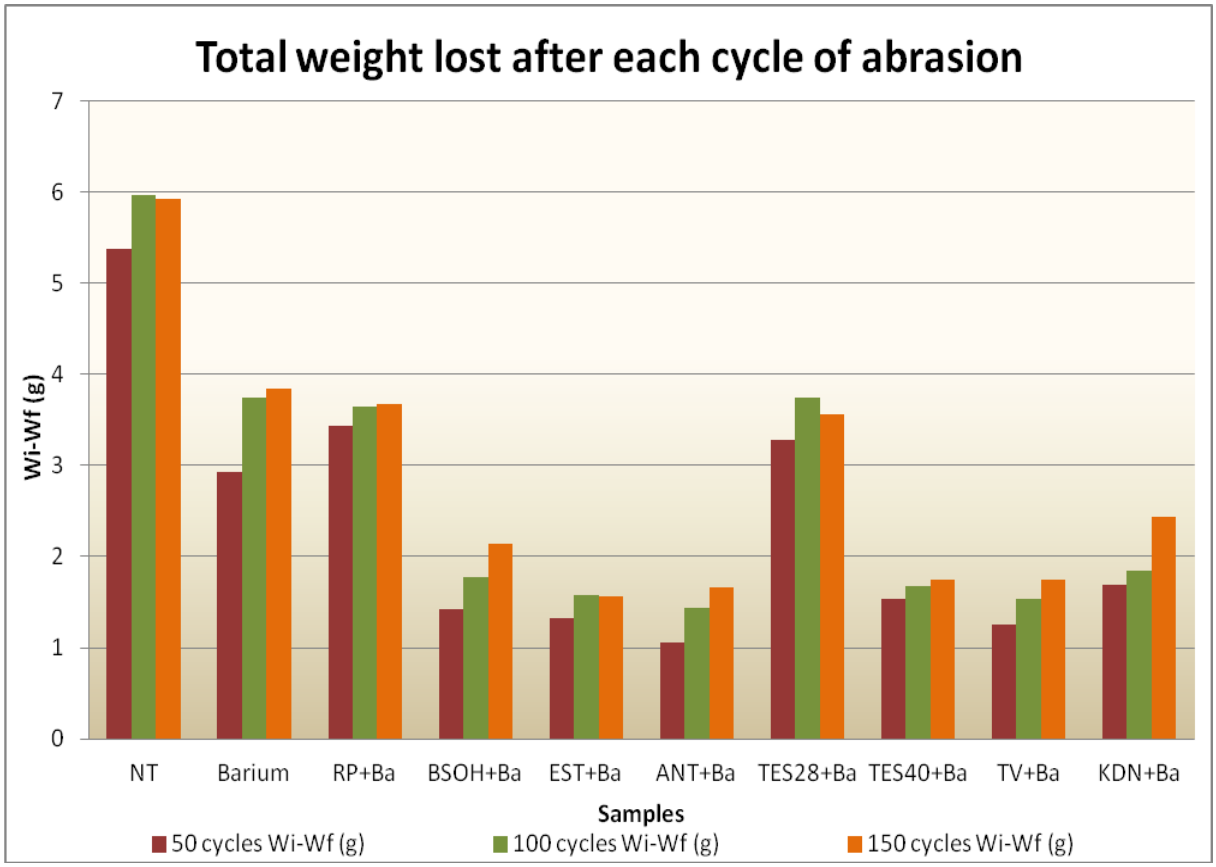

Fig.8.Total weight lost after surface abrasion test on samples treated with barium hydroxide added to ethyl silicates.

The results of deep abrasion tests are in agreements with the Taber tests (see Tab. 5 and Fig.9). All samples show good resistance to abrasion, and thus good consolidating effect respect with untreated samples and the ones treated with barium. At the same time, these samples show greater resistance to deep abrasion than samples treated with the same ethyl silicate, but an exception is given by RP silicate treatment. Indeed, its strengthening power seems to get worse when barium treatment is applied [Tab.6].

The better treatment results, if coupled with barium poultice ones, were given by ESTEL1000, while good consolidating effects are shown by BSOH, TV, ANT, KDN and TES 40 added to barium. In the case of TES 28 and RP, which gave the best behavior if used by themselves, they show only a small strengthening effect.

The treatments made by only application of barium poultice show a good increase in resistance compared to untreated, *i.e.* a consolidation effect.

	CAP (mm^3)					
Samples	**5 cycles**	**10 cycles**	**20 cycles**	**30 cycles**	**40 cycles**	**50 cycles**
	(10g)	**(20g)**	**(40g)**	**(60g)**	**(80g)**	**(100g)**
NT	462	462	696	696	1062	*
Barium	345	409	481	649	938	1583
RP+Ba	238	361	393	672	880	1128
BSOH+Ba	165	227	345	409	696	1062
EST+Ba	184	194	316	361	500	672
ANT+Ba	194	302	376	500	582	626
TES28+Ba	288	316	345	462	649	1128
TES40+Ba	238	227	316	626	696	*
TV+Ba	215	275	288	520	520	880
KDN+Ba	184	288	330	462	626	880

Tab.5. Volume removed (expressed in mm^3) from the artificial samples treated with barium hydroxide and ethyl silicates at different cycles of deep abrasion. (*) No available values due to the rupture of the specimen during the analyses.

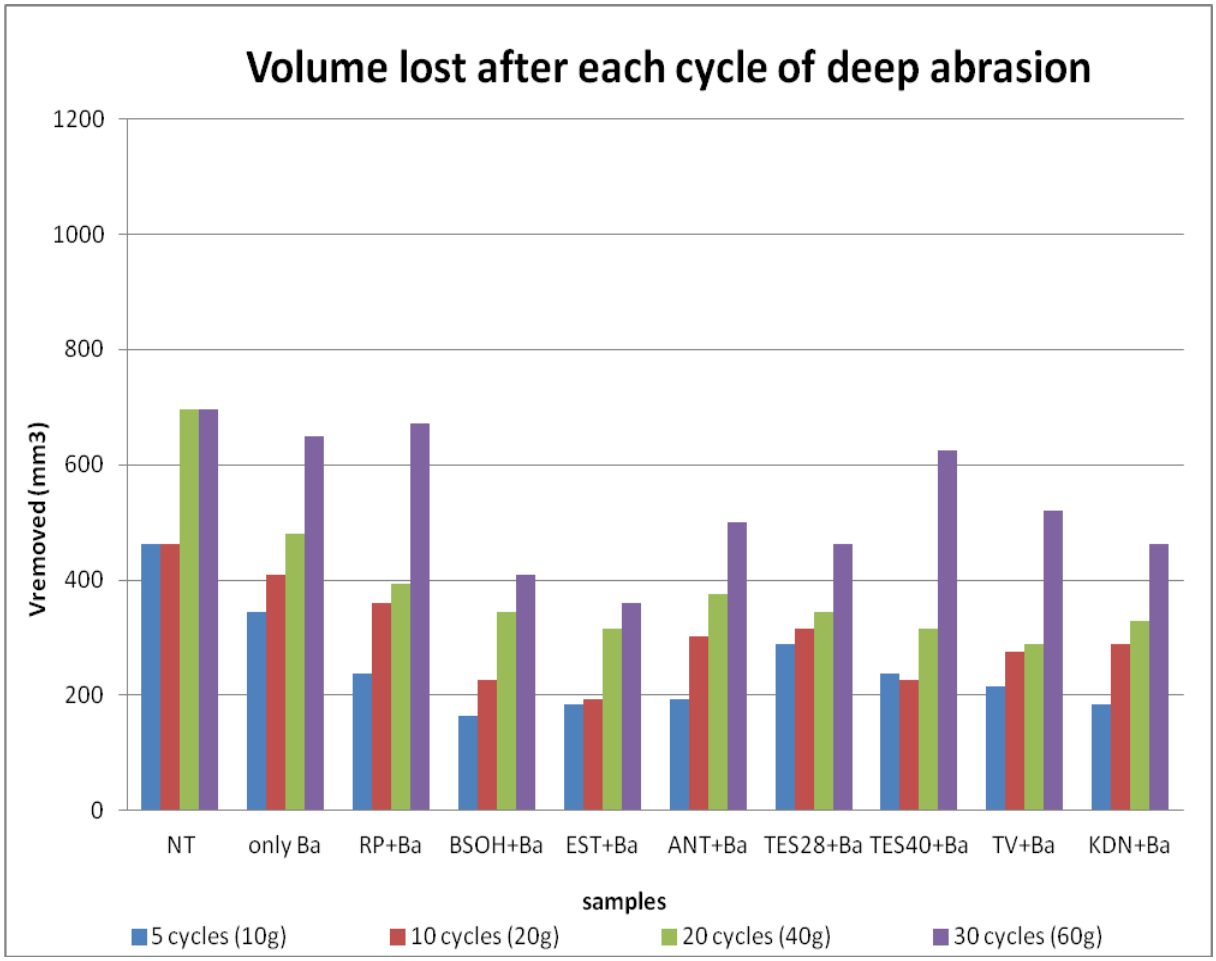

Fig.9. Comparison of the volume removed (expressed in mm^3) from artificial samples treated with barium and ethyl silicates, barium and untreated, after the early cycles of abrasion.

	CAP (mm^3)					
Samples	**5 cycles (10g)**	**10 cycles (20g)**	**20 cycles (40g)**	**30 cycles (60g)**	**40 cycles (80g)**	**50 cycles (100g)**
RP	205	250	462	649	672	1196
RP+Ba	238	361	393	672	880	1128

Tab.6. Comparison between RA tests of RP and RP+BA with CAP method.

The comparison of RA values derived from Taber test at 50 cycles between one treatment (like the only application of ethyl silicate or barium hydroxide), and the double treatment based on barium hydroxide and ethyl silicate, lead to the following percentages [$(RA_{NT}-RA_{treated})/RA_{NT} \cdot 100$]:

Samples	Barium	RP	BSOH	EST	ANT	TES28	TES40	TV	KDN
Ethyl Silicate	/	23%	38%	38%	39%	18%	0%	32%	0%
Ethyl Silicate + Barium	45%	36%	74%	75%	80%	39%	72%	77%	69%

The table must be interpreted as following: high percentages correspond to greater consolidating effects. Thus with the double treatment very high consolidating effects are noted, in most cases they are between 70 and 80 %.

Conversely, the treatments with ethyl silicate show small consolidating effects, between 20 and 40 %. TES 40 and KDN show values close to zero, when the value of surface abrasion of treated samples exceed the untreated, because treatment should not get worse than the situation of untreated samples.

The comparison between the results of water absorption tests and resistance to surface and deep abrasion, in addition to the solvent-free composition of some ethyl silicates, suggests the application of BS OH 100, Tegovakon V 100, RP and TES 28 like individual treatments based on ethyl silicate. BSOH and TES 28 show a not excessive consolidation effect, while RP and TV have the best characteristics of resistance to surface and deep abrasion.

When barium poultice is added to the silicate, the best abrasion resistance is given by BSOH+Ba and TV+BA, while the application of only barium or barium poultice added to RP and TES 28 give rise to a consolidating effect similar among these three products.

However, there are doubts on the reliability of the deep abrasion tests used for this evaluation. Most of the samples treated with only ethyl silicate have shown no strengthening effects and indeed, weaken the cohesion (i.e. the abrasion resistance) of the treated samples. This behavior does not seem to have a plausible explanation.

7.3. *Physical-chemical analyses*

These analyses were employed to determinate the new chemical binders and mineralogical compounds formed after the consolidation treatments, the strengthening of treated samples, and the penetration depth of barium into the artificial sample after the application with the poultice method.

The analytical techniques employed for these purposes are XRD, SEM-EDS, and XRF.

7.3.1. *XRD analysis*

This technique was used to determine if new mineralogical phases were developed after the treatments based on Barium Hydroxide together with Ethyl Silicate [Figs.10-18], such as Witherite ($BaCO_3$) and the different form of Barium Silicates like $BaSiO_3$ (Barium Metasilicate) and Ba_2SiO_4 (Barium Orthosilicate) that should be formed by the reaction of barium hydroxide in water solution with the silica surface of the stone and with the TEOS. These compounds should continue to react with silica matrix of the stone, and thus can give rise to the formation of more complex barium silicates, which $BaSi_2O_5$, $BaSi_3O_7$, $BaSi_4O_9$, $Ba_2Si_3O_8$, $Ba_5Si_8O_{21}$, $Ba_3Si_5O_{13}$, and so on.

The analyses confirm that barium silicate is formed through the reaction between barium hydroxide reaction and silica matrix of the specimen, while formation of barium carbonate ($BaCO_3$) is due to the reaction of barium hydroxide with the calcareous cement and calcareous minerals present in the artificial test pieces. However, formation of barium carbonate can lead to the formation of insoluble white areas on the surface of the sample that change its appearance.

The XRD analyses on samples treated with only ethyl silicate do not show the formation of new compounds, but they evidence a change in the intensity and widths of the peaks, sign of occurred changes within the matrix.

Also, XRD analyses were made on samples subjected to Taber analyses at 150 cycles, showing the same results of the artificial test pieces treated and not subjected to surface abrasion. This indicates that treatments have no effect of consolidation due to their penetration in the first 2 to 4 mm of the samples (range of thickness lost under 150 cycles of surface abrasion on specimen treated with different products and methods).

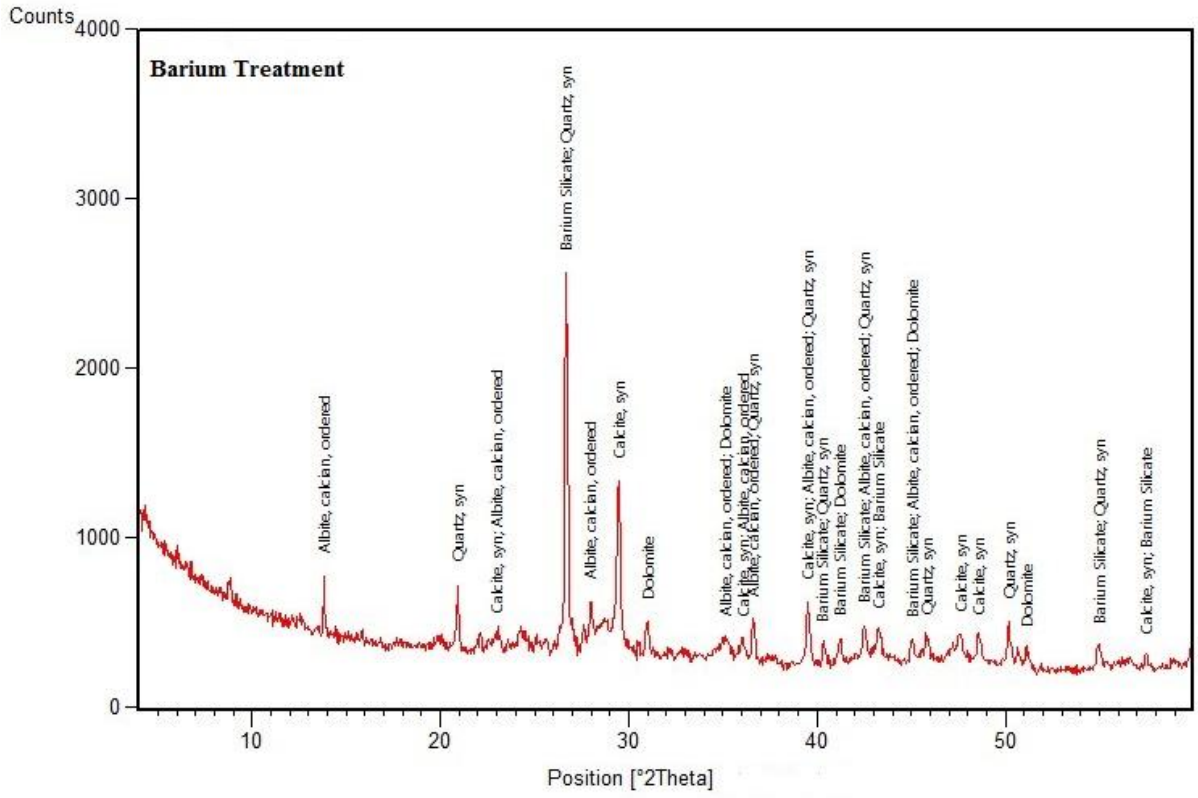

Fig.10. XRD spectrum of sample treated with Barium Hydroxide, showing Barium silicate peaks ($BaSiO_3$). In most cases the peaks of Barium silicate coincide with quartz and calcite peaks, i.e. the cases of the peaks at 26,67.

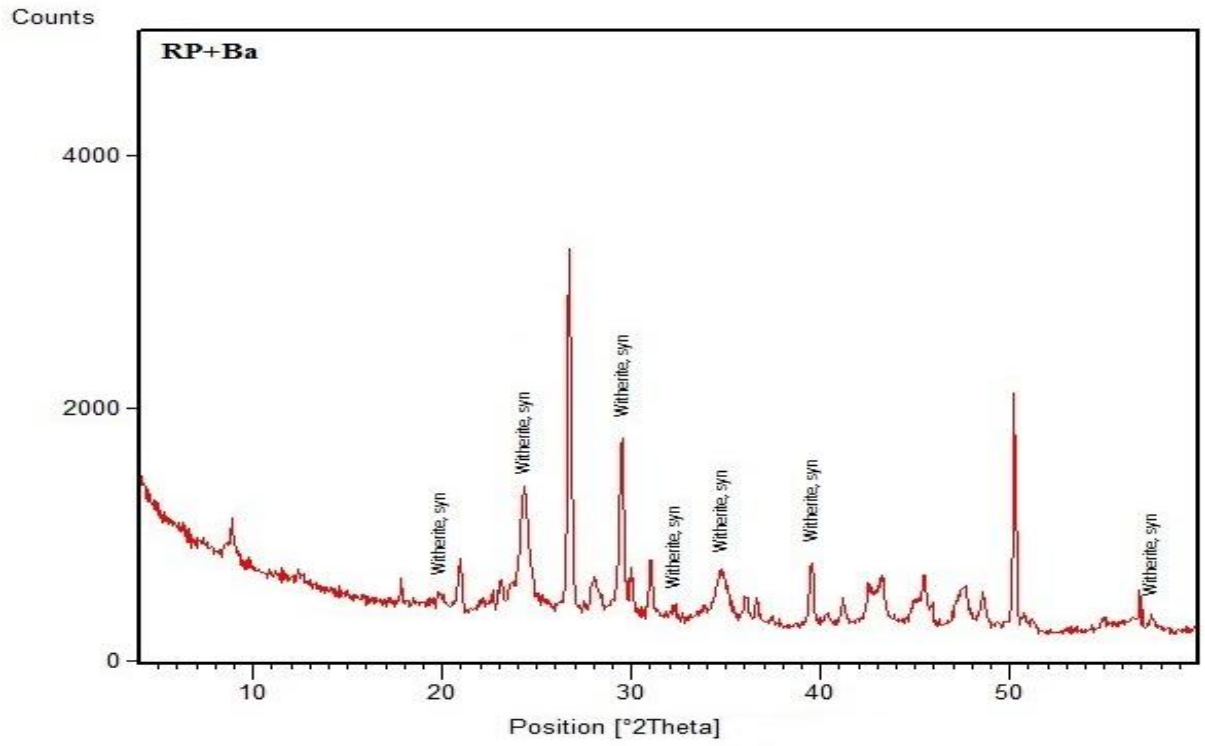

Fig.11. XRD spectrum of sample treated with RP+Ba , showing peaks of Barium Carbonate (Witherite).

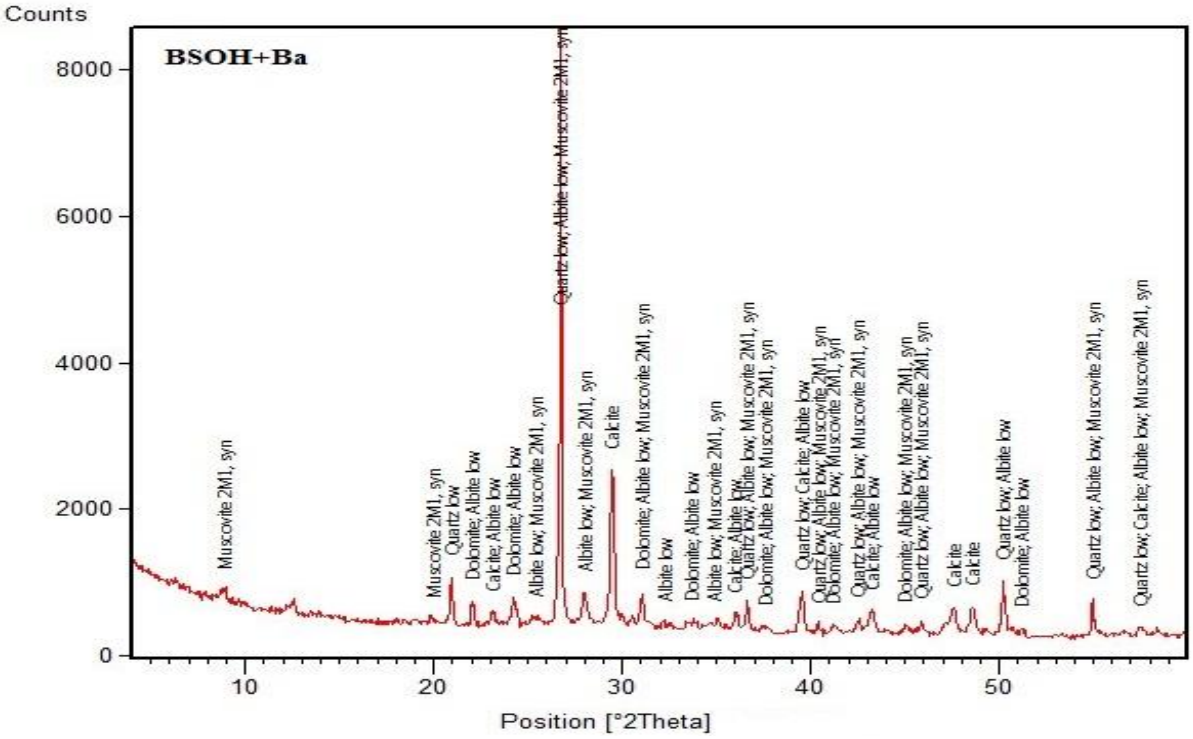

Fig.12. XRD spectrum of sample treated with BSOH+Ba, does not show the peaks of Barium compounds, possibly because barium compounds are in too low quantity on the surface of this sample.

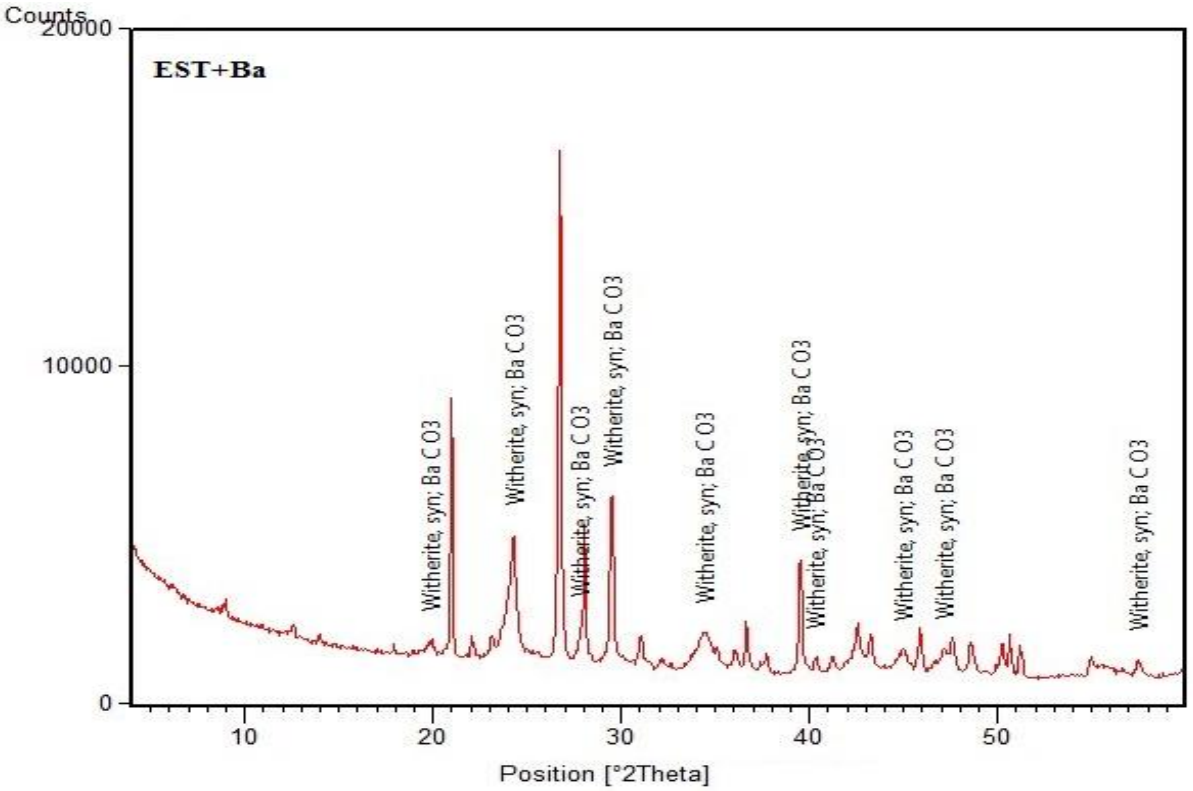

Fig.13. XRD spectrum of sample treated with EST+Ba showing peaks of Barium Carbonate (Witherite).

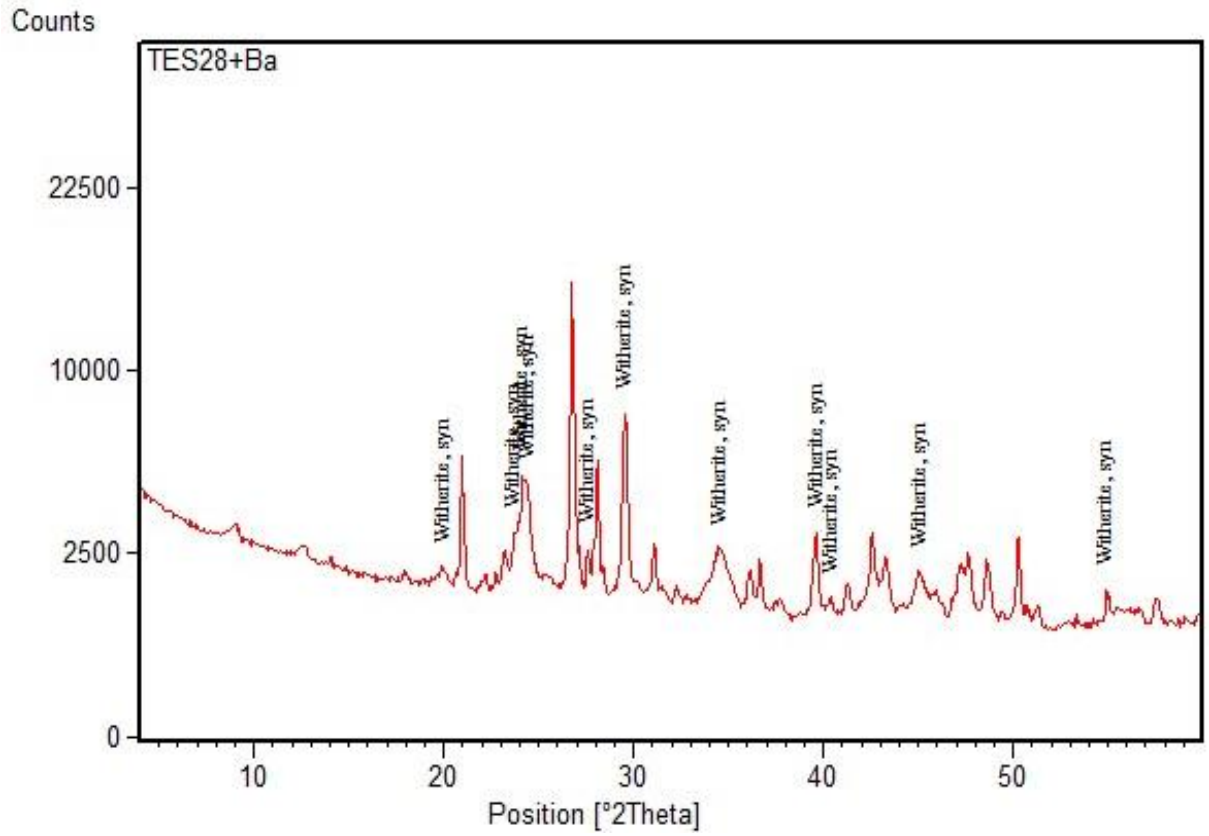

Fig.14. XRD spectrum of sample treated with TES 28+Ba, showing peaks of Barium Carbonate (Witherite).

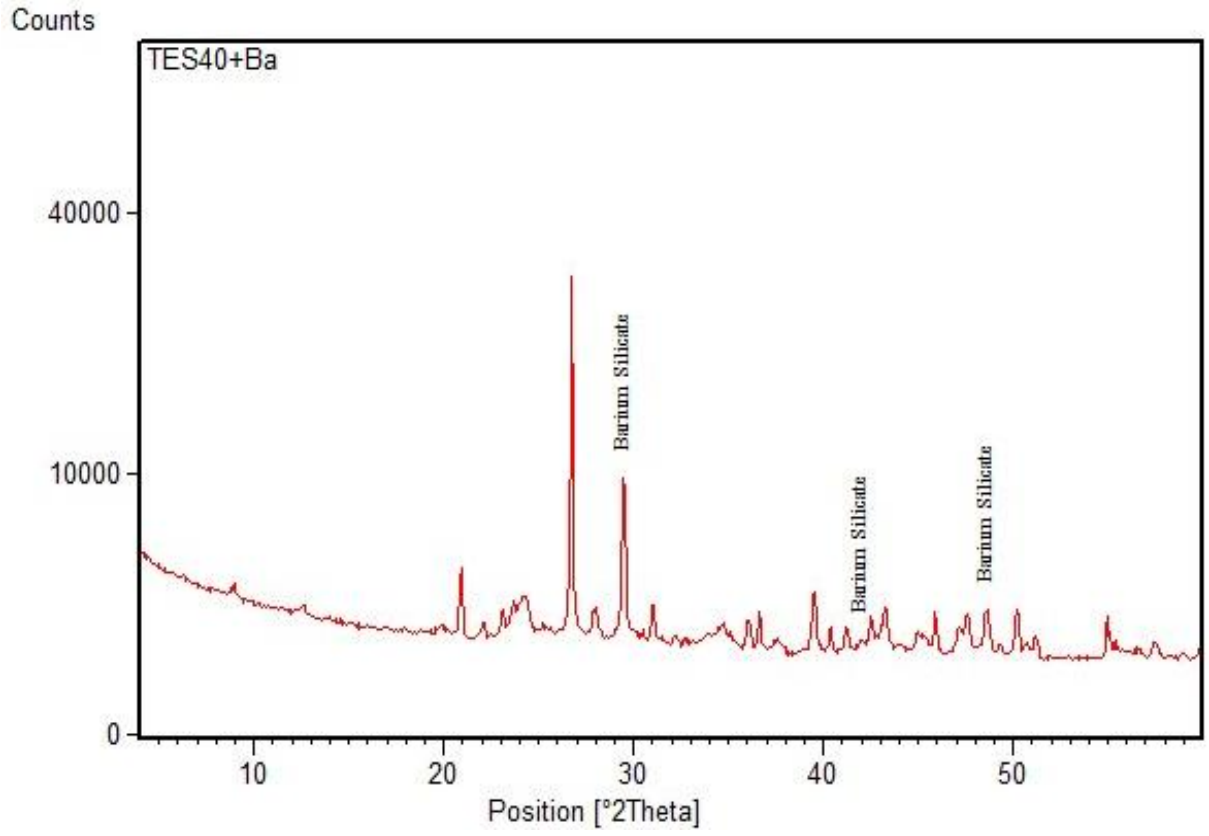

Fig.15. XRD spectrum of sample treated with TES 40+Ba, showing peaks of Barium Silicate.

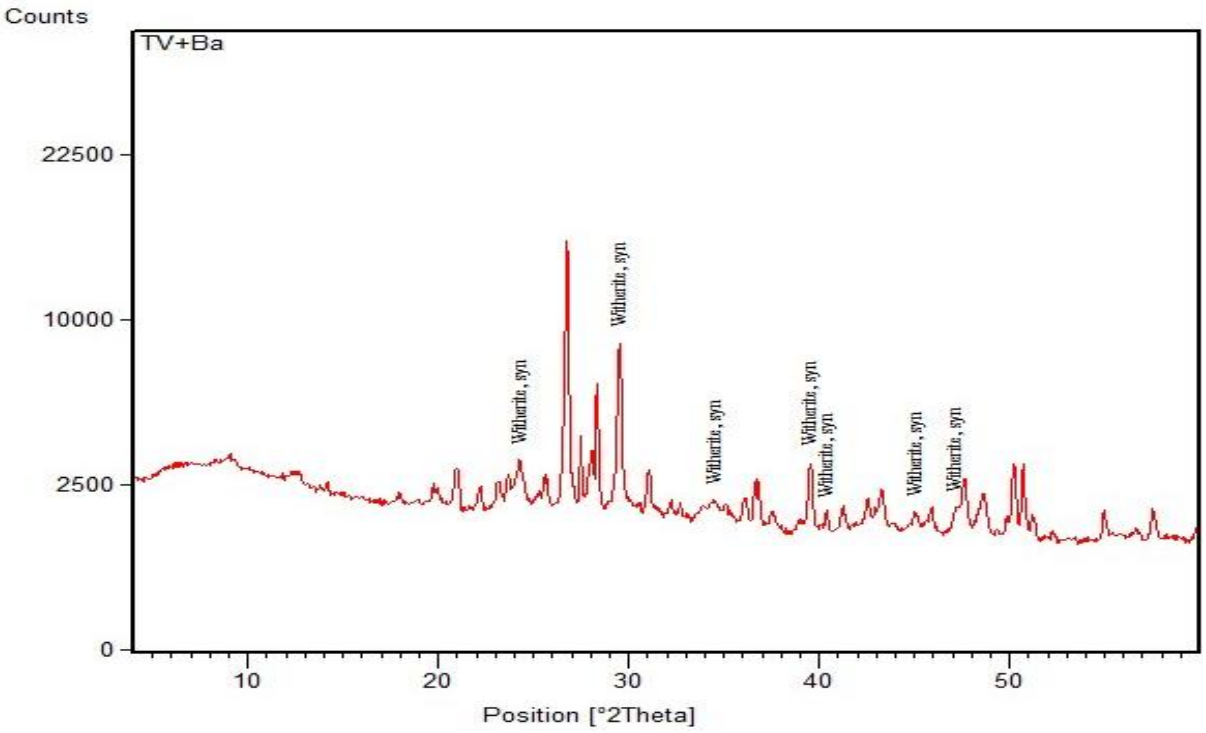

Fig.16. XRD spectrum of sample treated with TV+Ba - showing peaks of Witherite ($BaCO_3$).

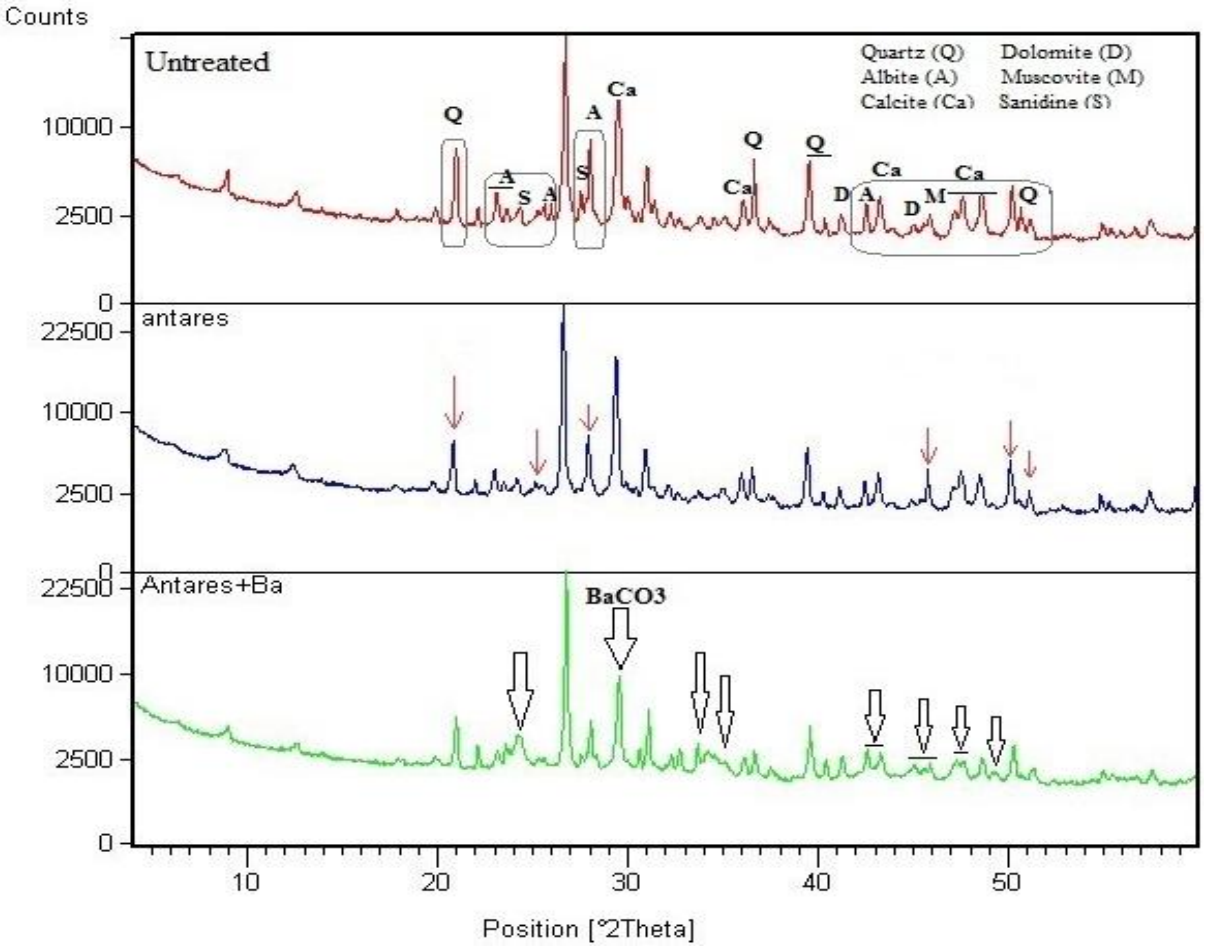

Fig.17. Comparisons between XRD spectra of Untreated, ANTARES, and ANTARES+Ba. The arrows indicate peaks that change intensity after the treatments. In the green spectrum, arrows suggest the formation of barium carbonate.

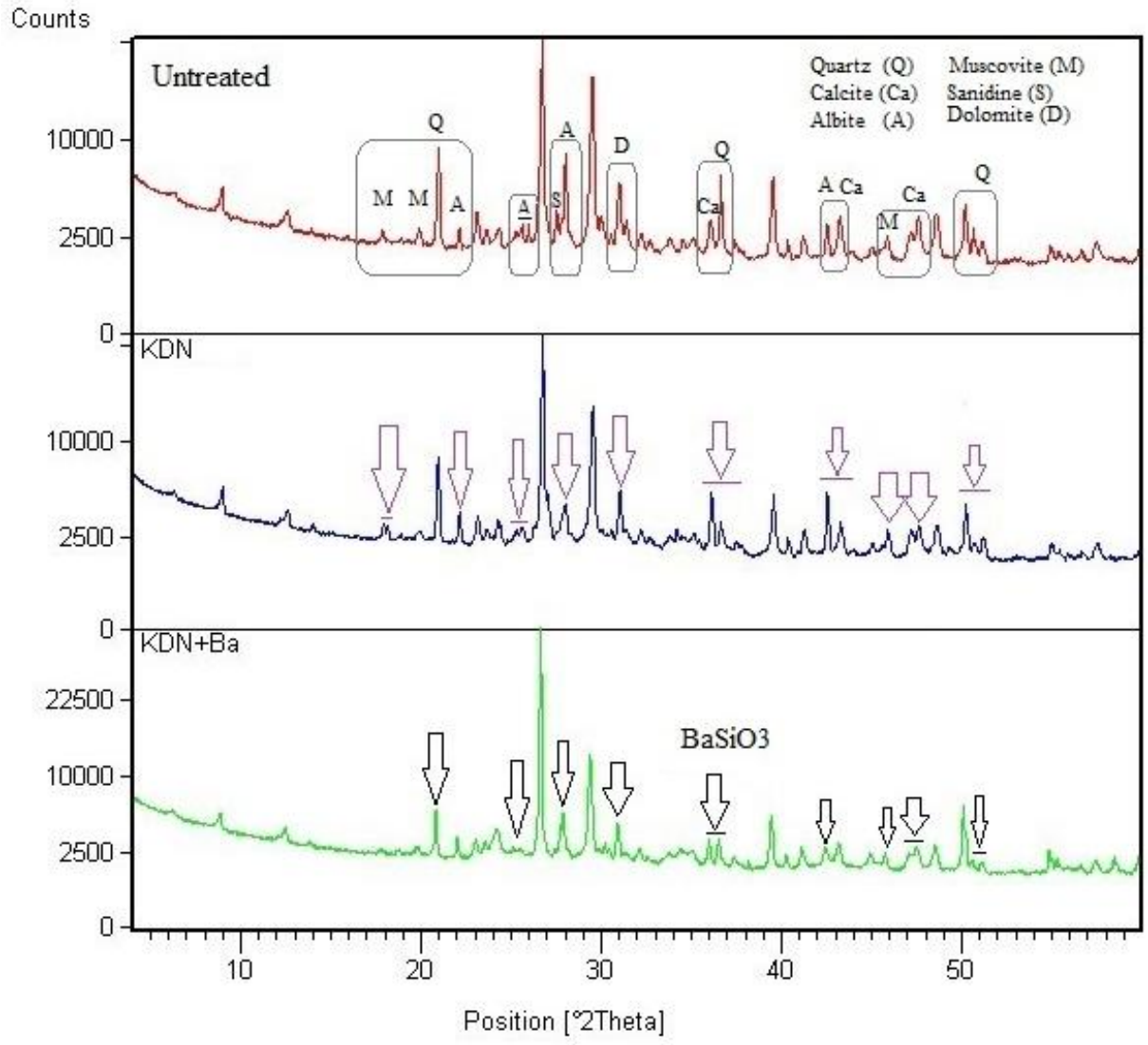

Fig.18. Comparisons between XRD spectra of Untreated, KDN, and KDN+Ba. The arrows indicate peaks that change intensity after the treatments. In the green spectrum, arrows suggest the formation of barium silicate.

7.3.2. *SEM-EDS analysis*

All samples treated with barium poultice were analyzed by Scanning Electron Microscopy from surface to the bottom through the division in sections of 20 μm of thickness and mapping their composition through microanalysis EDS [Fig.19-20].

Compound containing barium particles were observed at 2500x in high contrast, they are randomly distributed inside the samples with a size of about 1 μm.

SEM-EDS analyses show the presence of crystals of barium compounds (like carbonate and silicate) in the first millimeters down the treated surface of the samples [Fig. 21-24], and the results of barium penetration are available in Table 7.

Moreover the EDS analyses show an elemental composition of silicon, aluminum, calcium, potassium, and iron for all samples.

Samples	**Barium penetration**	**Note**
Only Ba	From treated surface (0) to – 0.2 mm within the sample	
BSOH+Ba	From 0 to – 0.6 mm,	particles of barium silicate were found during the analysis
Tes 40+Ba	From 0 to – 0.4 mm	
Tes 28+Ba	From 0 to – 1.6 mm	particles of barium carbonate were found during the analysis
Estel 1000+ Ba	From 0 to – 1.8 mm	particles of barium silicate were found during the analysis
Antares+Ba	From 0 to – 2.0 mm	particles of barium carbonate were found during the analysis

Tab.7. Results of barium penetration inside the samples treated with barium poultice by SEM-ESD analyses.

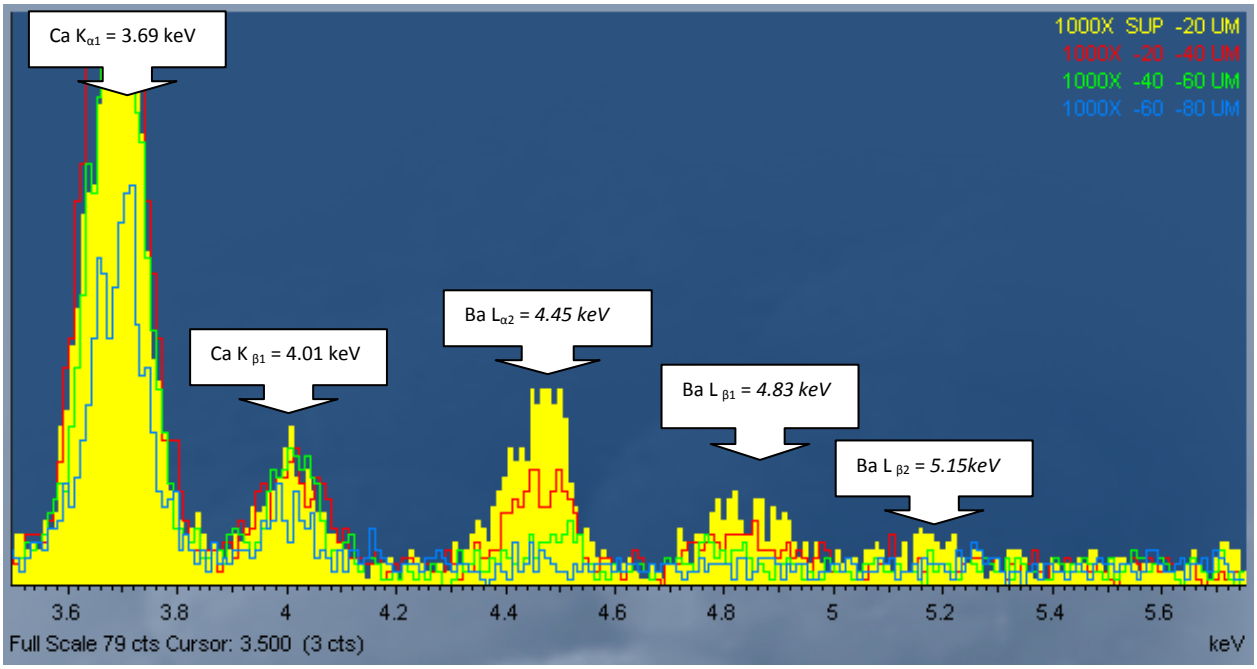

Fig.19. Stratigraphy from treated surface to – 0.8 mm on BSOH+BA sample with barium mapping.

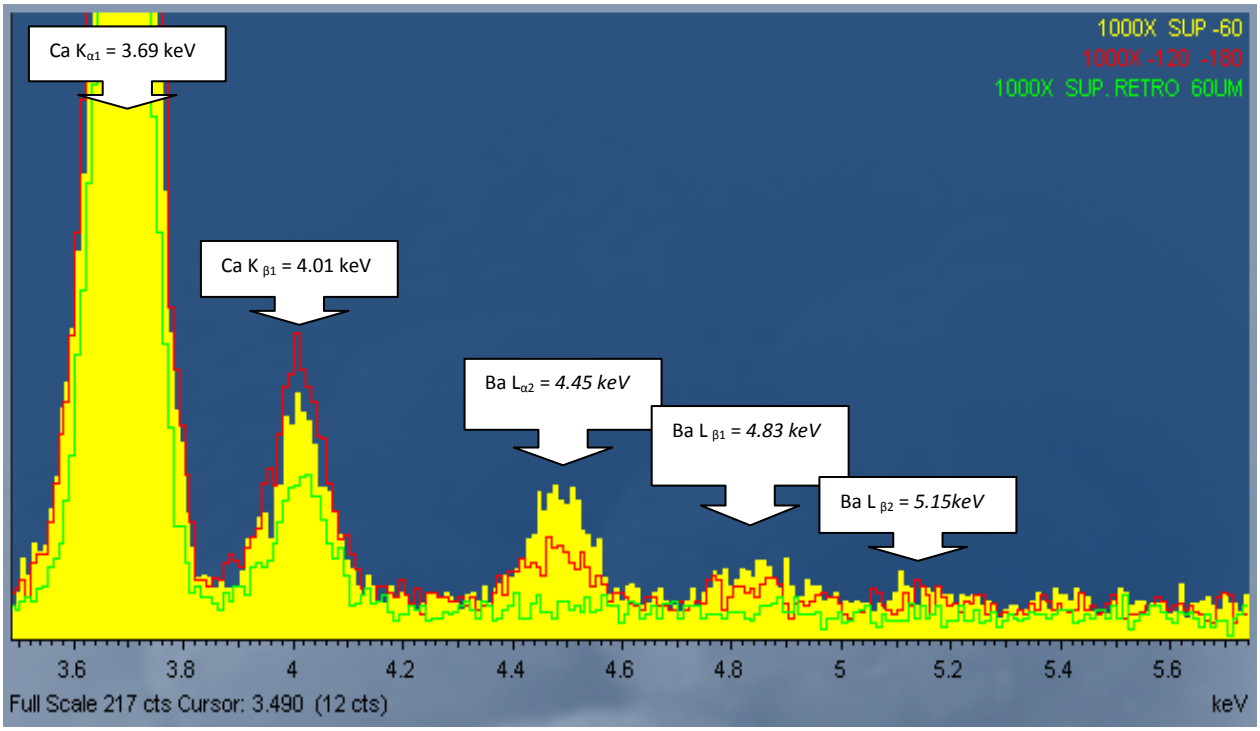

Fig.20. Particular of the stratigraphy from the treated surface to bottom with barium mapping of a ESTEL 1000+BA sample.

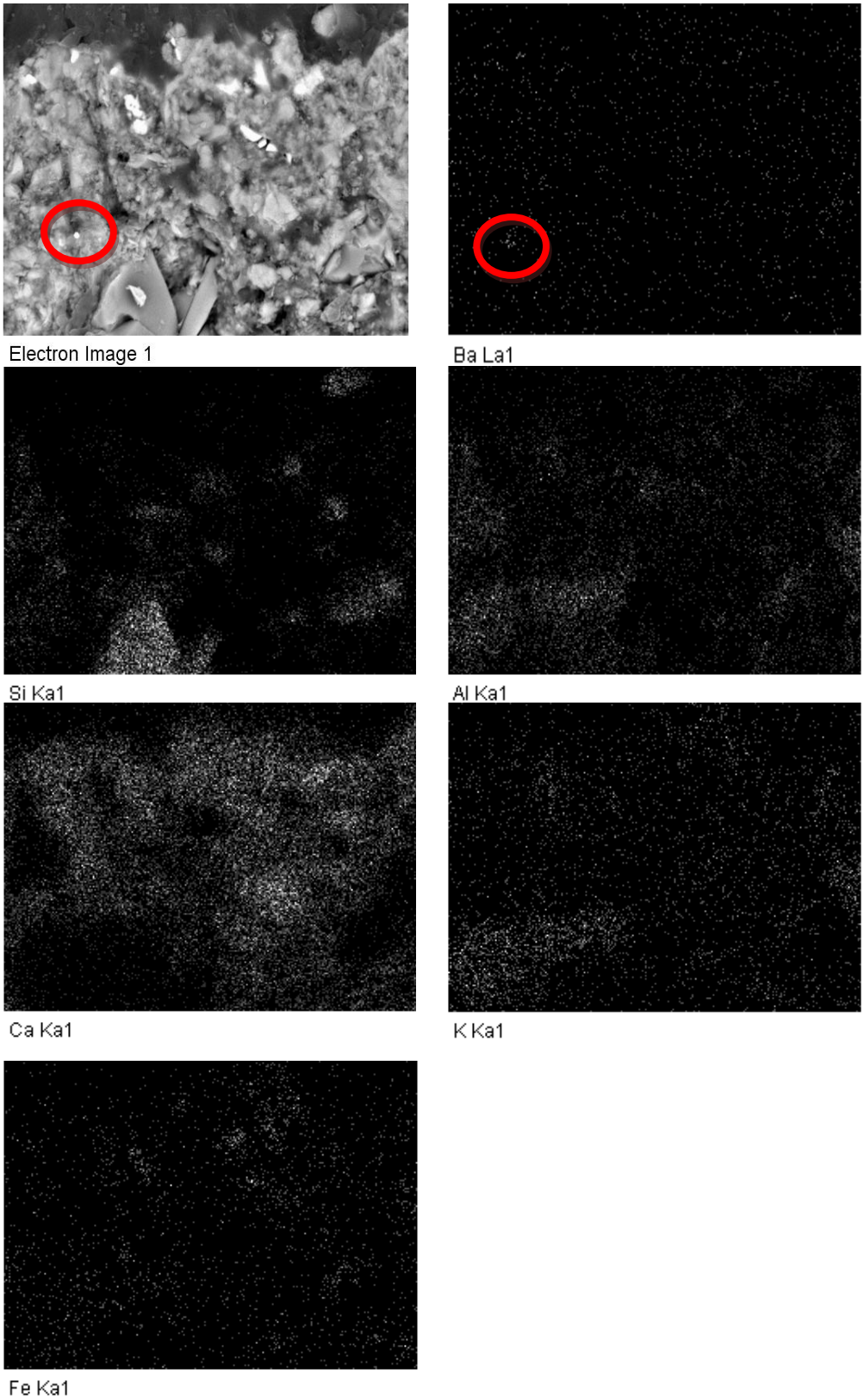

Fig.21. BSOH+BA sample, area at 1250x. SEM-EDS mapping of the composition of the area in Image 1.
It is barely possible to appreciate only some small particle Barium based (see the red circle in the firsts figures).

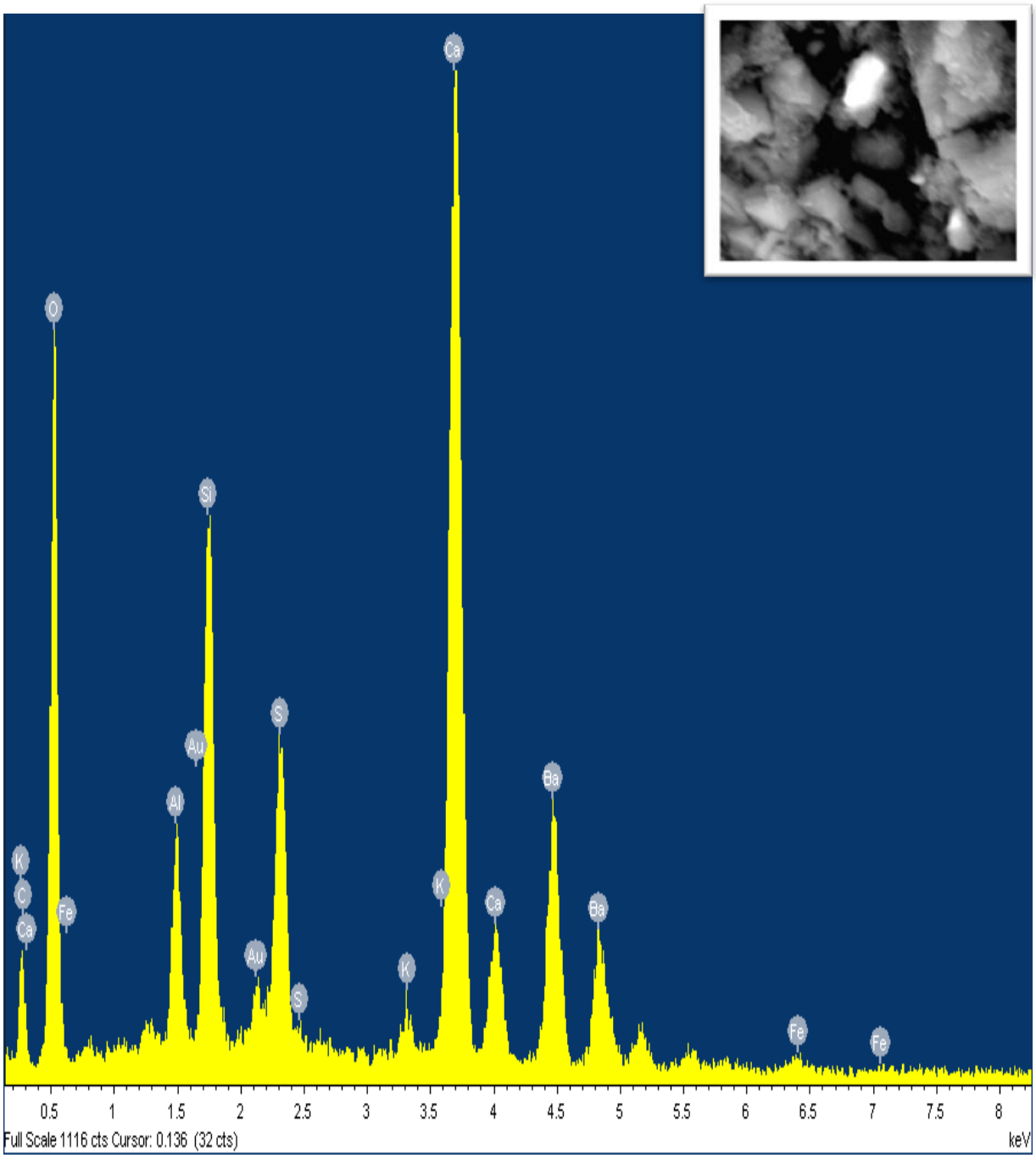

Fig.22. Composition of a white crystal of barium silicate at 64000x of a BSOH+BA sample.

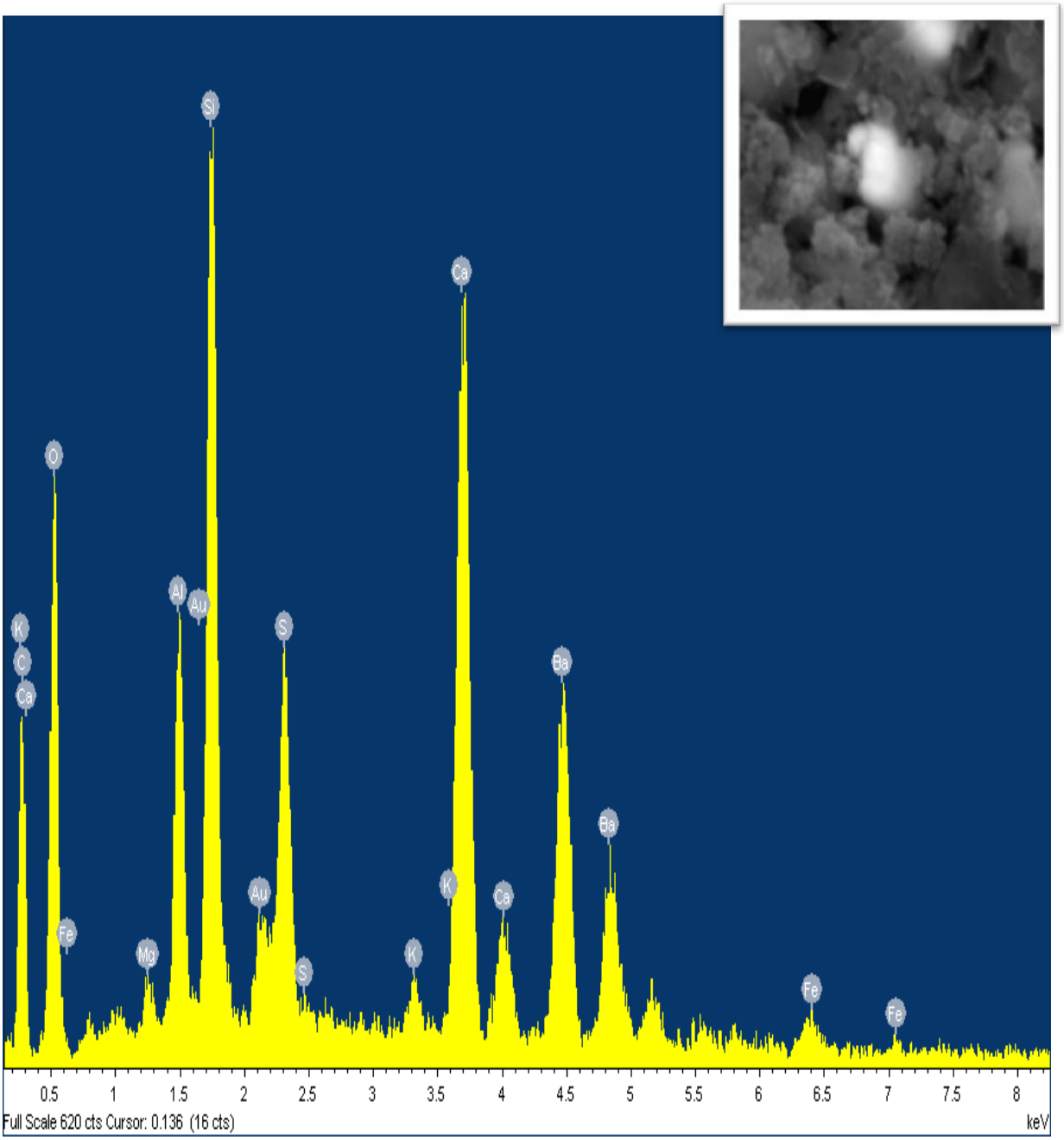

Fig.23. Composition of a white crystal of barium silicate at 18500x of a ESTEL 1000+BA sample.

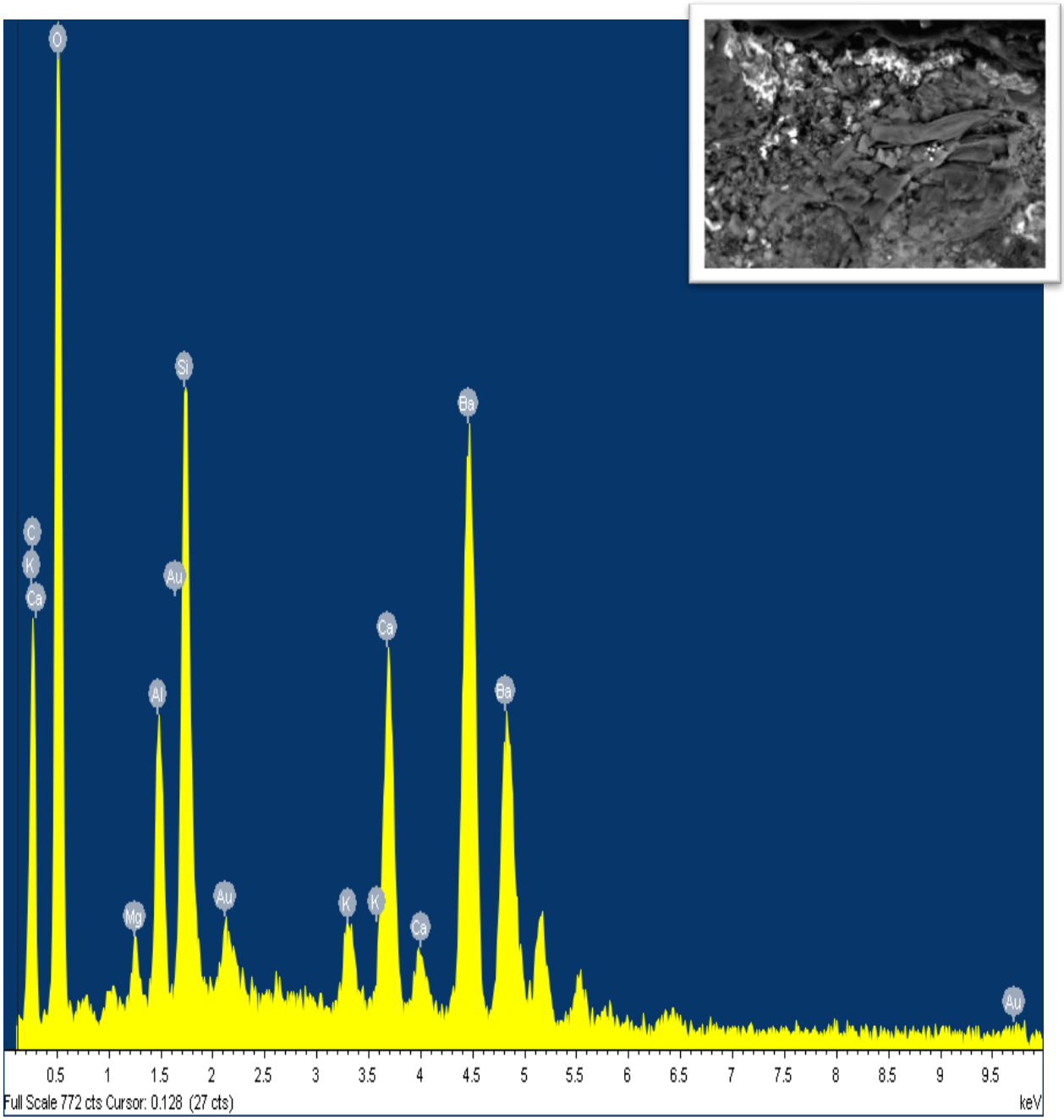

Fig.24. Composition of a white crystal of barium carbonate at 1000x found in the first micron under the surface of an ANTARES+BA sample.

7.3.3. *XRF analysis*

XRF analyses performed on a longitudinal section of the samples treated with barium poultice allowed an easy mapping of barium penetration into the sample.

The first peak of barium is found at 4.45 and 4.83 keV (L-alfa1 and L-beta1), while the main peaks are at 32.19 keV (K-alfa1) and 36.38 KeV (k-beta1), respectively.

All samples analysed show the presence of barium and generally its amount decreases from treated surface to bottom. An exception is provided by samples treated with Antares+Ba that show the three peaks of barium through the whole sample with constant intensity. A description of barium penetration is reported in Table 8.

In Figures 25-35 the comparison of XRF spectra of sections of samples treated with different methods is reported, with in blue the spectrum of treated surface (0 mm), in green the spectrum of the central section (-5.00 mm), and in red the spectrum of the bottom layer (-10.00 mm). Moreover, in each spectrum the peaks of silicon and barium are evidenced.

Samples	**Barium penetration (from surface to bottom)**
Only Ba	In all sections, barium is found from treated surface to untreated bottom. Principal peaks of barium are present till -5.00mm, and after its intensity decreases.
BSOH+Ba	All peaks of barium are found from surface to -5.00 mm, with a low intensity of the 3rd L peak.. Strong decrease of barium is observed between -5.00 mm to the bottom (only 1st peak present).
Tes 40+Ba	From surface to -5.00 mm the principal peaks are present, after barium intensity decreased till very low concentration in the bottom. The 1st and 2nd L peaks are still visible between -7.50 and -10.00 mm.
Tes 28+Ba	All peaks of barium are found from surface to -5.00 mm, while after their intensity decreases. Indeed, till -7.5 mm only 1st and 2nd L peaks are visible, while at -10.00 mm only the 1st peak is found.
Estel + Ba	All peaks of barium are found on the surface. At -5.00 mm1st and 2nd L peaks are visible, between -7.5 to -10.00 mm only the 1st peak can be observed. Barium presence decreases from surface to bottom.
Antares+Ba	In all sections, barium show its three peaks.
TV+Ba	Barium presence decreases from surface to bottom. On the surface the barium intensity is maximum.
KDN+Ba	All peaks of barium are found on the surface of the sample. After it decreases till -5.00 mm, where only the 1st and 2nd L peaks can be observed, and between -7.5 and -10.00 mm only the 1st peak is found. Thus, barium decreases from surface to bottom.

Tab.8. Results of barium penetration inside the samples treated with barium poultice.

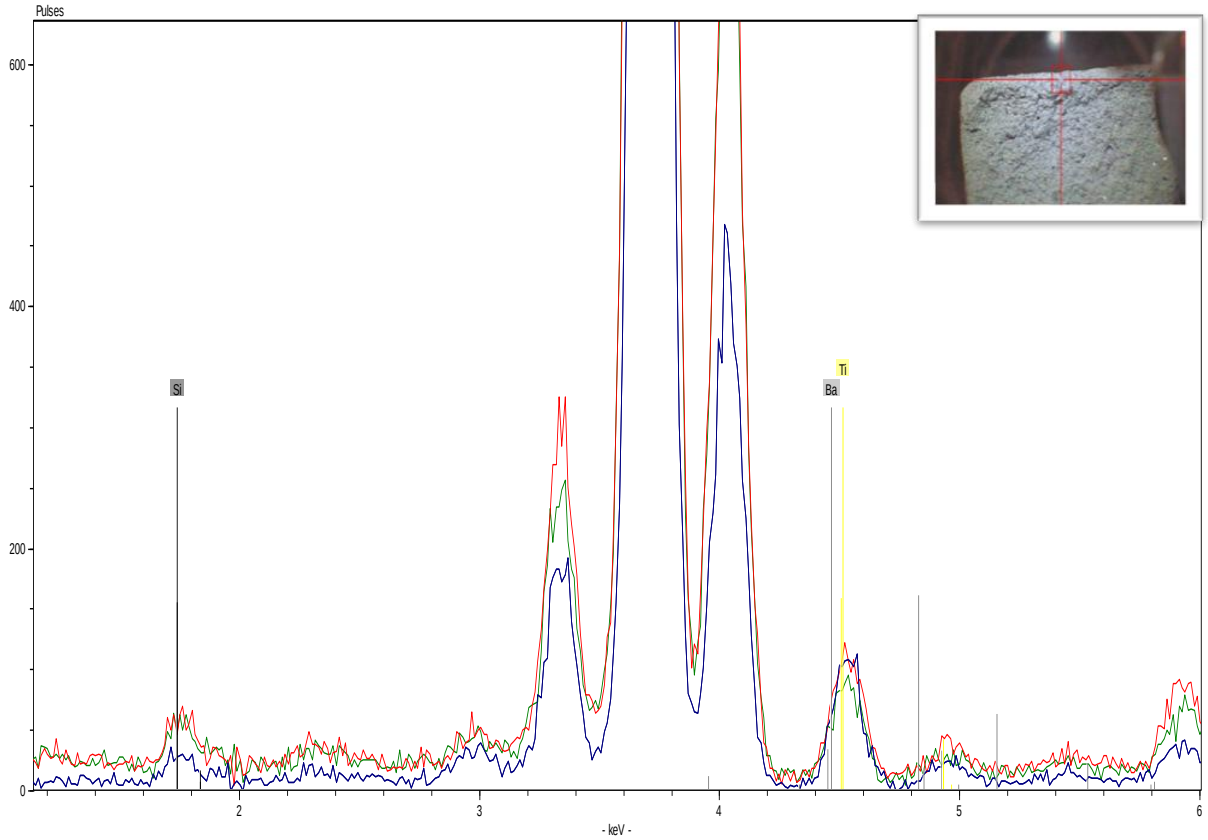

Fig.25. Comparison between XRF spectra of sections of an untreated sample.

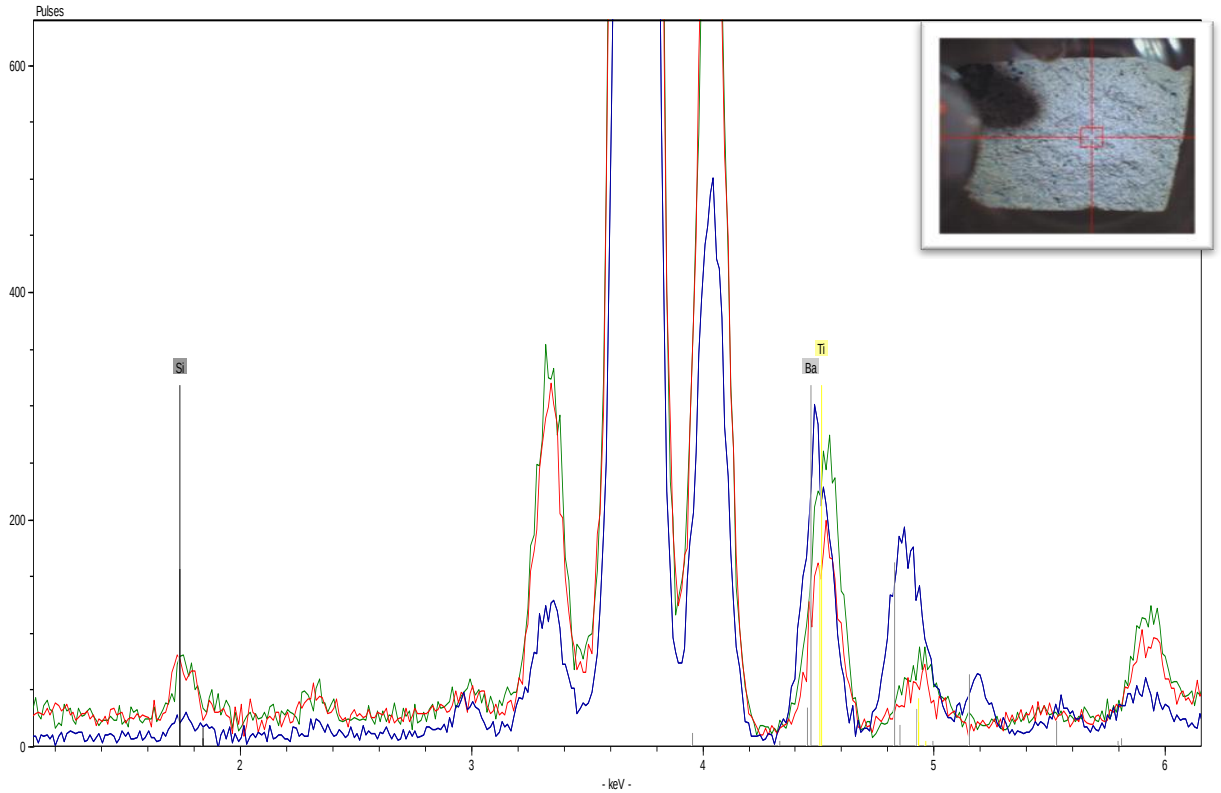

Fig.26. Comparison between XRF spectra of sections of a sample treated with barium poultice. The signal of barium is maximum on the treated surface.

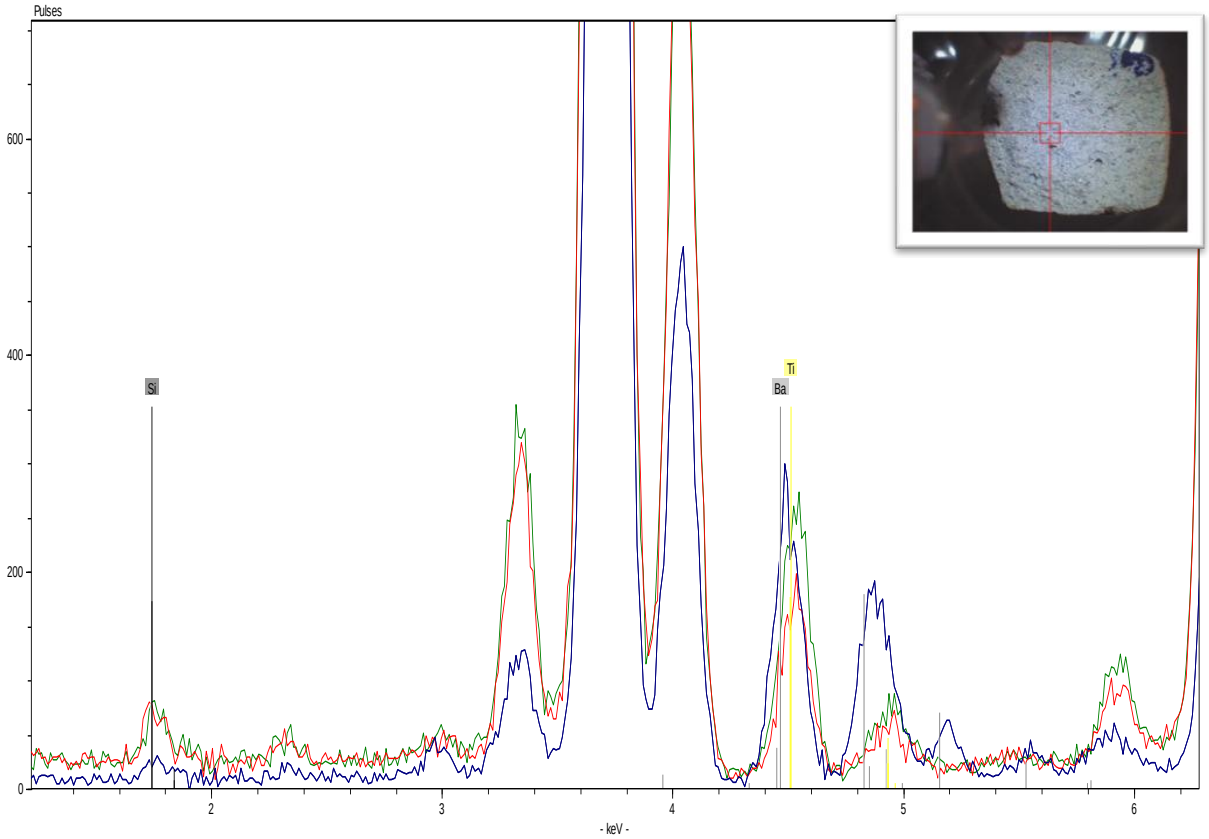

Fig.27. Comparison between XRF spectra of sections of RP+Ba. The peaks of barium show similar intensities both on the surface and in the middle section.

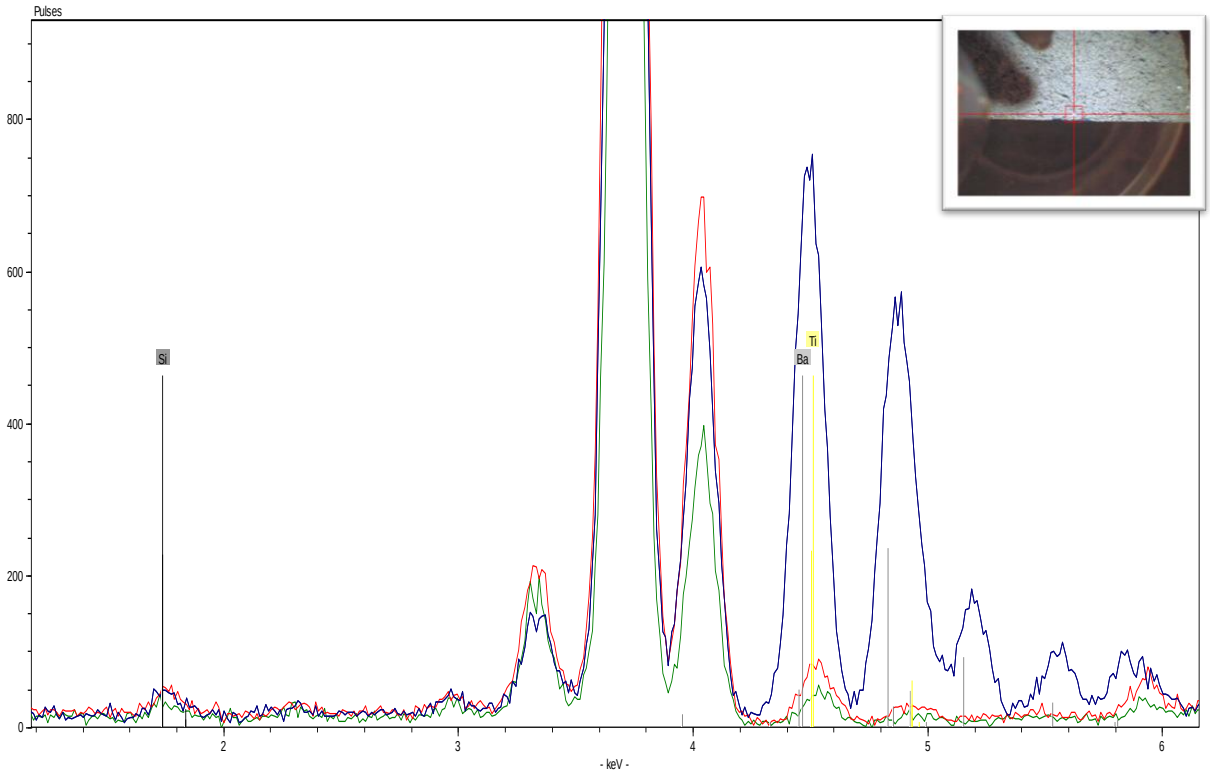

Fig.28. XRF spectra of sections of BSOH+Ba. The intensity of barium peaks decreases from the surface to the bottom.

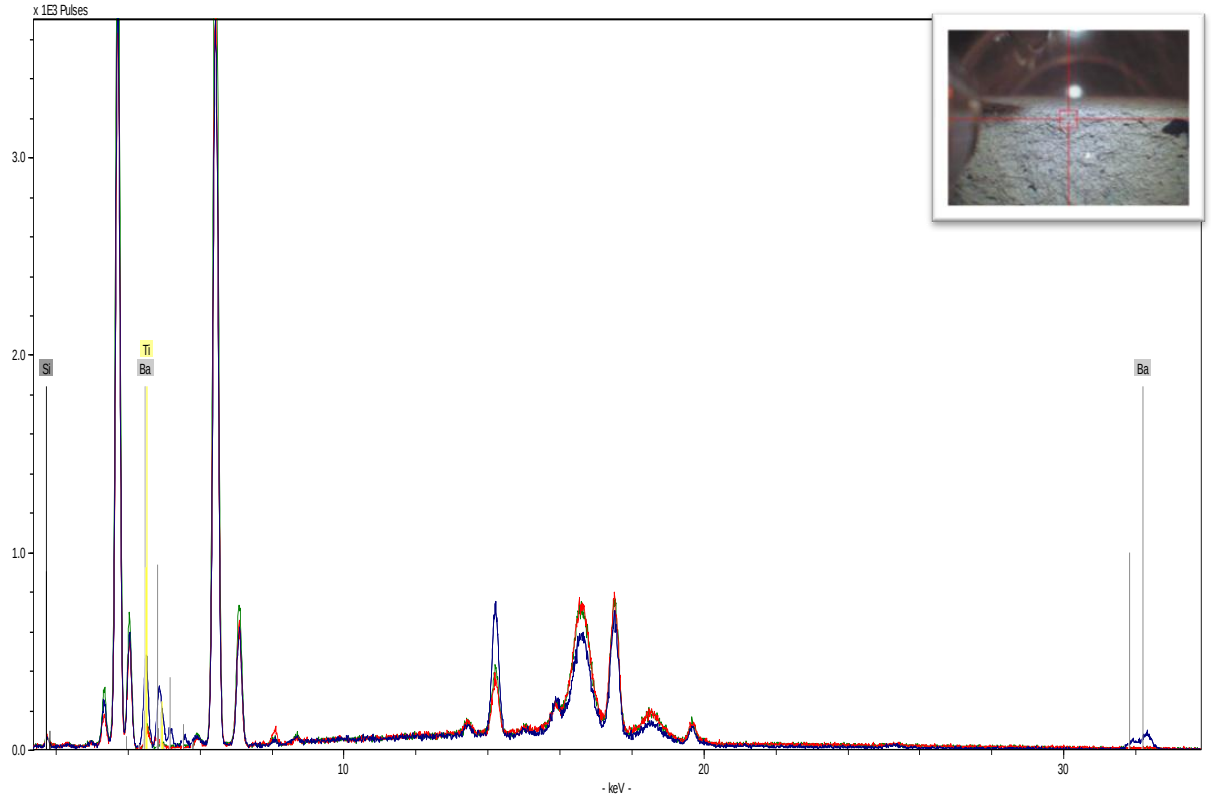

Fig.29. The three peaks of barium in XRF spectra of sections of ANTARES+Ba.

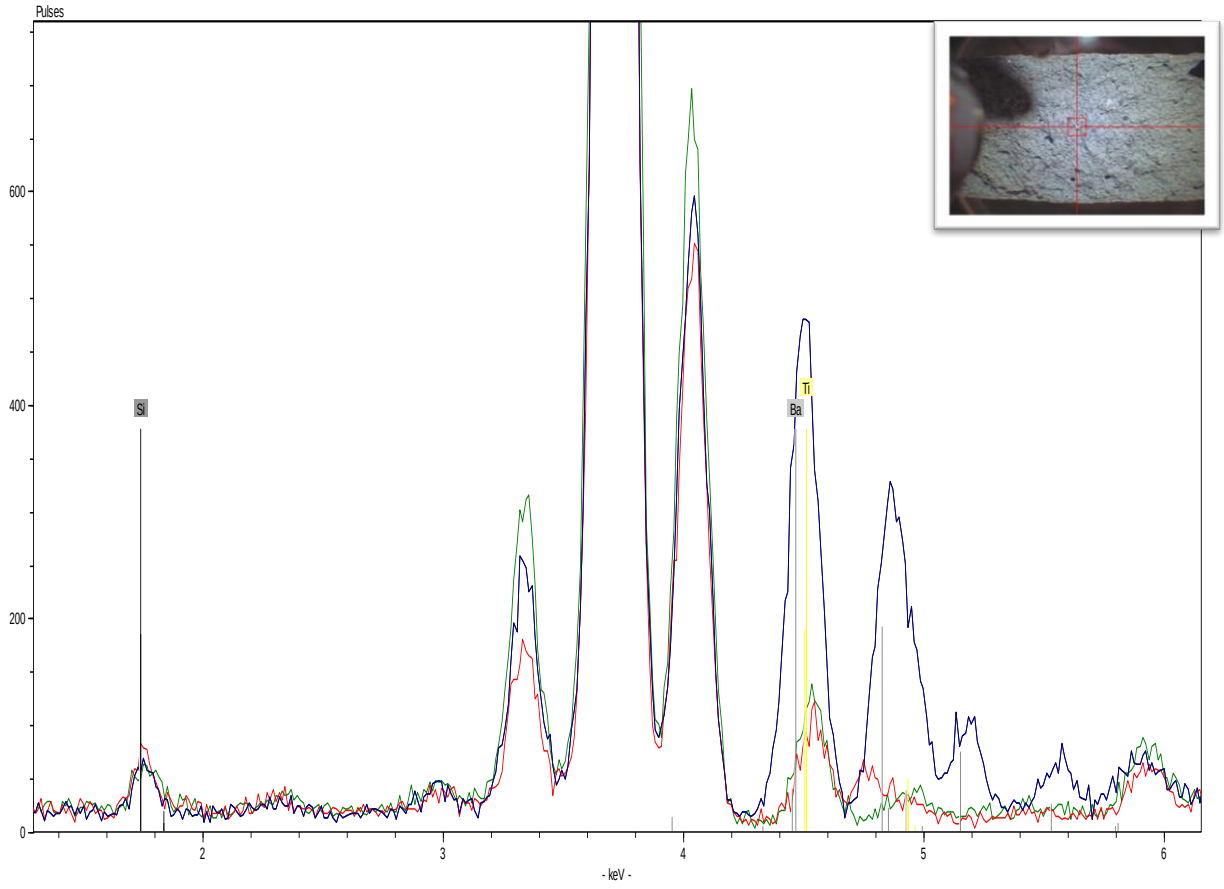

Fig.30. Particular of the comparison in the XRF spectra of sections of ANTARES+Ba.

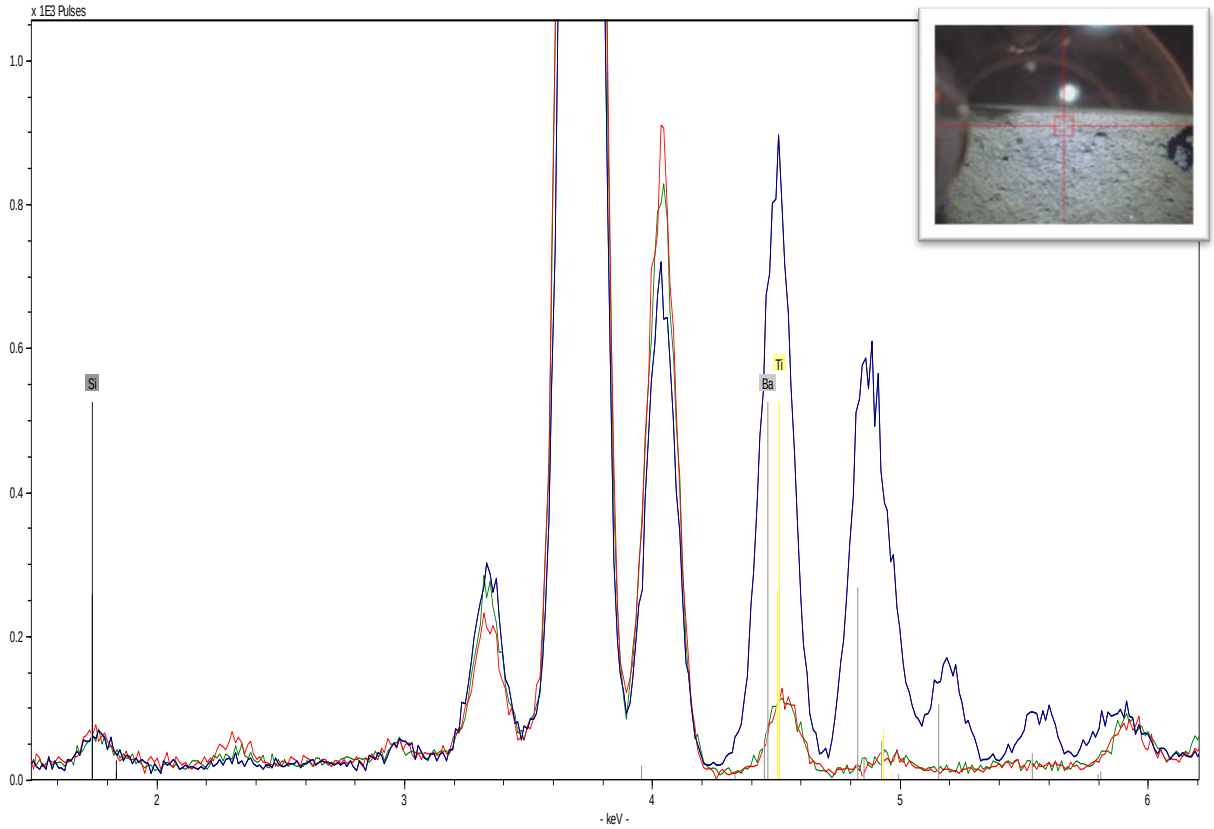

Fig.31. Comparison between XRF spectra of sections of EST+Ba. Barium peaks show the maximum intensity on the treated surface.

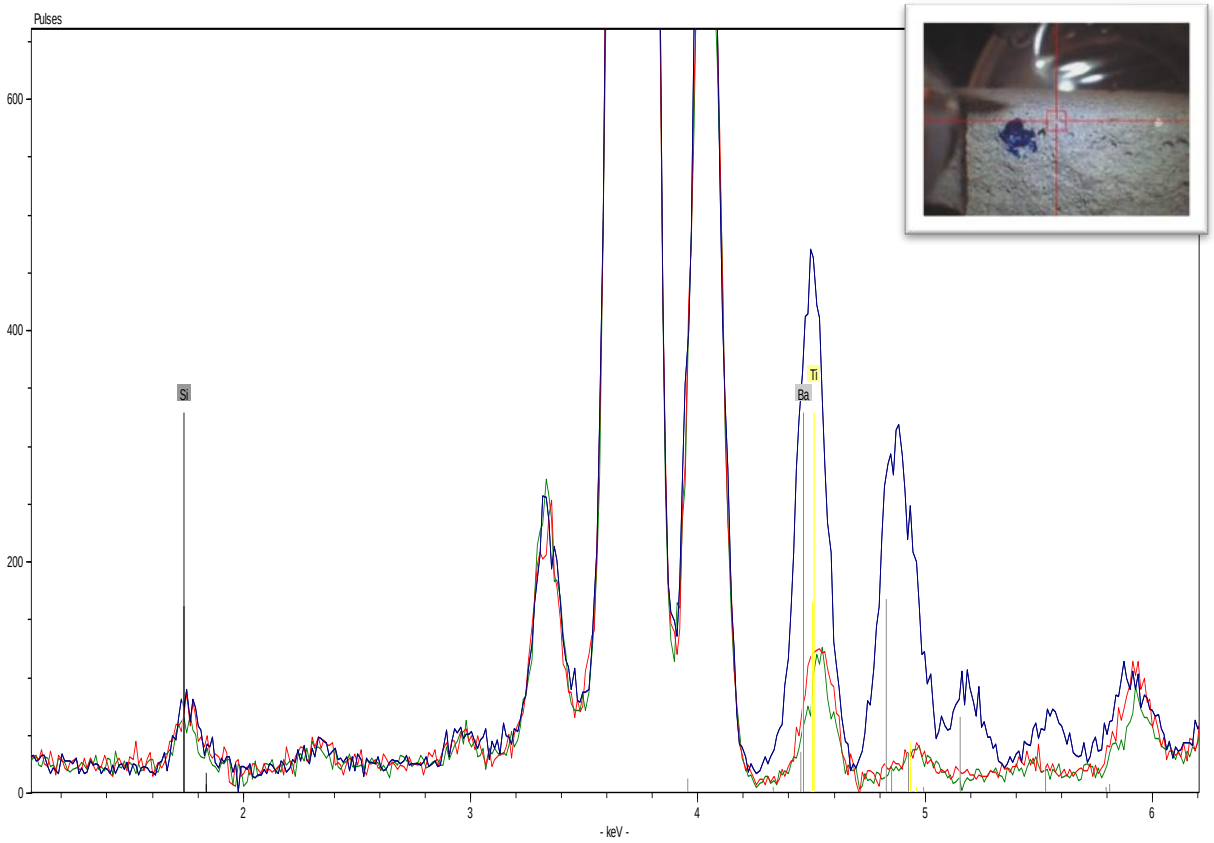

Fig.32. XRF spectra of sections of TV+Ba. Barium peaks have the maximum intensity on the sample surface.

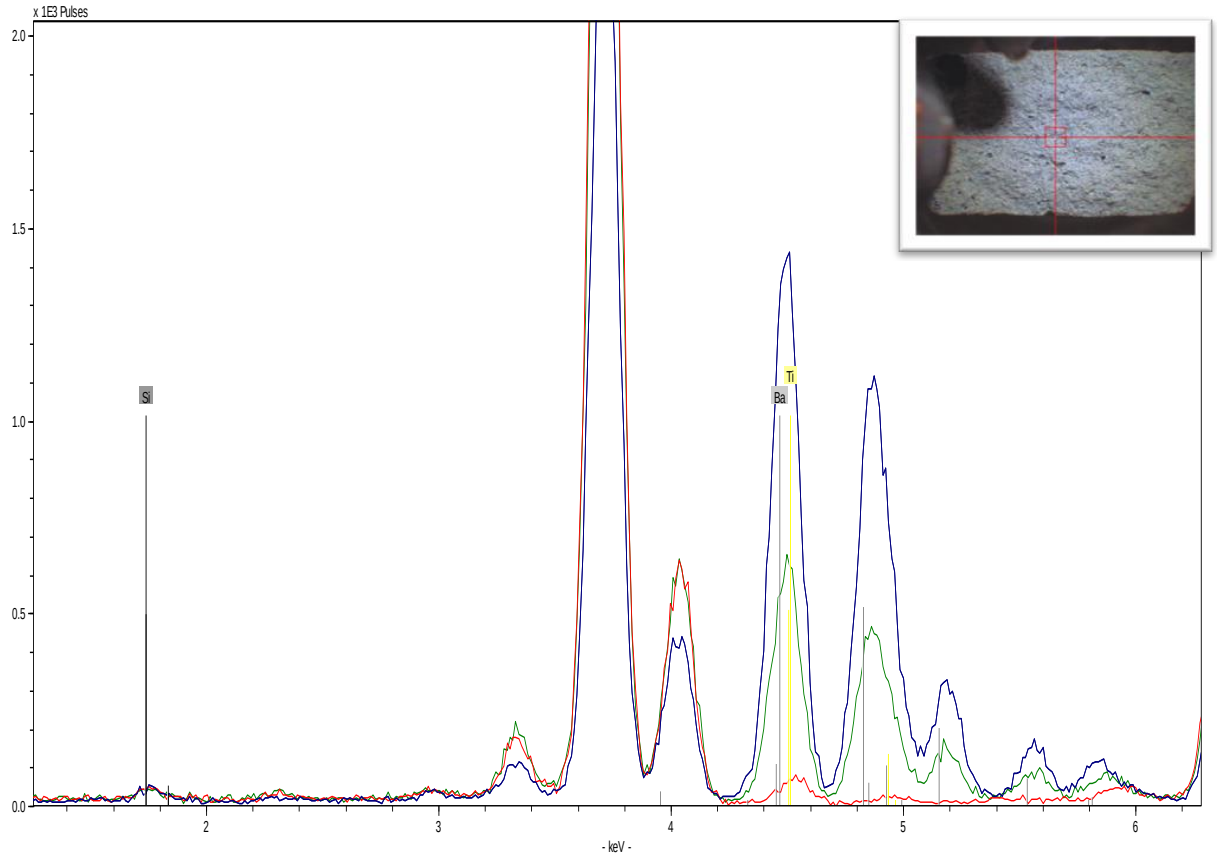

Fig.33. XRF spectra of sections of TES 40+Ba. Barium decreases from surface to the bottom of the sample.

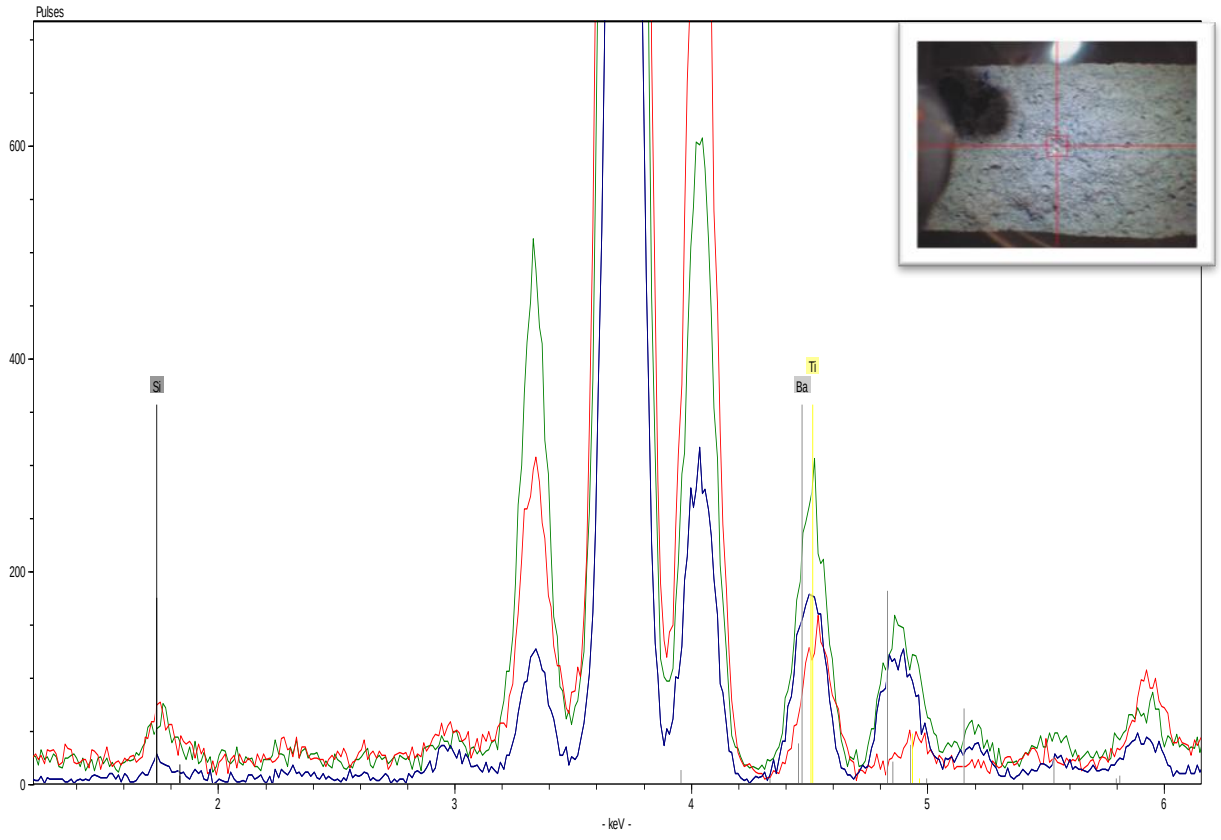

Fig.34. XRF spectra of sections of TES 28+Ba. Barium decreases from surface to the bottom of the sample.

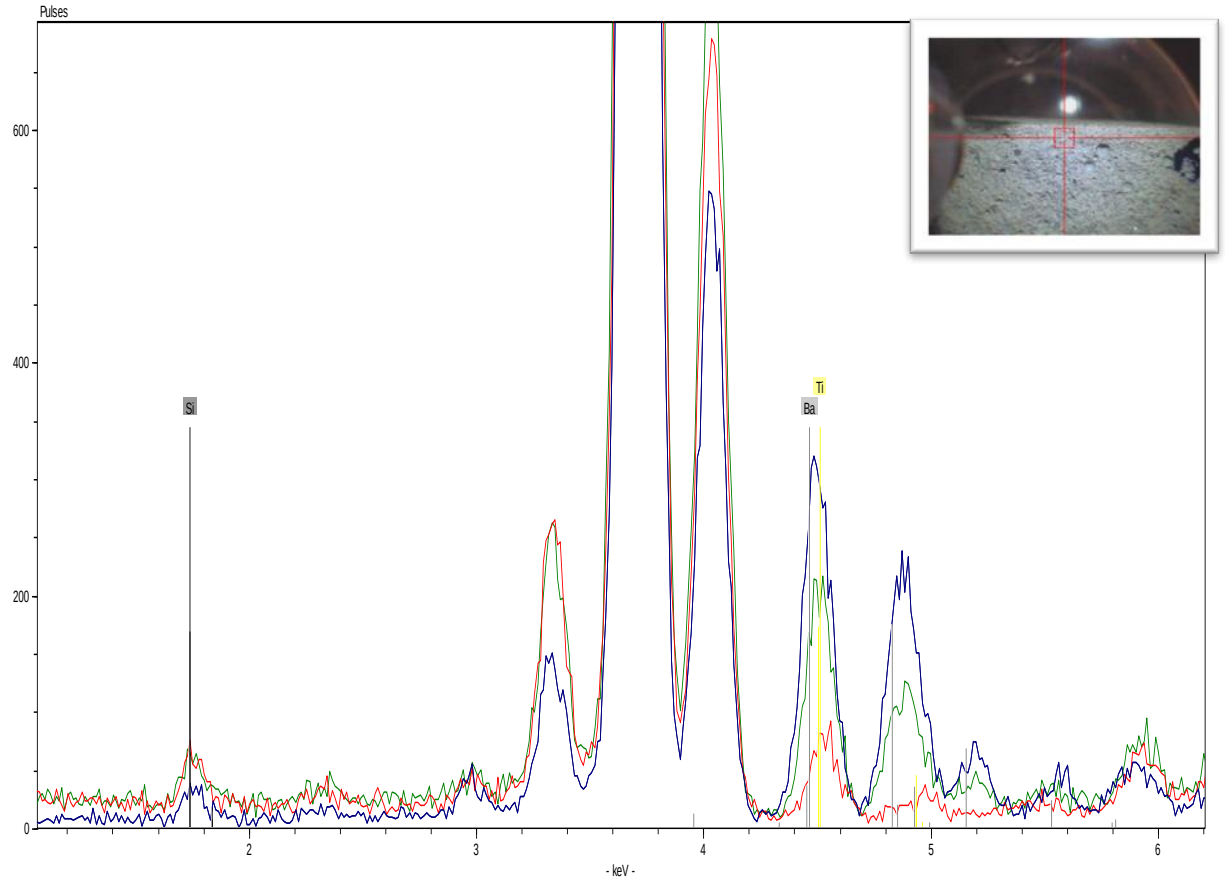

Fig.35. XRF spectra of sections of KDN+Ba. Barium decreases from surface to the bottom of the sample.

7.4. *Petrographic analysis*

Cross sections of all treated samples have been subjected to petrographic analysis in order to identify changes in the porosity of the sample matrix that might occur after the treatments, i.e. an indication of consolidation.

From the results obtained, treated samples seem to exhibit a slightly more cohesive matrix that untreated ones, and at the same time samples treated with barium seem more cohesive than the ones treated with only ethyl silicate.

Some of these observations at 2.5x in polarized light are now discussed, and examples are reported in Figs. 36-41. The pores of circular shape are due to the resin that penetrates where the sample was not consolidated, while the black areas in some samples (like BS OH 100) are due to the impregnation effect from the preparation of the cross-section, which shows a tendency to darken.

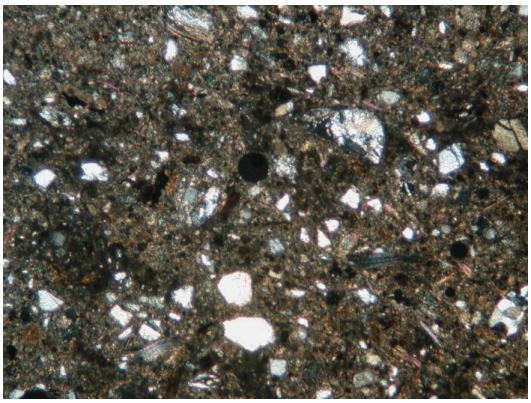

Fig.36. Petrographic section of an untreated sample.

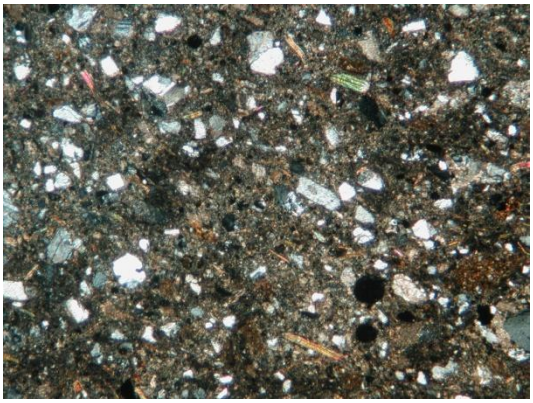

Fig.37. Petrographic image of a treated sample with barium.

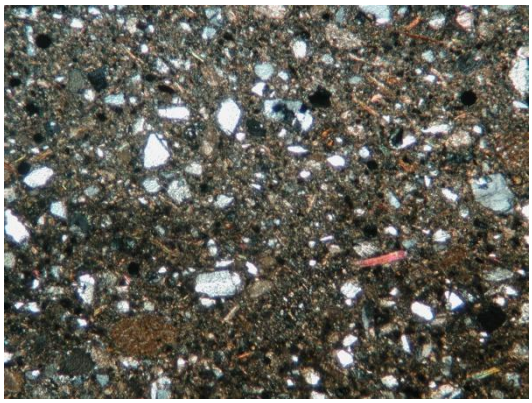

Fig.38. Petrographic image of a BSOH sample.

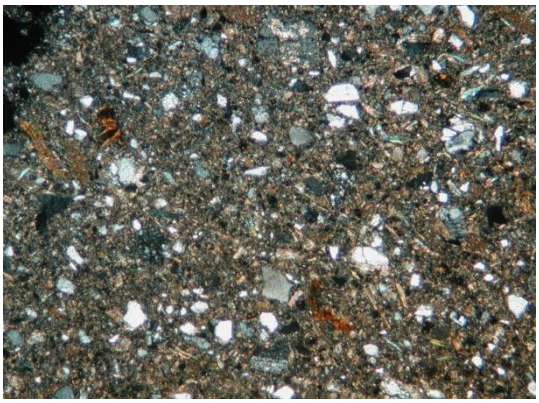

Fig.39. Petrographic section of a sample treated with BSOH+Ba.

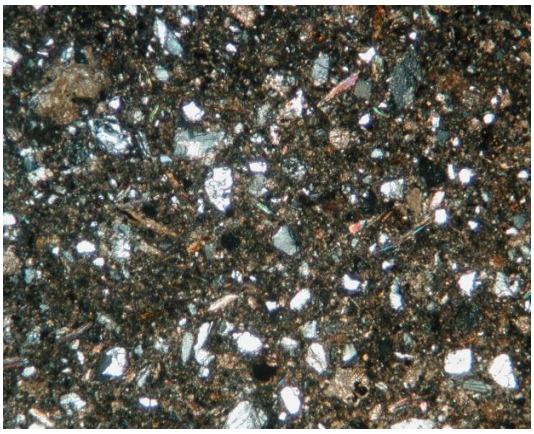

Fig.40. Petrographic section of an ANTARES sample.

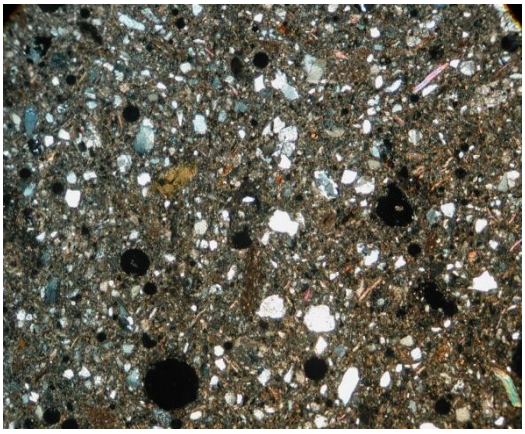

Fig.41. Petrographic section of an ANTARES+Ba sample.

7.5. *Treatement of Artificially Aged Stones*

Artificially aged stones were treated with the method of barium hydroxide added to ethyl silicate, in order to understand if some changes occur on low degraded sandstone surfaces.

The samples chosen for these tests belong to artificially-aged Colombino stone.

Due to the short artificial aging of samples treated, we tested only products that showed interesting results after the water absorption and mechanical abrasion tests on artificial samples. Therefore, we used Tetraethyl Orthosilicate (RP), Siler BS OH 100 (BSOH), Tegovakon V 100 (TV), ESTEL 1000 (EST), and ANTARES (ANT) as consolidants based on ethyl silicate. After that the poultice barium was added to these compounds.

Samples	**Untreated**	**RP+Ba**	**BSOH+Ba**	**EST+Ba**	**ANT+Ba**	**TV+Ba**
Wa (g/cm^2 min)	0.049	0.023	0.019	0.013	0.011	0.015

Tab.9. Results of water absorption test on artificially-aged Colombino samples treated with ethyl silicate and barium.

The water absorption and mechanical resistance tests made on these samples show good results for BSOH+Ba treatment [see Tab. 9-10, Fig.42]. This result confirms the observations made on the behaviour of artificial samples treated with this same product.

Surprisingly, a worsening of the properties can be observed with treatments based on Tetraethyl Orthosilicate (RP) and Tegovakon V 100 after the surface abrasion tests, which were supposed, instead, to improve their strength if compared to untreated samples.

Samples	**50 cycles Wi-Wf (g)**	**100 cycles Wi-Wf (g)**	**150 cycles Wi-Wf (g)**
Untreated	0.17	0.31	0.41
RP+Ba	0.18	0.34	0.52
BSOH+Ba	0.12	0.22	0.27
TV+Ba	0.16	0.36	0.56

Tab10. Results of TABER abrasion tests on treated Colombino samples.

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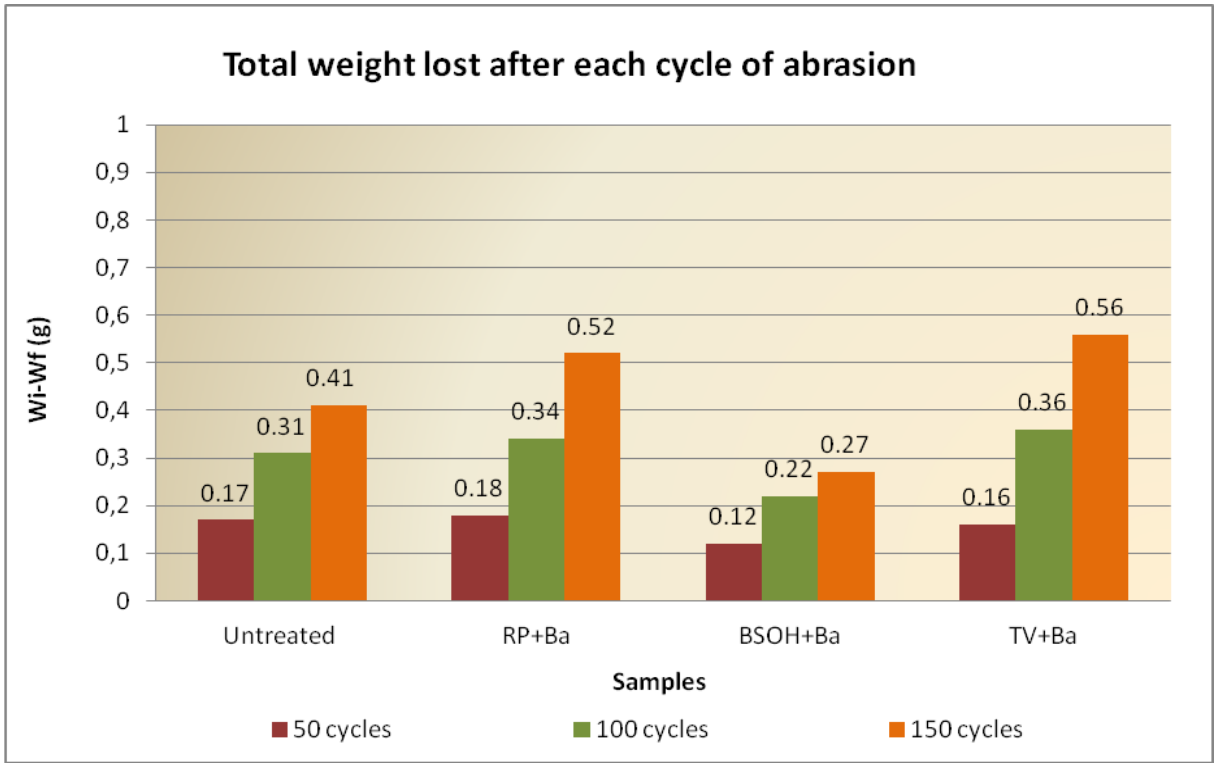


Fig.42. Total weight lost after surface abrasion test on treated Colombino samples

Chapter 8

HISTORICAL SAMPLES

The identification of a good treatment for the consolidation of the historical sandstone was the principal aim of this study.

Unfortunately, as it appears obvious, it was not easy to find proper sacrificial historical samples, so this last part of the work was based on the detailed study of a few samples, like a stair step from a Villa Medicea placed in Tuscan region and two building blocks from Montegibbio archeological site.

In this chapter we report the results of resistance to water absorption and physical-chemical and mineralogical characterizations of the degraded historical sandstone samples placed in their original context or available in the laboratory. These analyses were made to understand the level and the type of deterioration of these stones.

The samples were then treated with the methods, previously tested, that showed the best experimental results as consolidating effect towards the artificial samples (see Cap. 7), and in the last sections of this chapter we will report and discuss the results of these treatments.

8.1. *Description and characterization*

The historic sandstone samples consist of fragments of historic buildings, like part of columns (capitals, shaft, and base), and architectonical elements (such as building blocks and stair steps) from Toscana and Emilia Romagna regions in Italy.

These elements belong to different ages from II century B.C. to XVI century A.C.

The oldest samples are the two building blocks from archaeological site of Montegibbio (MO) probably belonging to a religious sanctuary dedicated to the goddess Minerva [on archaeological studies: Guandalini 2010] and entirely built by sandstone blocks.

These blocks were studied and treated in situ with the authorization of the director of Soprintendenza per i Beni Archeologici dell'Emilia-Romagna and the Director of the excavation, Dr. Francesca Guandalini.

Other degraded samples belong to monuments and buildings with civil and religious aims from different ages (some were made in XVI century A.C., while, for many others the age is unknown) and different places of Toscana region, belonging from restoration works of public

buildings and Villas, and consisting in the replacement with new elements. These deteriorated architectonical elements were originally made with sandstones from Toscana quarries, and were stored in depots of some sandstone suppliers of Firenzuola, which let us use these samples for our treatment.

All historical samples show different degradation elements like cracks, fissures, and loss of material made by action of weathering, animals organism, mosses, and lichens, Figs. 1-8 [Martuscelli 2007].

Fig 1. Capital_M and Base_M

Fig.2. Image of the back of Borghesiana 6.

Fig.3. Image of one side of Borghesiana 6.

Fig.4. Image of Borghesiana 5 sample.

Fig.5. Image of Borghesiana 7.

Fig.6. Stair step from Villa Medicea.

Fig.7. Architectonical element called C_M sample.

Fig.8. One of the two sandstone building blocks from Montegibbio site.

8.1.1. *XRD analysis*

All historic samples were studied through XRD analysis, showing a matrix based on Quartz, Feldspars (mainly Na-feldspars like Albite, and K-feldspars such as Microcline), Micas with Muscovite predominant on Biotite, and fragments from magmatic and metamorphic rocks (like Olivine in C_M sample, and minerals of Chlorite group in all samples). In all stones, the binder of the matrix was formed by calcite and dolomite [Figs. 9-10].

Moreover, XRD technique was used to identify the soluble salts extracted from these samples. Only the sample Borghesiana_5 shows the presence of this decay elements, mainly calcium sulfate ($CaSO_4$ found as Bassanite) [Fig.11].

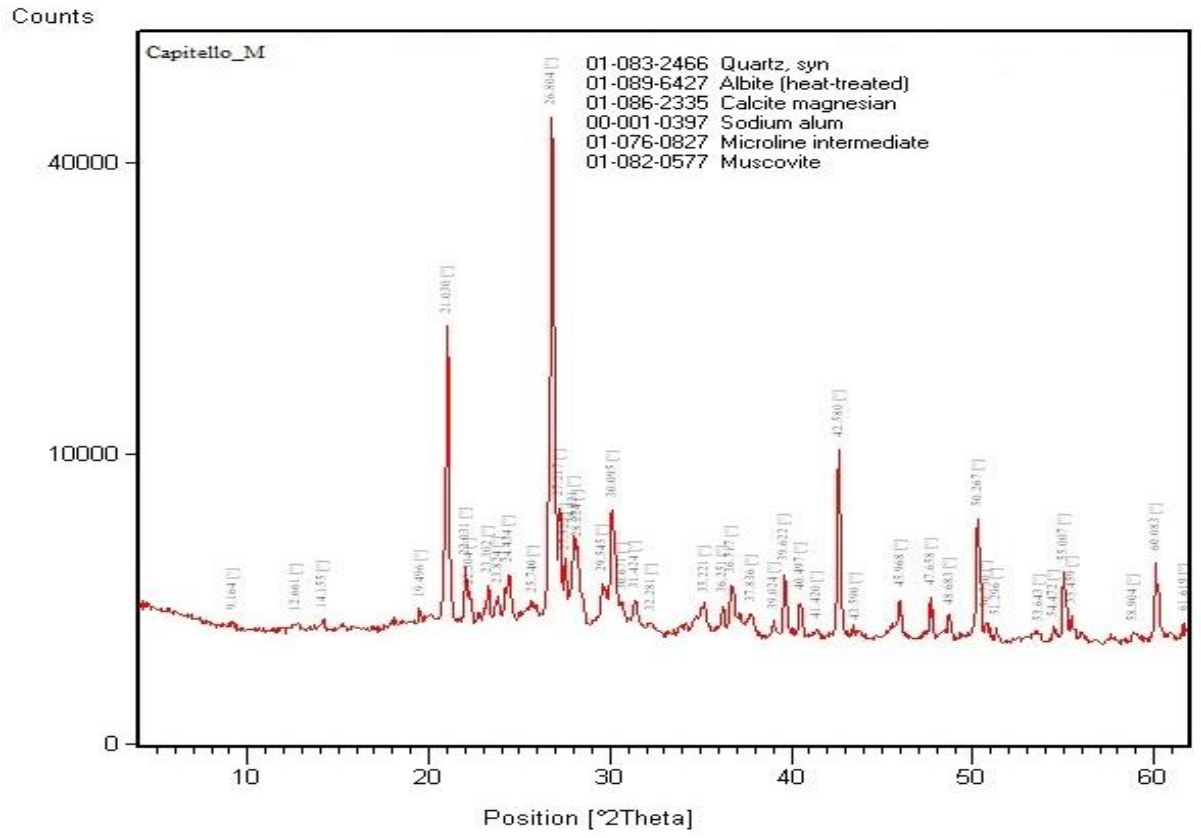


Fig.9. Mineralogical composition of Capital_M sample, after XRD analysis.

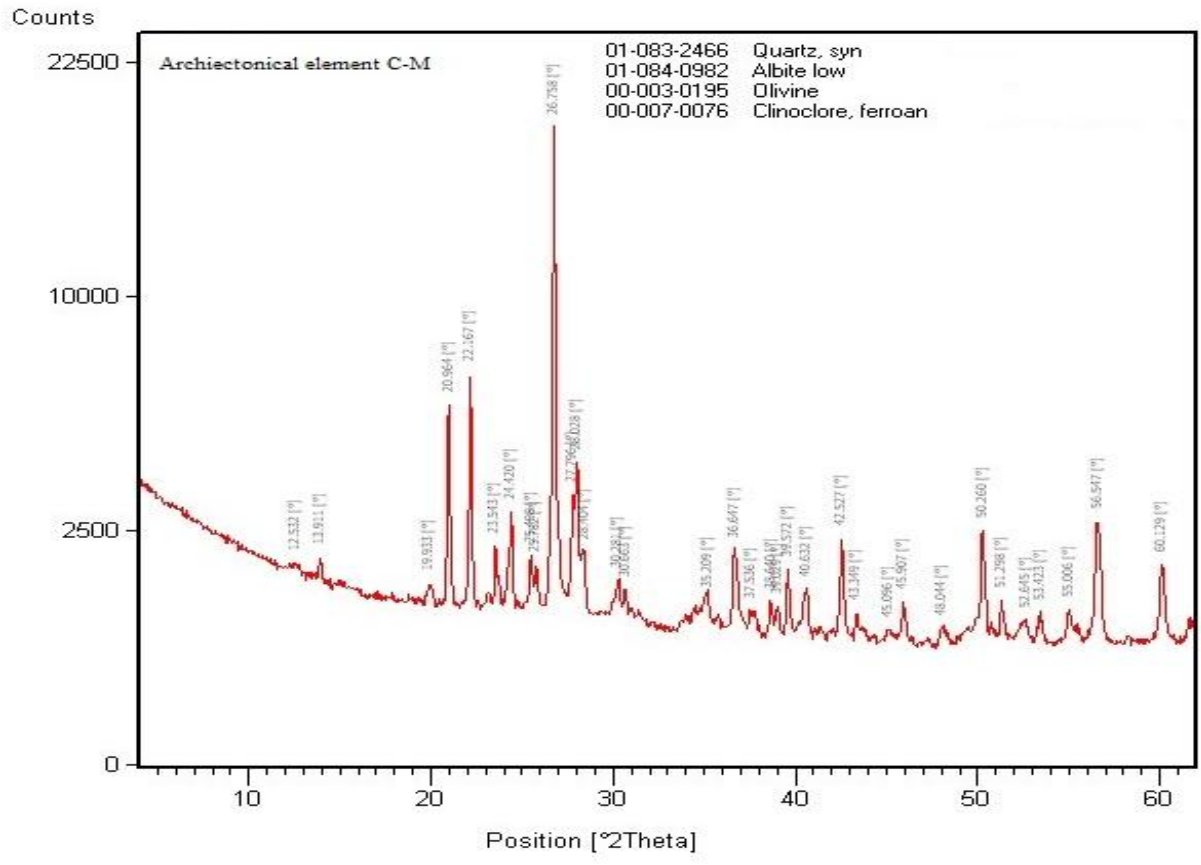


Fig.10. Mineralogical composition of architectonical element C_M, after XRD analysis.

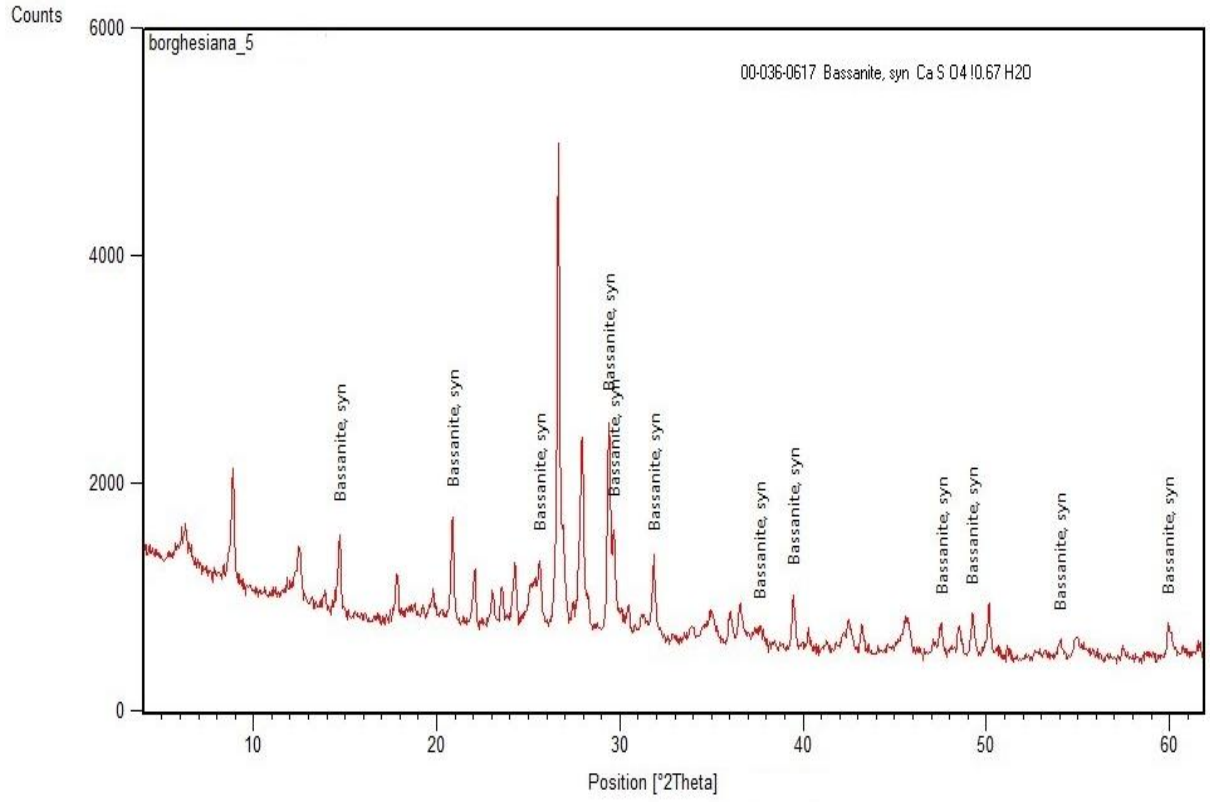


Fig.11. XRD spectrum of C_M architectonical element shows calcium sulfate (i.e. Bassanite).

8.1.2. *XRF analysis*

The results of XRDP analyses on historic samples are confirmed by XRF studies, which show an elemental composition based on Fe, Ca, and Si as main elements, followed by K, Na, Al, Mn, Mg, Ti, Sr, Cl, S, Ni, Rb, and Zn. We have already found this composition in all natural and natural aged stones, attributing these elements to the phases that form sandstone (see par. 6.2.3). Some examples are reported in Figs.12-13.

Historical samples, like natural aged stones, show also traces of P that can be due to exposition on environmental agents like residues of biological activity or animal excrements.

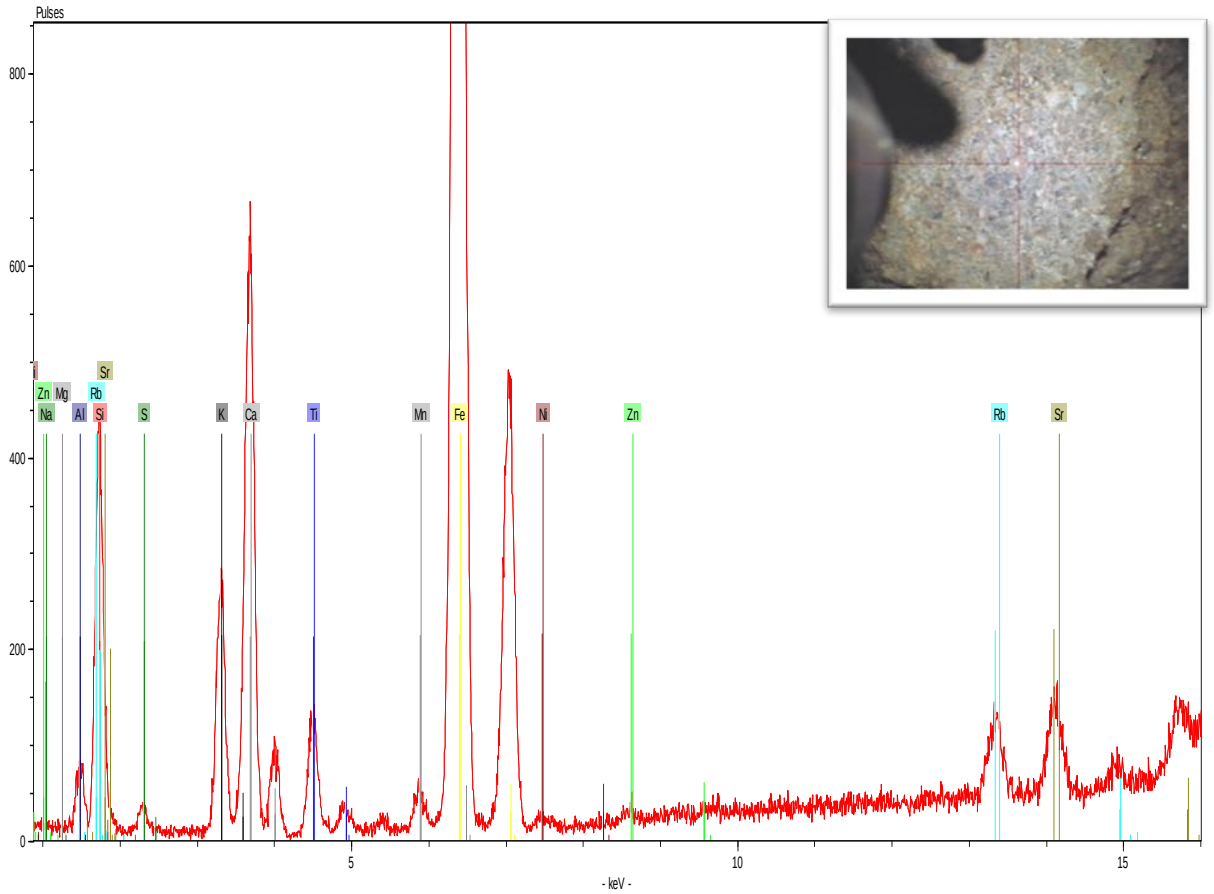


Fig.12. XRF spectrum of Capital_M showing a composition based mainly on Ca, Fe, Si, K, Sr , Rb, Ti (and minor Na, Mg, Al, S, Mn, Ni, Zn).

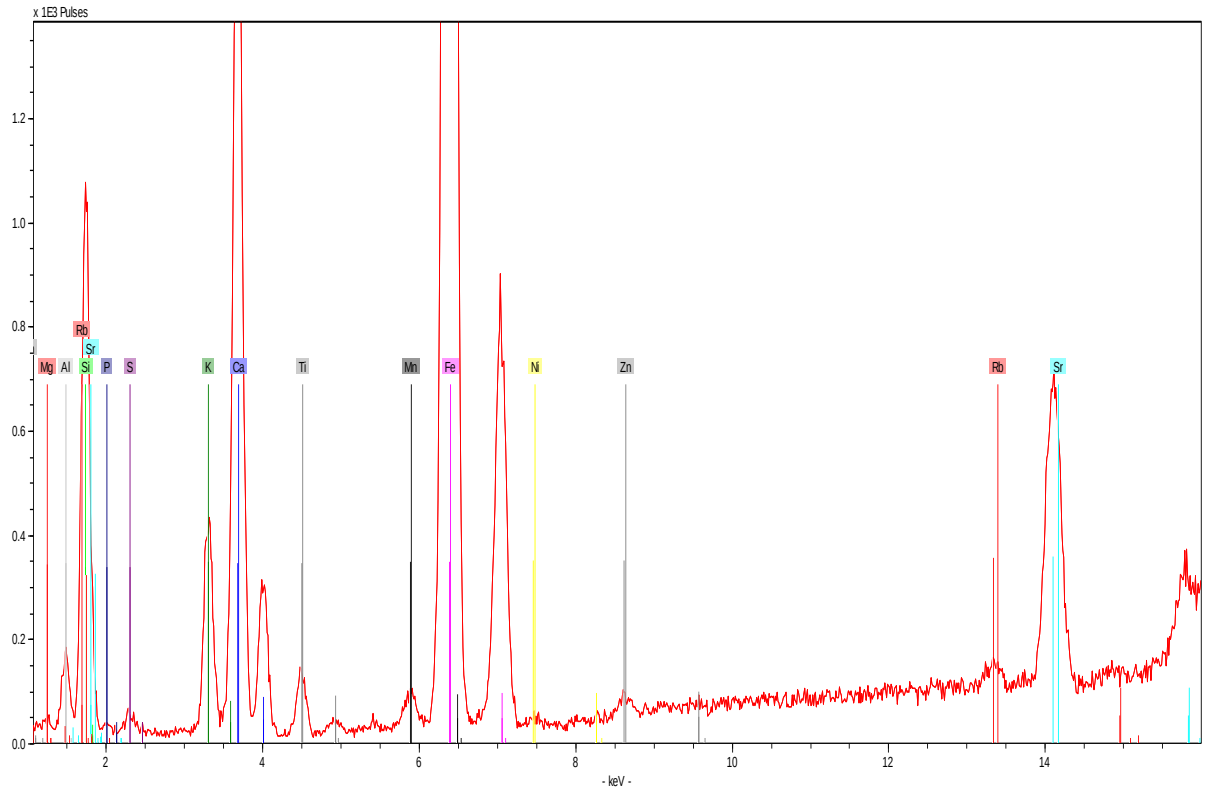


Fig.13. XRF composition of sandstone block from Montegibbio site [Fe, Ca, Si (P, K, Mg, Mn, Ti, Sr, Al, S, Ni , Zn, Rb)].

8.1.3. *Petrographic analysis*

Petrographic observations on historical stones are made at 2.5x and 6.3x in polarized light, and some examples are reported in Figs. 14-17.

These sandstones show the same mineralogical composition of Firenzuola sand, and in some cases fragments of other minerals are present, for example: flint, feldspars altered to clay, granitic rocks from the Alps, biotite altered to chlorite, garnet, carbonates, erosive materials from the Alps, and sulphates. Matrix shows low degree of cement obtained by carbonates.

In most cases, the texture of the historic samples consists of silico-clastic material with very large grains that are bigger than the grains found in artificial samples. Conversely, Capital_M shows a texture with silicoclastic material with smaller grains than the other historic samples, and very low cement. For this reason, this sample shows little cohesive strength and tends to easily loose material, showing a high level of degradation.

The sample called Base_M shows a typical distribution of crystals with different sizes, in which very large grains coexist with very small ones. Moreover, the Borghesiana_6 shows low porosity than artificial samples. The results of petrographic analyses are available in Table 1.

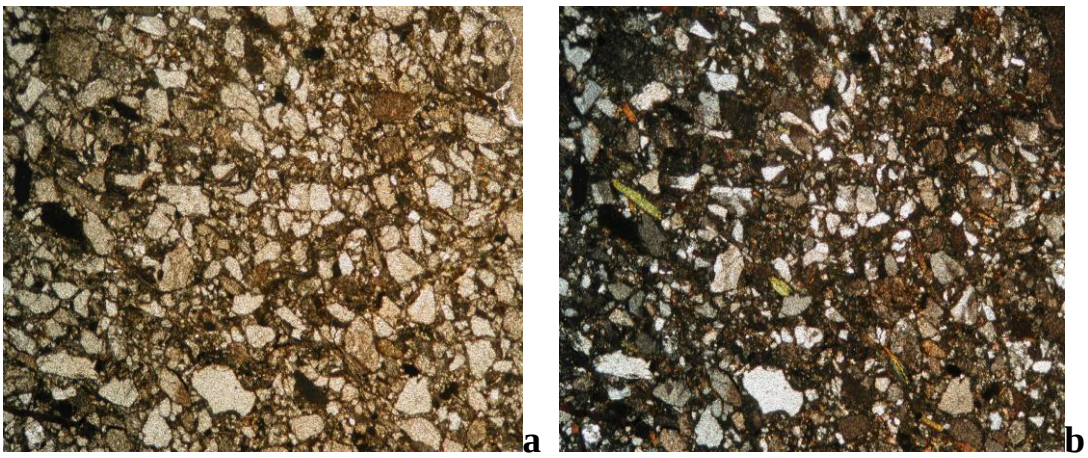


Fig.14a-b. Petrographic images at 2.5x of the texture of Borghesiana_5 sample.

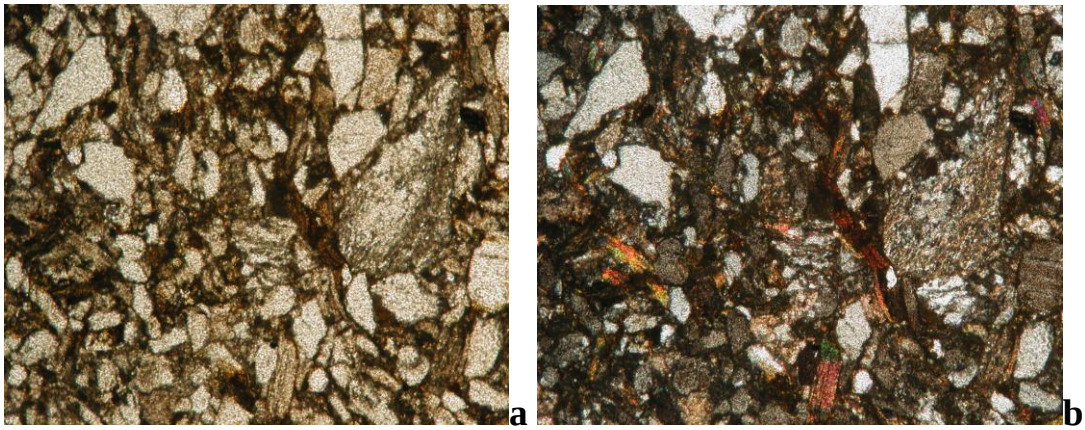


Fig.15a-b. Petrographic images at 2.5x of the texture of Capital_M.

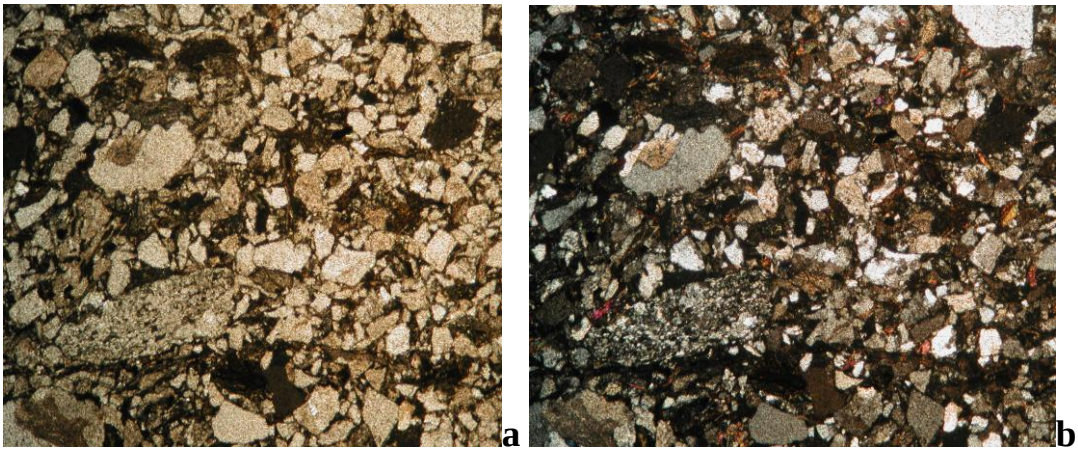


Fig.16a-b. Petrographic images at 2.5x of the texture of stair step.

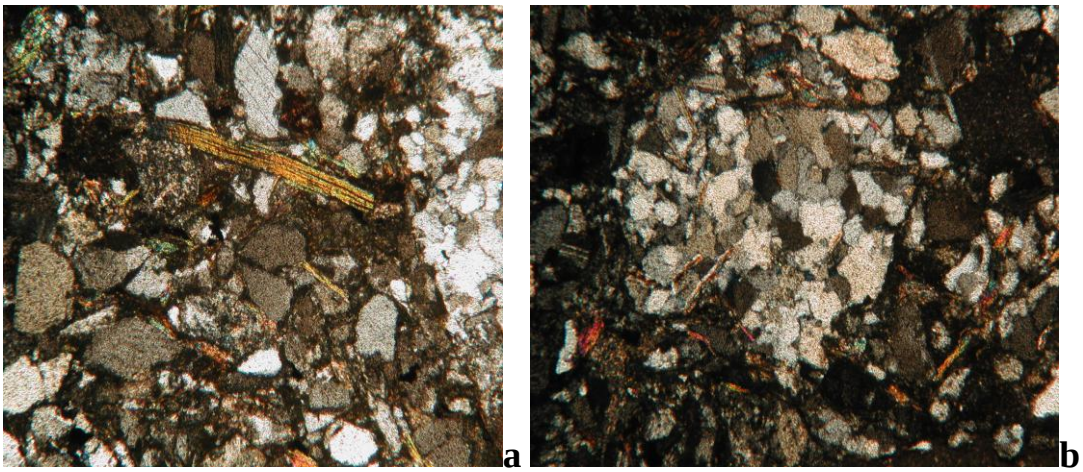


Fig.17a-b. Petrographic images at 6.3x of the texture of stair step sample.

Samples	Description	Sandstone texture	Mineral composition	Matrix
Borghesiana_5	Shaft of column	Silico-clastic material with very large grains. They are bigger than grains in artificial samples	The same of Firenzuola sand	Low degree of cement.
Borghesiana_6	Base of column	Dense accumulation of silico-clastic material, very large grains. Lower porosity than artificial samples	The same of Firenzuola sand	Very low degree of cement.
Borghesiana_7	Base of column	Silico-clastic material with very large grains with respect to Borghesiana_5	The same of Firenzuola sand, with fragments of flint	Low degree of cement.
Capital_M	Capital of column (XVI century A.D.)	Silico-clastic material with smaller grains than other historical samples	The same of Firenzuola sand with fragments of feldspars altered to clay, and granitic rocks from the Alps	Low degree of cement.
C_M	Architectonic element (XVI century A.D.)	Silico-clastic material with large grains	The same of Firenzuola sand	Low degree of cement.
Base_M	Base of column (XVI century A.D.)	Silico-clastic material, with very large and very small grains	The same of Firenzuola sand	Low degree of cement.
Stair Step	Stair step from Villa Medicea (XVI century A.D.)	Silico-clastic material with grains very large	The same of Firenzuola sand with fragments of biotite altered to chlorite, garnet, carbonates, erosive materials from the Alps, and sulphtes.	Low degree of cement.

Tab.1. Results of petrographic analyses on historical samples.

8.1.4. *pHmetry and Conductimetry tests*

These analyses were made to determine the presence of soluble salts into the historic samples.
Conductibility values of historic sandstones are lower than modern and natural aged stones. They exhibit values between 164.95 µS/cm (Borghesiana_6) and 55.8 µS/cm (Capital_M), meaning that the ions due to soluble salts found in water solution are very low.
In the case of pH analysis, the same behavior on both modern and aged stones was observed. Indeed, the pH values of historic samples are between 8.04 (Capital_M) and 7.52 (Borghesiana_7), close to neutrality. These values are similar to natural aged stones.
The results of pHmetry and conductimetry tests on historical samples are reported in Table 2.

Sample	Conductimetry (µS/cm 25 °C)	pHmetry
Borghesiana_5	164.9	7.56
Borghesiana_6	61.8	7.67
Borghesiana_7	71.8	7.52
Capitello_M	55.8	8.04
Base_M	79.3	7.92
Stair Step	66.7	7.57
Montegibbio	113.2	7.96

Tab.2. Results of conductimetry and pHmetry tests on historical sandstones.

8.1.5. *Water absorption tests*

The water absorption analyses were made on historical sandstones using the contact sponge method test (UNI 11432:2011), but in some cases, due to rough surfaces of the architectonical samples, this method could not be applied or, if applied, gave unreliable values, as the sponge did not adhere well to the stone surface and consequently, the water absorption was limited. This occurs in many samples like Borghesiana_5 and Borghesiana_7, Base_M, Capital_M, C_M, and Montegibbio.
In some historic samples, these tests were made in two different points of the surface and the values were compared.
The values of historic samples where the sponge adhered well are between 0.24 (Borghesiana_5) and 0.06 g/cm^{2}·min (Borghesiana_6 and stair step), similar to natural aged samples. The results of water absorption tests were reported in Table 3.

sample	Description	Wa ($g/cm^2 \cdot min$)
Borghesiana_5	external surface	**0.11***
	internal surface	**0.24**
Borghesiana_6	internal surface	**0.06**
	external surface	**0.12**
Borghesiana_7	external surface	**0.08***
Capital_M		**0.17***
Base_M		**0.02***
C_M	external surface	**0.11**
Stair step	internal surface	**0.09**
Stair step	external surface	**0.06**
Montegibbio	external surface	**0.05***

Tab.3. Water absorption tests on natural and historical sandstone samples.
* = sample with incomplete adherence of the sponge to the surface.

8.2. *Consolidation Treatments*

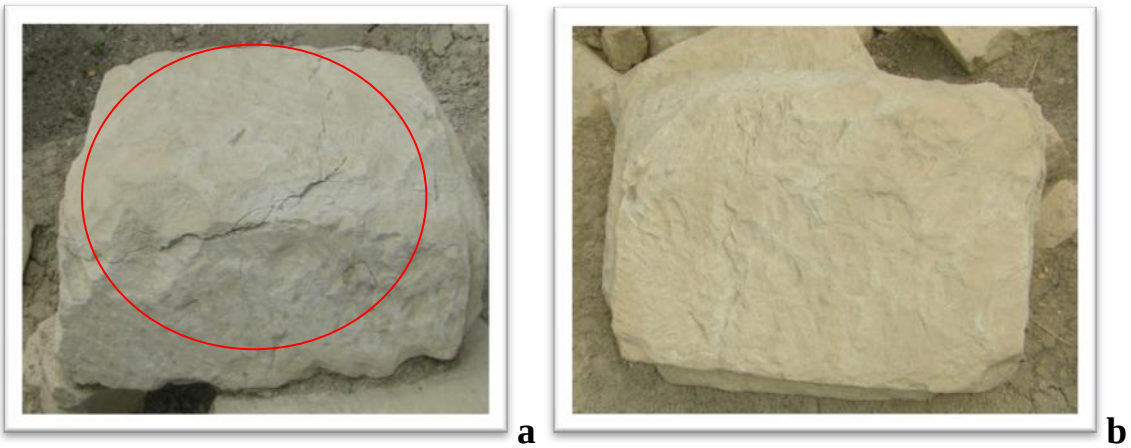
The greatest problem of degraded historical samples available in laboratory was their irregular and limited surface that do not allow to obtain homogeneous data about their phisycal-chemical and mechanical properties on different point of the sample, together with their limited number that do not permit a statistical analysis of samples. The most interesting results were obtained by an historical stair step from a private home placed in Toscana region and belonging to XVI Century A.D. In this case, due to the irregular surface, the stair step was cut into six slabs of about 9.0 × 9.0 cm, which were used for the analyses in laboratory condition.

At the same time, the consolidation methods were applied on two sandstones building blocks placed in archeological site of Montegibbio (near Modena), on the hills of Emilia Apennine. These pieces are large blocks that show irregular surface areas of 2924 (block n.1, Fig.18) and 2655 cm^2 (block n.2, Fig.19) with scaling, flaking, exfoliation, granular disaggregation, and

cracks due to exposition to the environmental conditions (like weathering and rising damp from the ground, close to a water source).

On the historical sandstones, some of the methods of treatment that gave good results on artificial test samples and artificially aged samples were applied and evaluated. So, the application of ethyl silicate by brushing the stone surface (Tetraethyl Orthosilicate of Sigma-Aldrich and Siler BS OH 100 of Wacker-Chemie), were followed by the application of a poultice of saturated solution of barium hydroxide. The results of these trials are available in the next paragraphs.

Fig.18. Block n.1 from Montegibbio site.



a **b**

Fig.19a-b. Block n.2 from Montegibbio site, with in evidence the cracks on the surface.

8.3. *Laboratory and field application*

The stair step samples were treated in laboratory condition (i.e. 20 - 25 °C), with RP+Ba and BSOH+Ba methods [Fig.20], with the same procedures used for the treatment of artificial test pieces.

The contact sponge methods show that the treatment with BSOH 100 and barium hydroxide greatly reduces the water absorption (0.006 g/cm^2 min) than samples treated with neat TEOS and barium hydroxide (RP+Ba method, 0.01 g/cm^2 min) and untreated ones (0.09 g/cm^2 min) [Tab.4]. Therefore BSOH+Ba shows a reduction of the porosity of the surfaces because of the closure of the pores, nevertheless the system may remain hydrophilic and the water might be absorbed slowly over time (see par. 7.2.1.).

Fig.20. Stair step samples treated with the two different ethyl silicates.

Resistance abrasion tests were made on treated stair step samples in order to verify the strengthening power of the treatment.

The results of Taber test show low values of weight loss after each cycle of abrasion for the treated samples. Moreover these values appear similar for both treatments. Unfortunately, the comparison between the results of treated and untreated samples was not possible, due to the rupture of untreated samples during the execution of the central hole for the accommodation of the specimen on the instrument.

The behavior of the treated samples was evaluated at 50, 100 and 150 abrasion cycles, and their results are reported in Table 4.

	TABER			Contact Sponge Methods
Samples	**50 cycles Wi-Wf (g)**	**100 cycles Wi-Wf (g)**	**150cycles Wi-Wf (g)**	**Wa (g/cm^2 min)**
Untreated	----	----	-----	**0.09**
RP+Ba	0.40	0.65	0.87	**0.01**
BSOH+Ba	0.47	0.76	0.97	**0.006**

Tab.4. Results of RA tests with Taber method

The results of deep abrasion test (CAP) show no strengthening effects at 5, 10, and 20 cycles of abrasion, while resistance effects appear at 30, 40, 50 cycles for both the treatment methods [Tab.5]. This appears as very strange, and it is probably due to a sure unhomogeneity of the samples.

In the previous chapter, we already mentioned that there were doubts on the reliability of the deep abrasion tests used for the evaluation of strengthening effects after the treatments.

	CAP (mm^3)					
Samples	**5 cycles (10g)**	**10 cycles (20g)**	**20 cycles (40g)**	**30 cycles (60g)**	**40 cycles (80g)**	**50 cycles (100g)**
Untreated	**44**	**65**	**123**	**227**	**288**	**330**
RP+Ba	131	89	---	109	227	262
BSOH+Ba	57	77	227	147	205	262

Tab5. Comparison between deep abrasion tests of RP+BA, BSOH+BA, and untreated samples with CAP method.

Physical and chemical analyses were made on treated and untreated samples of the stair step.

XRDP analyses show the formation of Barium Carbonate (i.e. Witherite) in all treated samples, and Barium Silicate in the samples treated with RP silicate [Figs.21-22].

XRF analyses were employed to mapping the penetration of barium inside a longitudinal section of the treated samples.

As already reported in the previous chapter, this was obtained evaluating the first peak of barium at 4.45 and 4.83 keV (L-alfa1 and L-beta1). The analyses showed low penetration of barium inside all samples because this peak was not fully focused in the spectra.

In Figures 23-25 the comparison of XRF spectra of sections of samples treated with different methods is reported, with in blue the spectrum of treated surface, in green the spectrum of the central section, and in red the spectrum of the bottom layer. Moreover, in each spectrum the peaks of silicon, barium, and titanium were put in evidence: the latest is also interfering to a clear attribution on Ba.

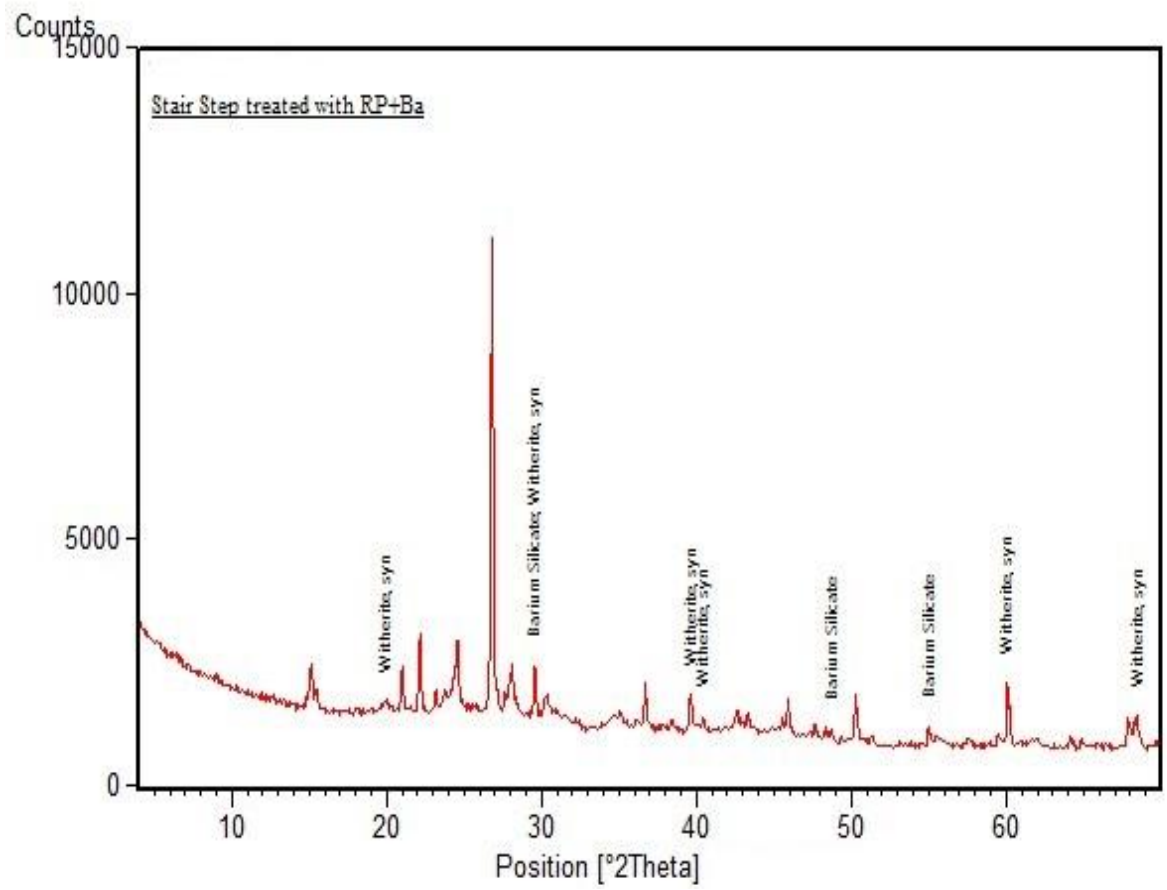


Fig.21. XRD spectrum of sample treated with RP+Ba showing peaks of Barium Silicate and Barium Carbonate.

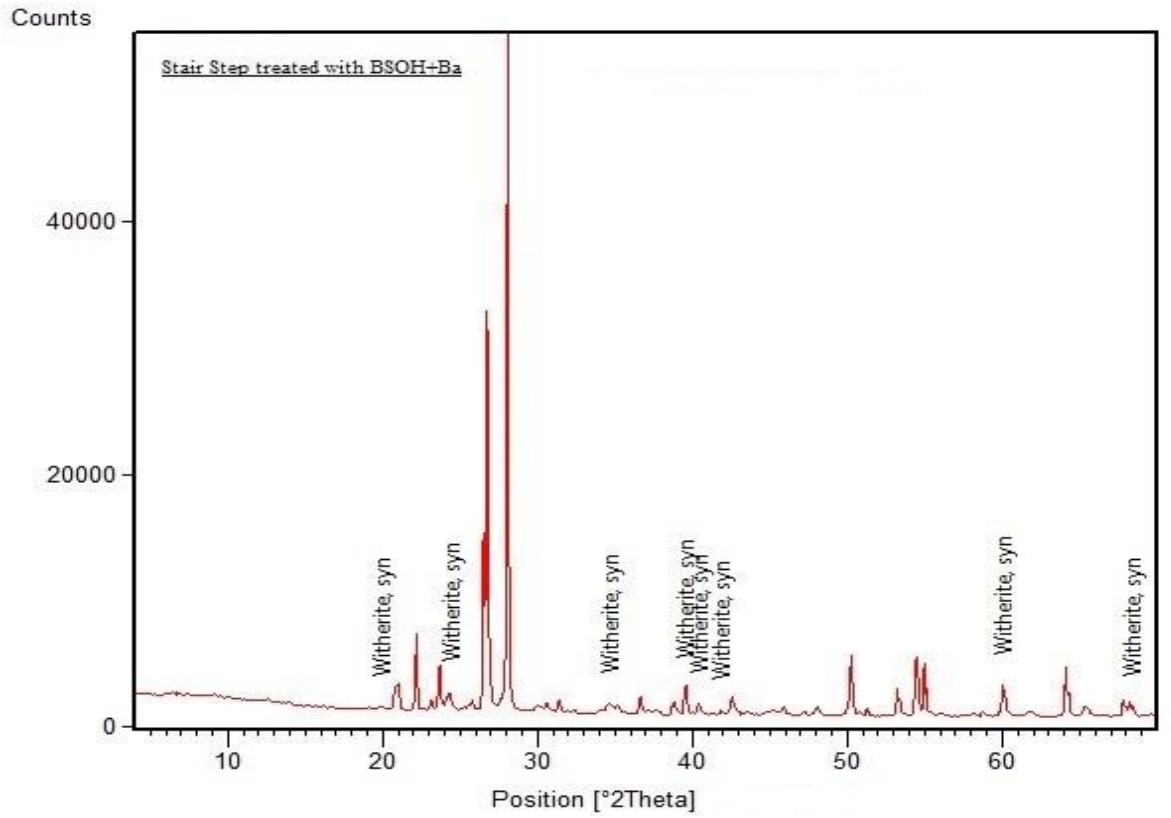


Fig.22. XRD spectrum of sample treated with BSOH+Ba showing peaks of Barium Carbonate.

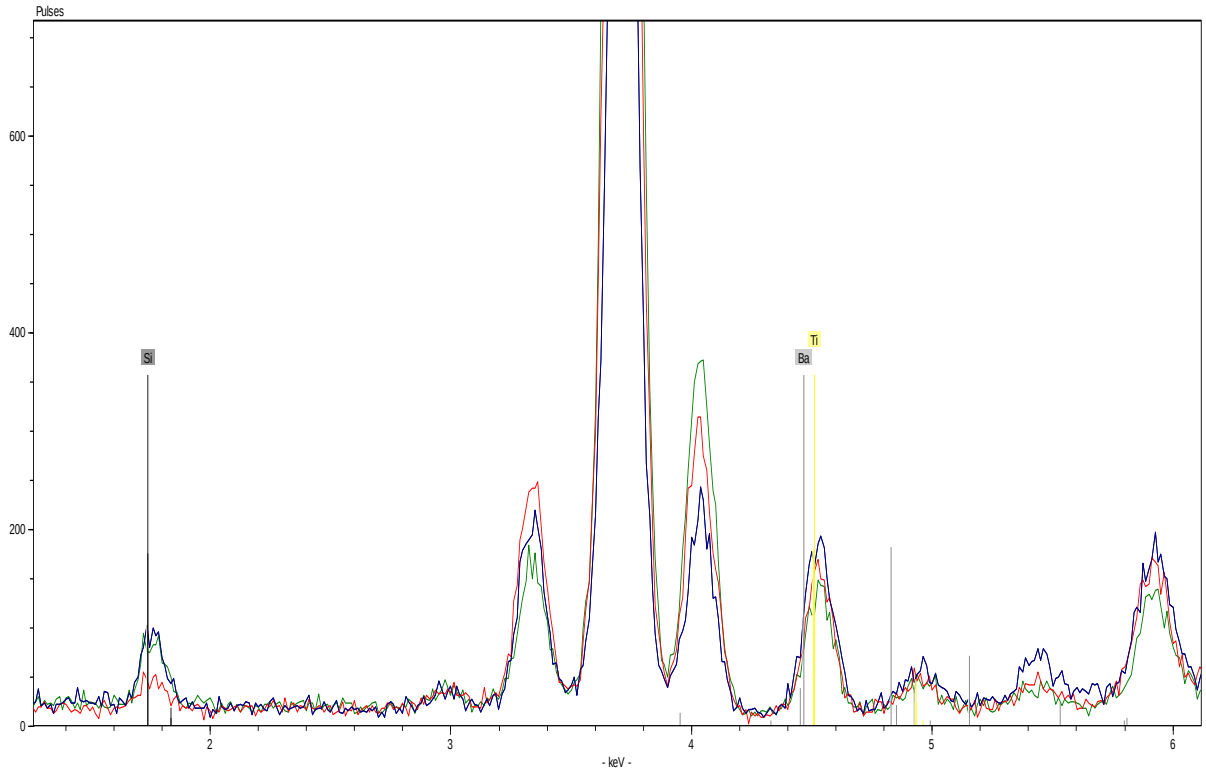


Fig.23. Comparison between XRF spectra of sections of an untreated sample.

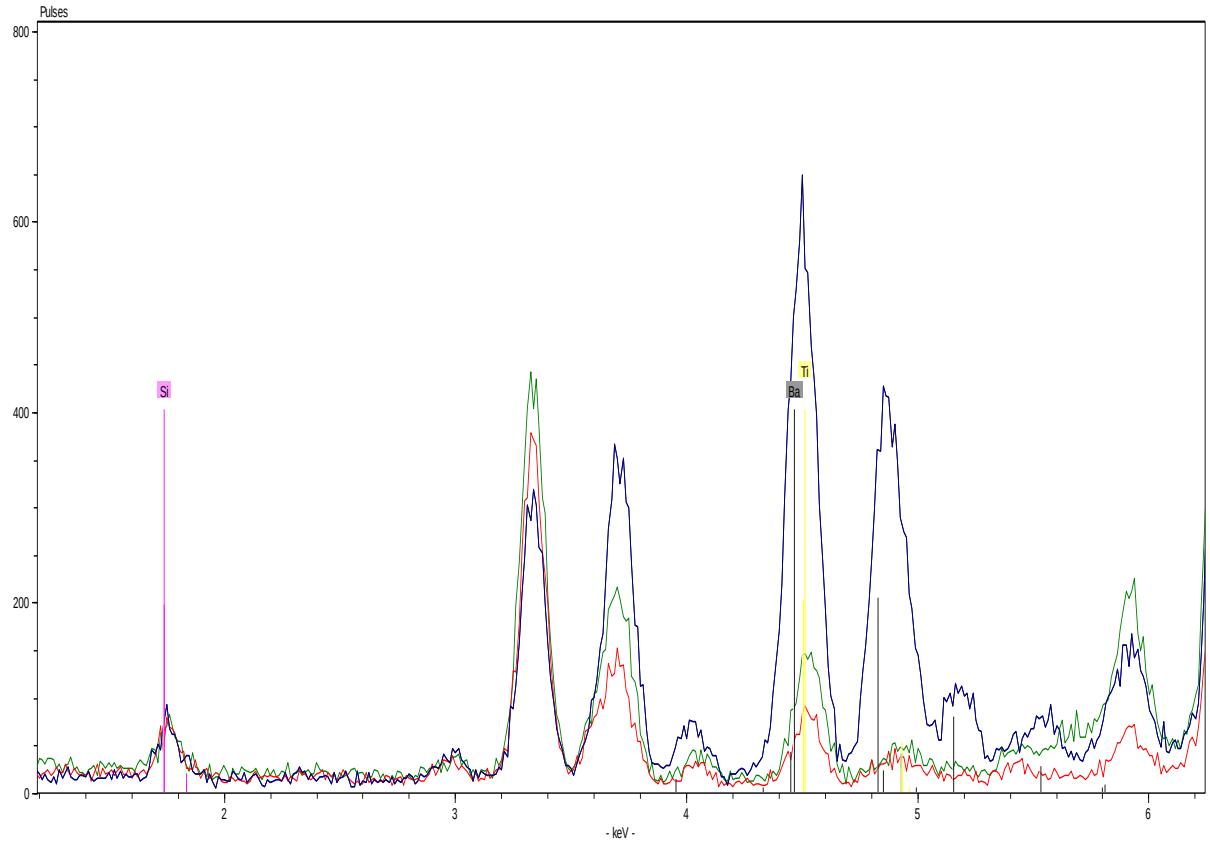


Fig.24. Comparison between XRF spectra of sections of sample treated with RP+Ba.

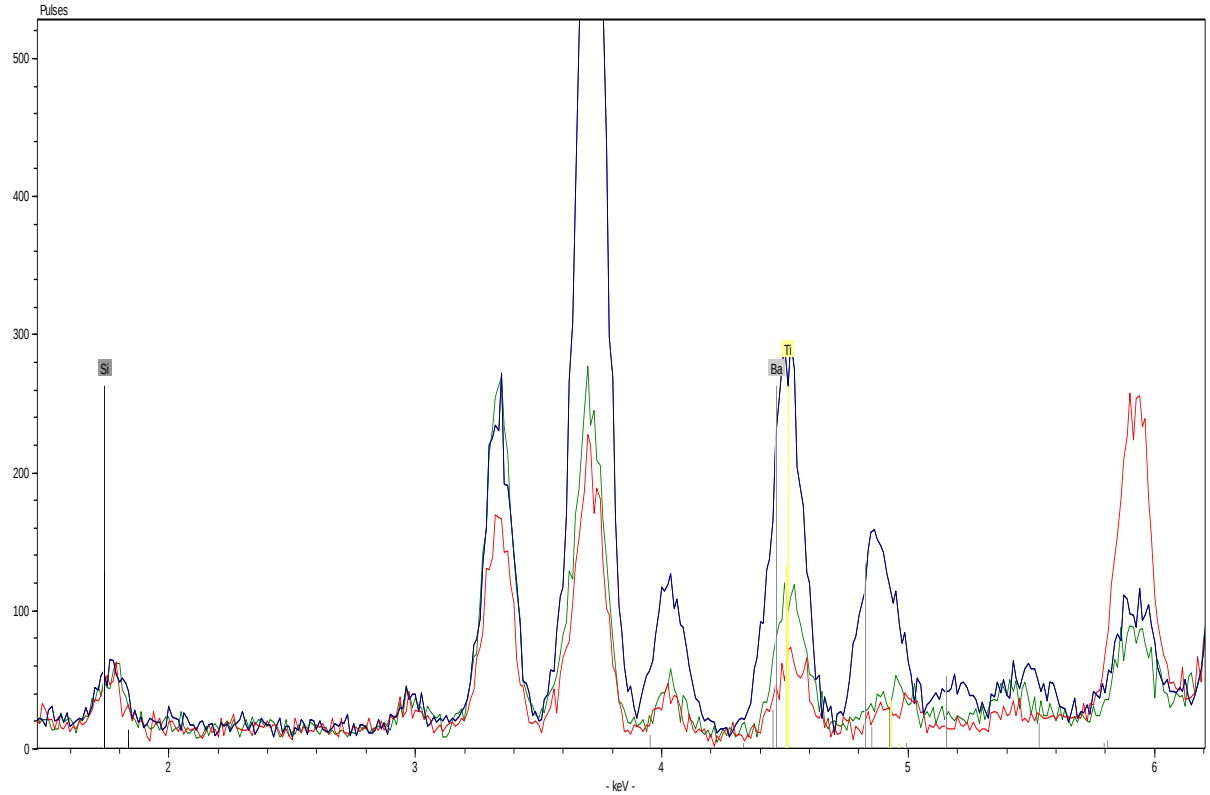


Fig.25. Comparison between XRF spectra of sections of sample treated with BSOH+Ba.

In the archeological site of Monteggibbio, two building blocks that show cracks of different sizes, detachments and granular disgregation are treated at enviroment condition (27-30 °C), and allowed to dry in air, with no direct exposition to sun. One block was treated with BSOH 100 and barium hydroxide, while the second block was treated with net TEOS (RP) and barium hydroxide. The poultice was left to dry for the same time as the trial in laboratory.

On these treated samples it was not possible to make distructive tests (like resistance tests) due to their great dimensions and because they belong to an archeological site , neither water absorption test with contact sponge method, due to their irregular surface.

So, physical-chemical analyses were made on some fragments detached at ten and thirty days after the treatments. After this time the block n.2, that appeared the most degraded before the treatment, showed the detachment of some scales of stone in correspondence of the cracks with larger dimensions. Some of these fragments were taken for laboratory evaluation throught XRDP and XRF analyses. The little creacks present before the treatment appeared, anyway, consolidated.

After thirty days the situation appeared worse in the parts already compromised while appeared stable in corrispondance of the little cracks.

XRF analyses were employed to mapping the penetration of barium inside the treated fragments, showing the three main peaks of barium. In Fig. 26, the spectrum of the detached fragment after ten days is reported in red, while the spectrum of the detached fragment after thirty days is reported in green.

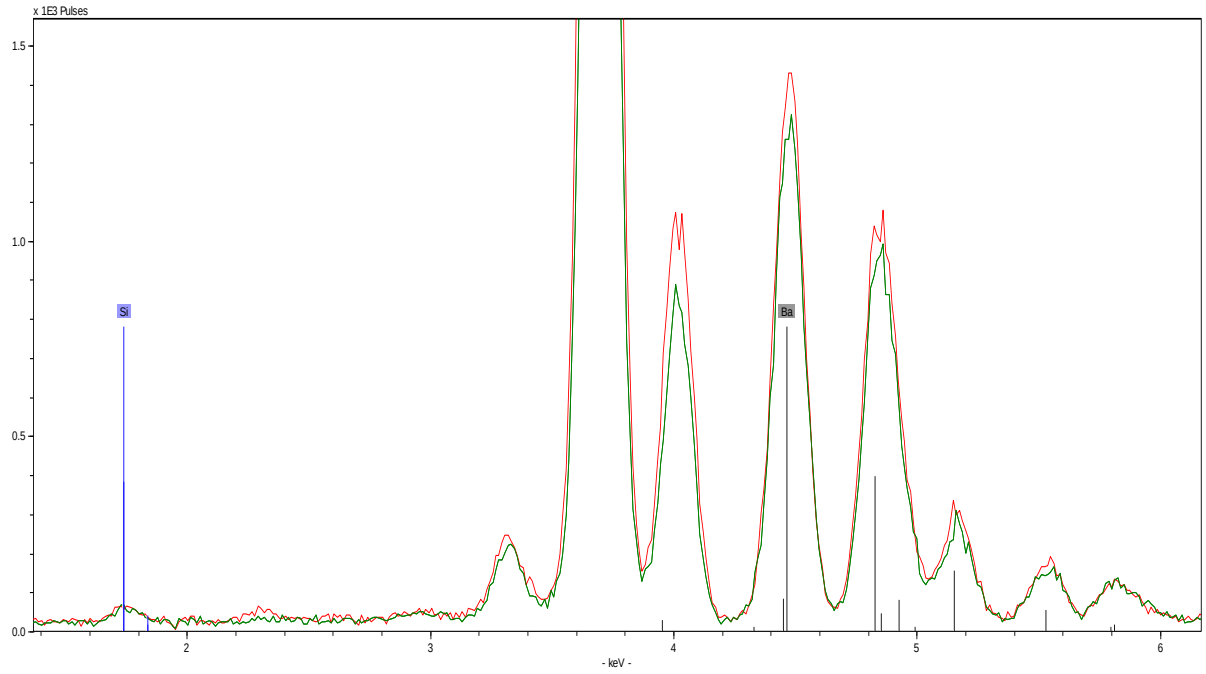


Fig.26. Comparison between XRF spectra of the fragment detached after ten days (red) and after thirty days (green).

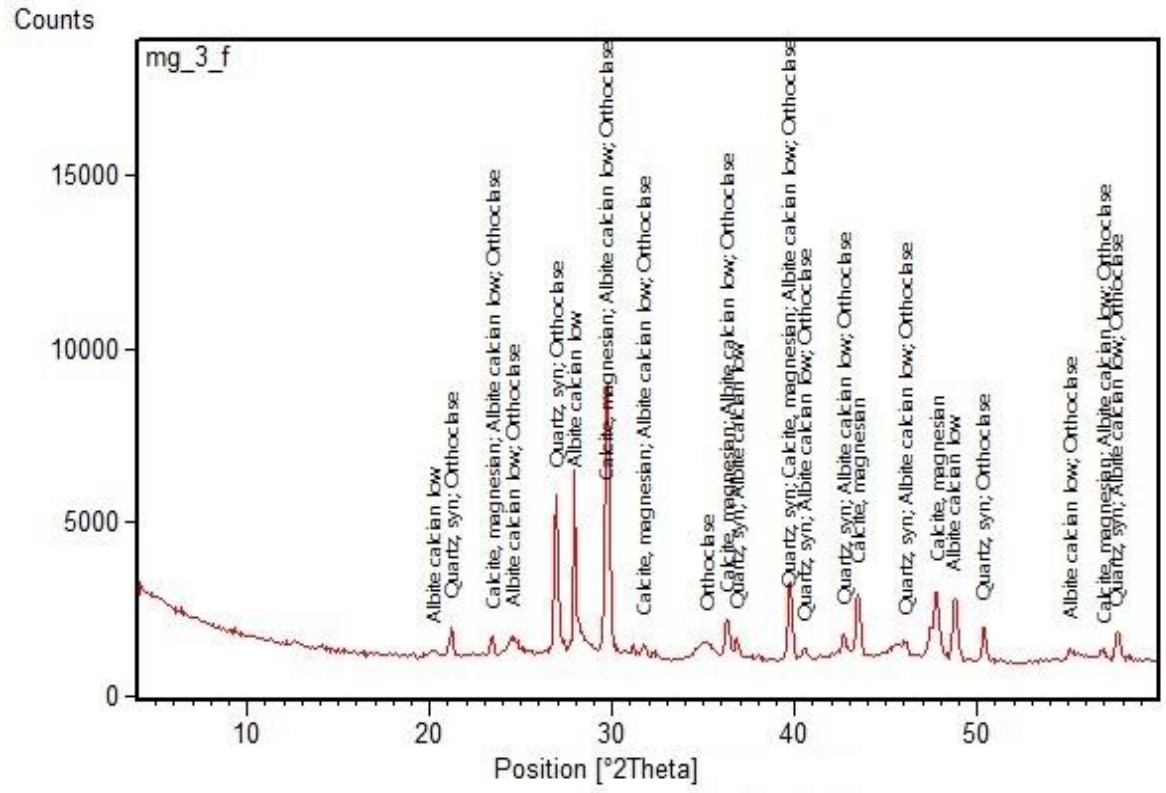


Fig.27. XRDP spectrum of the fragment detached after thirty days.

XRD analyses do not show the presence of barium in neither of the two samples, this means that the barium is present in very low amounts on the surface of the samples in quantities not detectable by X-ray diffraction analysis. The spectra show a composition of the fragments made by of calcite, quartz, feldspars.

8.4. *Conclusions*

Historical Sandstones treated with ethyl silicate and barium hydroxide show a low penetration of the treatment, only in the first millimetres of the samples. Moreover this method is not suitable for the consolidation of samples that present deep cracks, as after treatments the samples even continue to degrade.

On the contrary, the treatment appears ideal to block the small cracks and stop their future development into bigger cracks, as the analyses on the Montegibbio samples clearly show.

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CONCLUSIONS

In these work have been studied and evaluated new treatments and methods for the conservation of degraded sandstones.

Sandstones samples coming from industries of the historical area of Firenzuola (FI, Italy) and belong to natural quarries placed along the Tuscan-Emilian Apennine or in other country of Europe and commercialized by industries of Firenzuola, were studied.

These stones are classified like modern natural stones and natural aged stones, on the basis of their different degrees of deterioration and aging due to weathering agents. Modern natural samples are the stones newly extracted and processed that do not show deterioration. Modern aged stones are extracted and worked in the past, and they have been stored in factory's yards, being subjected for decades to natural aging due to the action of weathering agents over the time.

The physical-chemical and mineralogical-petrographic analyses of these stones showed the same composition for all natural stones samples, i.e. Quartz, Feldspars (like Albite, Microcline, Sanidine, and Orthoclase), Micas (Muscovite and Biotite), and magmatic and metamorphic rocks fragments (like Olivine, Chlorites, and so on). Other clay minerals were found in traces, such as Illite and Montmorillonite. Calcite and Dolomite are the natural binder of the matrix.

Modern natural sandstones show a compact, slightly porous, and more resistant matrix than Modern aged stones. These last reveal the same a compact matrix with some porosity but a lower resistance to deterioration due to their prolonged contact with weathering, pollution, and biological agents.

Therefore, all natural stones have a good compact and resistant structures without or with very little loss of cohesion compared with the really historical samples of sandstone, belonging from many centuries ago.

Thus the excessive strength of these samples, on which to perform tests of consolidation, and the need of obtain a large number of degraded samples have led to try thermal chock treatments on modern natural stones, with the aim to deteriorate their cohesive matrix, so that to behave similar to the decohesive matrix of the degraded historical stones.

These artificially aged samples exhibited still low water absorption and thus a good cohesion of the matrix, demonstrating to be not suitable for the consolidation lab. attempts. Consequently, artificial test pieces have been produced with the same or very similar cohesion properties of degraded sandstones, and on which to perform the consolidation tests.

Artificial test pieces were based on Firenzuola's sandstone powder and a special Portland cement.

The chemical and mineralogical composition of this samples were investigated by XRD, XRF, SEM-EDS and petrographic analyses. All results are in agreement between them and showed a composition based on Quartz, Chlorite, Feldspars (which Albite, Muscovite, and Microcline), Calcite, and Dolomite, i.e. the same composition of the all natural sandstones.

The internal structure of the artificial specimen appears very porous, with a variety of grain sizes of Quartz, Feldspars, and Micas; in petrographic analyses the dark matrix based on Carbonate in the natural sandstones was replaced by the compounds belonging from the special Portland cement used to bind the sand.

Permeability to water and abrasion resistance tests (superficial and deep) were investigated for these artificial samples, and showed high permeability and a linear loss of weight when increasing the depth of surface abrasion. These results correspond to what would be expected by extremely porous sandstones. Deep abrasion tests on untreated samples showed data that are not easily interpretable, probably due to the weak matrix of the sample itself, that tends to be too much easily abraded by this test. Moreover, the fact that the tests are performed on different areas of the specimen, can lead to incoherence of data. However, even if deep abrasion tests were made on all samples, it was finally decided to focus the attention on the results obtained from surface abrasion tests.

Artificial test pieces showed similar porosity and behavior of the degraded historic sandstones. Therefore a substantial number these specimens (more than 200) was made for the experimentation of the different consolidant methods.

At the same time eight commercial ethyl silicates, employed by the Restorers [see Table 1 on pag. 73], were studied preliminary by different analytical techniques (like FT-IR and NMR) with the aim to understand their composition, characteristics and properties.

NMR analysis exhibit a clear and clean spectrum for RP TEOS of Aldrich, TES 28, and TES 40. ESTEL 1000 and, mostly, ANTARES show small peaks probably corresponding to silicone components present in low concentration. In some products like BS OH 100, the presence of pre-polymerization products based on ethyl silicate, was suggested. Moreover, solvents and

dispersing agents with low molecular weight could be detected, probably belonging to the family of ethanol, white spirit, dichloropropane, iso-propanol, methilethilchetone, toluene, and so on.

The innovative treatment proposed by this work consists in the attempt to synthesize barium silicate inside the stones, acting as consolidant for the conservation**.** We have supposed that barium hydroxide in water solution, applied just after ethyl silicates, should react with silica matrix of the stone and the applied silicate forming some quality of barium silicate, based on Ba-Si–O–Si-Ba linkages that show good physical-chemical affinity and compatibility with the internal structure of the sandstone, and do not change the physical appearance of the stone.
Barium silicate should lead to an improvement of the hardness and abrasion resistance of treated sandstones respect with the effect of traditional consolidants based mostly on TEOS, tetraethylorthosilicate.
Therefore, have been tested and evaluated treatments based on the application Ethyl Silicates, Barium Hydroxide, and Barium Silicate (obtained from the addition of Barium Hydroxide to TEOS), through physical-chemical analyses, permeability (like contact sponge method) and mechanical resistance tests (i.e. surface and deep abrasions) on artificial samples. The level of impregnation and distribution obtained and the possible chemical interaction was checked by SEM-EDS, FT-IR, XRF, XRDP techniques.
Preliminary checks were made by the application of ethyl silicates only, by brushing: some of them showed no decrease or low decrease of water absorption (like RP and TES 28), while others show a strong decrease (i.e. ANTARES, DN-Consolidant, TES 40, ESTEL 1000, BS OH 100 and Tegovakon V 100). Thus, it must be assumed that the latter products contain some water-repellent substances that cause no absorption of water, like silicone additives (probably this is the case, from NMR data, of ANT, KDN, and EST that contain partially unknown solvents). Ethyl silicates that show strong decrease of water absorption were considered negatively for the purposes of this research, because their water repellency blocks access to water, so to the subsequent treatment with Barium Hydroxide solutions. BS OH 100 and Tegovakon V100 exhibited low values of water absorption, but none of them contains water-repellent products. After water absorption tests, the best results were given by RP and TES 28.
The situation changes with the application of treatments based on poultice of Barium Hydroxide. Referring to water absorption, BS OH 100 showed a little increase compared to the others Wacker products, while Tegovakon V 100 undergoes a further decrease.

The products that showed good water absorption results after ethyl silicate treatment only, now undergo a sharp decrease of Wa (*i.e.* RP and TES28), thus confirming the presence of an interaction between Ethyl Silicate and Barium on the surface samples.

Treatments based on the application of only Barium Hydroxide were also made, showing that the water absorption decreased at less than a half, if compared to the value of untreated samples, and therefore some interactions with the matrix of the stone occurred.

The treatments based on Barium Hydroxide cannot lead to water repellency. Thus, the further reduction of water absorption in some samples probably is due to the precipitation into the pores of some new material produced by the interaction between stone silicates and barium Hydroxide (like barium silicate, i.e. a mineral and hydrophilic product).

The comparison between the results of water absorption tests and resistance to surface and deep abrasion, in addition to the solvent-free composition of some ethyl silicates, suggests the application of BS OH 100, Tegovakon V 100, TEOS RP and TES 28 like individual treatments based on ethyl silicate. BSOH and TES 28 show a not excessive consolidation effect, while RP and TV have the best characteristics of resistance to surface and deep abrasion.

When barium hydroxide poultice is added to the silicate, the best abrasion resistance is given by BSOH+Ba and TV+BA, while the application of only barium or barium poultice added to RP and TES 28 give rise to a consolidating effect similar among these three products.

However, there are doubts on the reliability of the deep abrasion tests used for this evaluation. Most of the samples treated with only ethyl silicate have shown no strengthening effects and indeed, weaken the cohesion (i.e. the abrasion resistance) of the treated samples. This behavior does not seem to have a plausible explanation.

Thus, ethyl silicate treatments appear to improve the cohesion properties of the treated samples, as evinced by the results of water absorption and mechanical resistance tests. Correspondingly, the physical-chemical analyses of treated samples through XRD show spectra with a change in the shape and intensity of silica minerals peaks (like albite, quartz, muscovite, and sanidine) respect with untreated samples. This could mean that some reactions between ethyl silicate and silica matrix of the samples occurred.

In the specimens treated with different ethyl silicates, mapping of ethyl silicate penetration into the sample matrix with XRF and SEM-EDS techniques revealed to be quite impossible, because of the silicatic matrix of the stone. We then tried to map this penetration with Phenolphthalein, an acid-base indicator that colors of fuchsia the basic solution, like ethyl silicate. The results of these tests were not good because since both the surface and the longitudinal sections appeared colored with the indicator.

So, in the case of the application of barium salts to artificial specimens, their surface appeared more cohesive than the surface treated with ethyl silicate.
On the contrary, the treatment based on barium poultice applied after ethyl silicate increases the consolidation action of this last compound and promotes the strengthening of the stone matrix, hindering its mechanical degradation. Therefore, barium hydroxide should lead to the formation of chemical bridges between silica matrix of the stone and TEOS-based consolidant.
The XRD and SEM-EDS, used to verify the formation of barium compounds, like barium silicate and barium carbonate in the first millimeters of the specimens, were, unfortunately, not effective. The increasing of the mechanical features of the surfaces confirms, anyway, that the reaction between barium hydroxide and silica matrix has occurred.
XRF analyses were employed to map the penetration of barium into the samples, if applied through the section of treated samples. The results of these analyses were very useful to understand the penetration of the treatment inside the specimen.
Finally, interesting results on the consolidation of the matrix were showed by the application of ethyl silicate only (like RP TEOS of Aldrich, Siler BS OH 100, Tegovakon V 100, and TES 28).

Artificially aged stones were also treated with the method of barium hydroxide added to ethyl silicate, in order to understand if some changes occur on low degraded sandstone surfaces. On these samples have been tested the methods which have shown the most interesting results after the water absorption and mechanical abrasion tests on artificial samples such as the application of barium poultice added to ethyl silicate products (i.e. TEOS RP, BSOH, TV, EST, and ANT).
The water absorption and mechanical resistance tests made on these samples show good results for BSOH+Ba treatment, which confirms the observations made on the behaviour of artificial samples treated with this same product.
The treatments based on Tetraethyl Orthosilicate (RP) and Tegovakon V 100 showed a worsening of their properties after the surface abrasion tests, which were supposed, instead, to improve their strength if compared to untreated samples.

All these tests led to the identification of some treatments to use for the consolidation of the historical degraded sandstone, that is the principal goal of this work.

Passing to the experiments on real cultural heritage materials, all the few historical samples studied showed different degradation elements like cracks, fissures, and loss of material made by action of weathering, animals organism, mosses, and lichens.

Unfortunately, as it appears obvious, it was not easy to find proper sacrificial historical samples, so this last part of the work was based on the detailed study on a stair step from a Villa Medicea placed in Tuscan region and two building blocks from Montegibbio, archeological site near Modena. In addition, also the characterization of seven architectonical sandstone fragments, such as part of column (base, shaft, and capital) and architectonical elements was made.

The greatest problem of degraded historical samples available in laboratory was their irregular and limited surface that do not allow to obtain homogeneous data about their physical-chemical and mechanical properties on different point of the sample, together with their limited number that do not permit a statistical analysis of samples.

XRD analysis showed the same mineral composition of all sandstone samples studied in these work. These results are confirmed by XRF studies and petrographic observations.

Water absorption analyses were made on historical sandstones using the contact sponge method test, but in some cases, due to rough surfaces of the architectonical samples, this method could not be applied or, if applied, gave unreliable values, as the sponge did not adhere well to the stone surface and consequently, the water absorption was limited.

Therefore, the consolidation treatments were applied on two sandstones building blocks placed in archeological site of Montegibbio (near Modena), which showed scaling, flaking, exfoliation, granular disaggregation, and cracks due to exposition to the environmental conditions (like weathering and rising damp from the ground, close to a water source), and on the stair step preserved in the laboratory.

The treatment methods chosen for the consolidation of these historical materials consist in ethyl silicate applied by brushing on the stone surface (i.e. Tetraethyl Orthosilicate of Sigma-Aldrich and Siler BS OH 100 of Wacker-Chemie), were followed by the application of a poultice of saturated solution of barium hydroxide.

Surface abrasion tests were made only on treated stair step samples in order to verify the strengthening power of the treatment. Similar results (like low values of weight loss) are showed for both treatments.

XRD analysis on treated samples show the formation of Barium Carbonate (i.e. Witherite) in all treated samples, and Barium Silicate in the samples treated with RP silicate.

XRF analyses showed, only on the surface samples, the presence of the barium treatment.

On two building blocks treated from Montegibbio site, it was not possible to make distructive tests after the treatments due to the great dimensions and because they belong to an archeological site, neither water absorption test with contact sponge method, due to their irregular surface.
So, physical-chemical analyses (like XRDP and XRF) were made on some fragments detached at ten and thirty days after the treatments. The little creacks present before the treatment appeared, anyway, consolidated ten days after the consolidation.After thirty days the situation appeared worse in the parts already compromised while appeared stable in corrispondance of the little cracks.
XRF spectra show the penetration of barium treatment in the early millimeter into the surface treated.
Therefore, all historical sandstones treated with ethyl silicate and barium hydroxide showed a low penetration of the treatment, attributable to the first millimetres inside the samples. So, this method is not suitable for the consolidation of samples that present deep cracks, as after treatments the samples even continue to degrade.
On the contrary, the treatment appears ideal to block the small cracks and stop their future development into bigger cracks, as the analyses on the Montegibbio samples clearly show.

The proposed methods are innovative, and they were very extensively tested on a large amount of artificial samples, having the best match is possible to natural products. The obtained results showed that these methods mostly could be used for the preservation of sandstone surfaces and not as wide consolidating treatment, according to the intrinsically low absorption capacity of compact sandstones. If the problem is the one to consolidate badly weathered samples, showing flakes, creeps etc., these methods were found not suitable for a deep consolidation.

Anyway a further experimentation of these method such as preservation treatment of sandstone is, in our opinion, strongly recommended.

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