MINERALOGICAL AND PETROGRAPHIC CHARACTERIZATION OF CALCITE-ALABASTER. THE CASE STUDY OF BUSCA ONYX

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INTRODUCTION

Busca Onyx was one of the most appreciated ornamental stones in Piedmontese art and architecture. Its main area of diffusion is NW Italy and it was employed especially in the city of Turin, the ancient seat of the House of Savoy, where it was used since the XVII Century. Generally, the applications of *Busca Onyx* were limited because of the characteristics of the material; in fact, it was mainly used for decorations in churches, royal residences and aristocratic palaces and for small decorative objects as vases and statuettes, decorative wall panels, furniture cover plates, columns, and balustrades.

This work is focused on the project for the characterization of the ornamental stone and quarry. The case study is presented through a multidisciplinary approach with the purpose of covering a wide range of aspects beside the mineralogical and petrographic description. The characterization aim was to relate geosciences to cultural heritage conservation and geo-touristic applications. Main topics are: description of the quarry site, reconstruction of its history, study of the depositional environment, mineralogical and petrographic characterization of the rock, and applications of *Busca Onyx* in cultural heritage. Furthermore, considering the geo-touristic potential of the quarry area, a valorization project was undertaken, finalized for the enhancement and the touristic fruition of the area.

Busca Onyx, despite its name, is a variety of calcite-alabaster. In this paper, calcite-alabaster is defined as a sedimentary orthochemical rock, generally layered, alternating opaque and translucent bands, composed mainly of calcite and rarely of aragonite. Calcite-alabasters can have hypogeal origin in karst environment or can also form subaerially in open fractures, occurring typically as reprecipitated calcite crystals in carbonate host rocks (Klemm & Klemm, 1991, Frumkin *et al*., 2014).

CHARACTERIZATION OF THE QUARRY

The *Busca Onyx* quarry is located in SW Piedmont (NW Italy), near the town of Busca, in the Cuneo province. The quarry is halfway from the entrances to Maira and Varaita valleys (Cottian Alps). It is located on the southeastern side of the "Eremo di Belmonte" hill, in an area called "La Marmorera", a name that refers to the quarrying activity. Canyons are hosted in a dolomitic marble, which belongs to the southern sector of Dora Maira Massif (Fig. 1a). The area is characterized by four artificial canyons obtained removing the carbonate concretion that constituted *Busca Onyx*. Canyons are a few meters wide and up to 35 meters high. Their length ranges between 50 and 100 meters (Table 1). The deposits are nearly parallel and oriented along a NW-SE direction (Fig. 1b). Most of the concretion had been extracted leaving the bare host rock (Fig. 1c), which is partially marked with the traces left by the extraction techniques.

At present, the quarry is no longer in activity. The extracted rock is known by the commercial names of *Busca Onyx Marble* (or the most common *Busca Onyx*) and *Busca Alabaster*.

Busca Onyx deposits consist of thick layers of carbonate concretions originated by water percolating into an ancient cave/fracture system and, as observed in similar cases (*e.g.*, Fairchild & Baker, 2012), the outcome is the coexistence of horizontal high flow component (flowstone) and vertical slow flow component (stalactites and stalagmites). In many areas of the quarry, the concretion was thick enough to be extracted in blocks and was thus used as an ornamental stone.

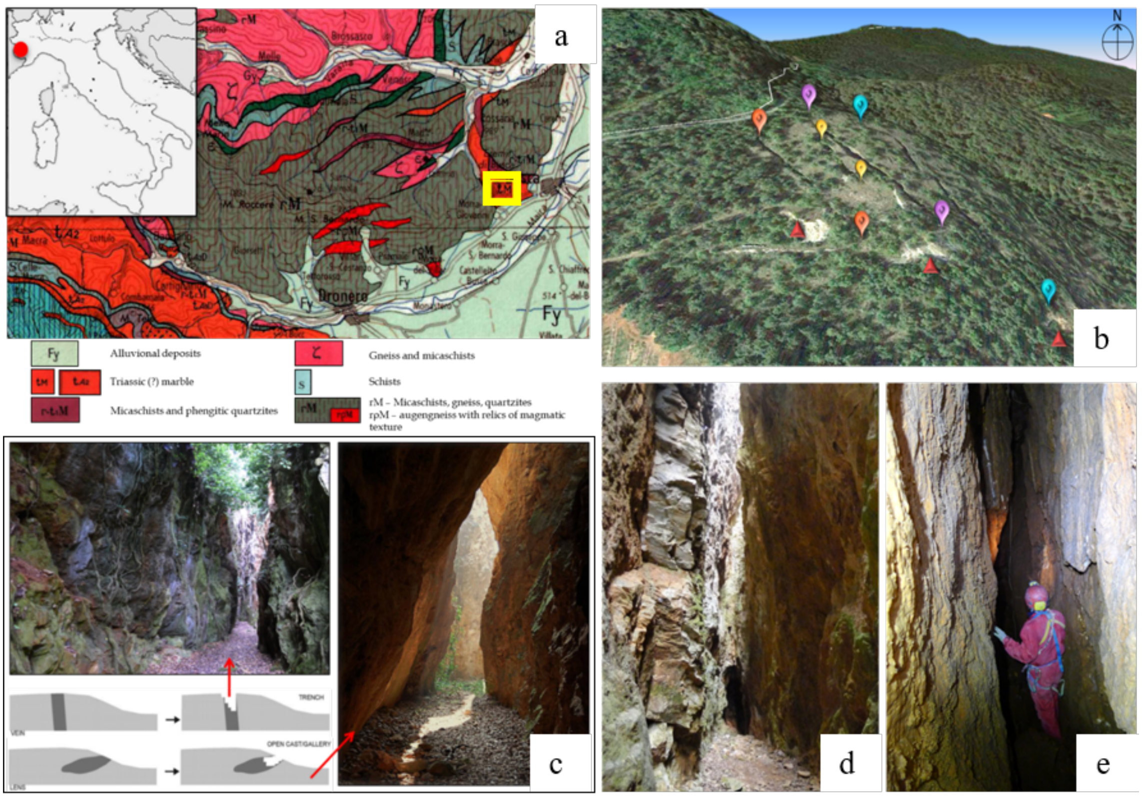

Fig. 1 - a) Geological map of the southern sector of Dora Maira Massif (Carte géologique de la France 1:250 000 - Sheet 32-10 Gap). Busca quarry area is highlighted by the yellow rectangle. b) Satellite image of quarry area: the colored pins are positioned at the entrance and at the end of every canyon; canyons are named from C1 to C4 from left to right (modified from Google Earth). c) Insights of the canyons. Their artificial morphology is intermediate between a trench and a gallery, due to the irregular shape of the original deposits. The ground plane was artificially leveled and flattened. d) Entrance to Marmorera cave. e) The narrow shape of the cave. Walls are covered in sub-vertical flowstone.

The only area that preserves the original morphology of the ancient carbonate deposit is represented by the *Marmorera cave*, which is located at the far end of canyon C4 (Fig. 1d). It has been explored and mapped for the first time by Spissu *et al.* (2000) and registered to the “Italian Caves Cadaster” (cave number PI CN 1195). It is a narrow cavity, around 10 meters in depth that develops for around 20 meters along NW direction (coherently with the direction of the canyons).

Table 1 - Coordinates and morphological features of the low-gradient canyons.

Canyon ID	Length (m)	Width (m)	Altitude (entrance)	Azimuth (entrance)	Coordinates (entrance)
C1a	27	1.4 - 2.4	688 m asl	315 N	44°31’02,341’’ N - 7°27’02.120’’ W
C1b	63	0.9 - 3.9	700 m asl	315 N	44°31’01,244’’ N - 7°27’00,129’’ W
C2	53	1.8 - 4.2	704 m asl	318 N	44°31’02,178’’ N - 7°26‘09,178’’ W
C3	78	1.6 - 3.6	689 m asl	320 N	44°31’02,771’’ N - 7°27’00,170’’ W
C4	96	1.9 - 4.0	660 m asl	323 N	44°31’01,270’’ N - 7°27’04,363’’ W

From field observations and considering the morphology of Marmorera cave, unexplored cavities could exist in the area but their entrances could be hidden by the vegetation, covered by quarry debris or not directly connected to the surface. In the cave, water is still drained through the roof and drips or flows on the walls; as a matter of the fact, draperies and principally sub-vertical flowstones are growing (Fig. 1e).

In 2015, following the indications of an excursionist who noticed tool marks on an outcropping rock block in the woods, another abandoned quarry site was discovered. It lies around 500 m West from the main quarry. So, the secondary quarry site, denominated C5, was described for the first time. The morphology of C5 is different compared to the canyon-like shape of C1-C4 since the original shape of the deposit should have been similar to a chamber. In some areas, rough trenches are still recognizable, but the extraction stopped before a further lowering of the ground plan.

Busca Onyx formed in a complex environment, which is no longer preserved, since the quarry altered the original morphology of the landscape. Typical features of karst environments are still recognizable in the area and the petrographic analysis, on both extracted material and samples collected *in situ*, confirmed its spelean nature (Marengo *et al.*, 2014). Therefore, beneath the land surface there was a cave system mostly destroyed by quarrying activity, unless for Marmorera cave. Calcite-alabaster characteristics are strongly dependent on the environmental conditions at the time of their deposition. For this reason, a complete characterization of the site and of the rocks requires a reconstruction of its formation mechanisms and of its evolution. Hypothetically, the deposits of carbonate concretion extracted as *Busca Onyx* formed in solution caves successively unroofed by erosional processes. In fact, the evidences observed *in situ* and the data obtained from the petrographic characterization of *Busca Onyx* samples proved that the area underwent to karst phenomena.

Exploitation history and applications of Busca Onyx

A further aspect considered in the characterization of the quarry was its history. To accomplish such task, researches in historical archives were done to reconstruct the chronology of the quarry from its opening in 1650 to its closure in 1961. The quarry belonged for the most part of its history to Savoy Royal Family, and the extracted material was exclusively reserved for their monuments and buildings. Its success is mainly due to Royal Architect Filippo Juvarra (1678-1736), who extensively used this material in the decorative apparatus of his masterworks. The rock was so appreciated that in many churches (especially in Piedmont) it was imitated by painting its particular pattern. Decreasing of the production happened in concomitance with the selling of the property to private citizens at the end of XVIII century. Major applications are in the Church of San Filippo Neri and in the Basilica of Superga in Turin. Other examples are the Beaumont Galley in the Royal Palace of Turin, the Royal Church of San Lorenzo (located nearby the Palace), and other churches in Turin as St. Teresa, St. Tommaso, and St. Francesco d'Assisi. An interesting example is St. Donato Cathedral in Mondovì (Cuneo), where the pillars of the central navy are painted imitating *Busca Onyx* pattern (the rock was used only in one of the lateral chapels). More information can be deduced also by the material remains derived from the different processes involved in its exploitation as a quarry. Features related to production (extraction and working of the rock), transport of the blocks and infrastructures (buildings and services) are still recognizable. Along with the information found in archives and historical reports, these data provide an interesting overview of technology, purpose and size of the activity.

By the observation of the tool marks and from the analysis of the leftovers of the social infrastructure it is clear that for almost all the time span in which the quarry was active, the extraction was carried out mainly by manual labor. This is also confirmed by the description of the activity wrote by Augusto Stella (1908): "*the quarry […] is managed in a primitive way, it certainly lacks any rational organization. It is unthinkable to make a high profit from this material, as it should be supposed to*" referring to the absence of adequate tools and efficient extraction methods. In the last period of activity (mid-1900), some machines as pneumatic drills and jackhammers were used to a small extent.

CHARACTERIZATION OF BUSCA ONYX

Materials and methods

Sampling was done considering the presence in the area of different kind of rocks and concretions, and the possibility to compare samples between different zones of the quarry site. Concerning the type of lithologic and mineralogical material collected, the three main categories of samples are the host rock (dolomitic marble), the interface (layer sometimes present between the marble and the concretion) and *Busca Onyx*. Speleothem material was possibly collected in the areas of the quarry where it was largely available and where genetic features as its original bedding and the growth direction of layers were still recognizable. In fact, sampling methods and the choice of sampling sites attained as much as possible to conservative criteria, massive sampling was avoided, taking into account the ongoing valorization project and the touristic enhancement of the area.

The analytical procedure is characterized by a multi-technique protocol; complementary non-destructive techniques were preferred in order to preserve samples for further analyses and to limit sampling actions in the quarry area. Mineralogical and petrographic characterization of calcite-alabaster samples and of concretion was done by means of optical microscopy, SEM-EDS, and micro-Raman spectroscopy. While geochemical analyses and trace element determination was carried out with XRF, and analyses of the organic content in calcite layers was done by IR spectroscopy.

Results and discussion

The host rock is a saccharoid micaceous marble, which according to European standard EN 12670:2001 can be classified as a calcitic-dolomitic marble. Dolomite-bearing rock are less prone to dissolution, so the relatively small extent of Busca calcite-alabaster deposits could be related to the composition of the host rock.

Mineralogical examination showed that host rock samples have a mixed composition, average contents of calcite and dolomite are 60% and 40%, respectively. Some portions are rich in white mica, suggesting a siliciclastic input into the formation environment during the early stages of carbonate deposition. Identification of main and accessory mineralogical phases was done by means of SEM-EDS and μ-Raman spectroscopy. Main components are thus calcite and dolomite, accessory minerals are muscovite, hematite and, at a lesser extent, fluorapatite. The rock shows an overall heterogeneous distribution of microporosity. Pores are generally localized at grain boundaries and have an average size of 10 μm, the total porosity is however very low.

Macroscopic description of *Busca Onyx* samples was carried out on both fresh-cut and polished samples collected in quarry sites from C1 to C5. The prominent characteristic of the material is its heterogeneity; in fact, the result of depositional processes is a complex aggregate of concretions and speleothem structures (mostly stalactite-like concretions and flowstones), as can be seen in Fig. 2.

The petrographic characterization of *Busca Onyx* was performed by means of optical microscopy and SEM-EDS and by the construction of microstratigraphic logs for the description of sequences of calcite fabrics (for fabric reference and definition see Frisia, 2015).

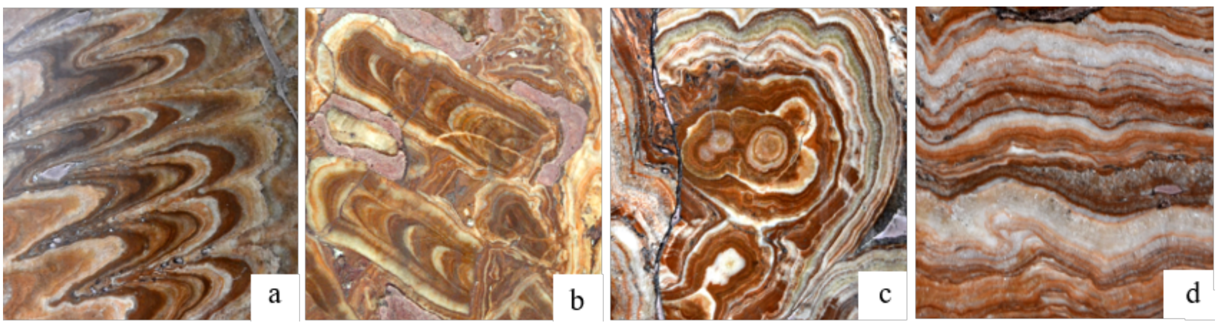

Fig. 2 - Polished slabs of *Busca Onyx*. a-b) Longitudinal sections of carbonate concretions in which the direction of accretion is clearly recognizable. Layers are composed of radial crystals of calcite. c) Orthogonal section of stalactite-like components. Clear and dark layers are disposed in a concentric arrangement. d) Typical flowstone component (vein cut). Calcite layers are nearly parallel and show variable thickness. Crystals grow, in this case, almost perpendicular to the substrate.

Busca Onyx is macroscopically and microscopically characterized by the alternation of subparallel clear layers and dark, reddish bands. The thickness of the layers is extremely variable, ranging from few microns to centimeters.

Clear layers are composed of calcite crystals that can be grown sub-perpendicular to the substrate, as in flowstones (Fig. 3a and b), or radially grown as in stalactitic/stalagmitic agglomerates (Fig. 3c). Chemical analysis revealed that clear layers are constituted by chemically pure calcite crystals. Features of calcite layers are related to the environmental conditions occurred in the formation setting at the time of precipitation. In general, the predominant calcite fabric observed in Busca samples is columnar type, suggesting a slow growth under low supersaturation conditions. Overall, the observed flowstone portions suggest cyclic changes in hydrological features through time, represented by the alternation of columnar/micritic pattern; in fact, the presence of smaller calcite crystals may indicate that the system experienced periods of reduced water input.

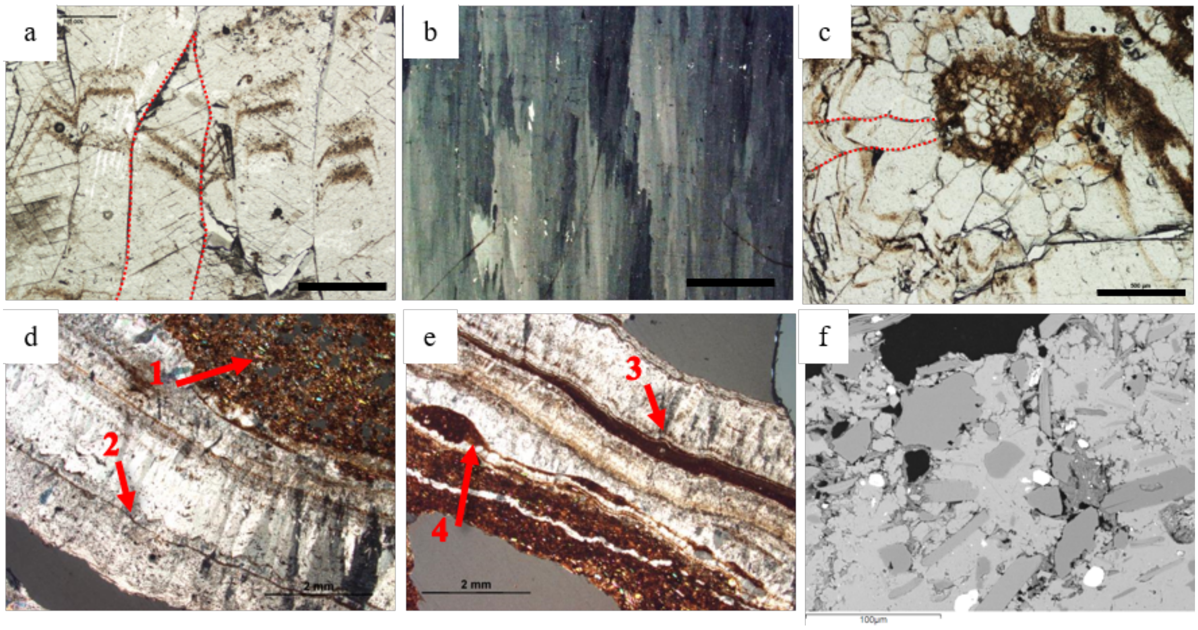

Fig. 3 - Upper row, clear calcite layers: a) Sample MN318 from main quarry site. Calcite crystals growing perpendicular to the substrate. b) Sample D1 from site C5. Calcite crystals which length/width ratio exceeds 10. c) Sample MN319 from main quarry site. Example of radial growth. Scale bars in a, b and c are 500 µm. Lower row, detrital layers: d-e) Variable thickness and porosity of detrital layers are well visible (red arrows). Arrow 1 indicates a 1 cm thick porous layer, contrarily, arrow 2 points a thin layer (30-40 µm thick), arrow 3 shows a 200 µm thick layer and arrow 4 indicates a layer characterized by variable thickness (from around 30 µm to a maximum of 500 µm). f) backscatter electron image of a detrital layer (corresponding to the layer pointed by arrow 3), mineral grains are embedded in a calcite matrix (field of view: 250 µm).

Darker layers are irregularly alternated to clear layers and are rich of impurities. They can be ascribed to two categories according to the nature of the impurities: layers rich in organic colloidal particles and layers rich in inorganic detrital particles. Layers with high organic input can be slightly colored and thus distinguishable by optical microscope from clear layers, but their mineralogical features are very similar. While the presence of inorganic detrital impurities leads to the formation of a completely different kind of layer (referred as detrital layers).

Detrital layers are composed of small isometric calcite crystals and mineral sediments (mainly clay-sized, sometimes bigger). These bands are almost opaque if observed under optical microscopy, unlike clear layers of calcite. Their frequency and distribution are irregular; the thickness can vary from several microns to centimeters

(Fig. 3d-f). During recurring rainfall periods, high recharge conditions occur and when turbulent waters flow into the depositional environment, suspended sediments (clay, silt, or sand) are loaded within. As the water drains away, part of the sediment settles out on the growth surface of the flowstone (as well as on the top of stalagmites). After their deposition, the clasts are interbedded between chemically precipitated calcite layers (Dasgupta *et al.*, 2010; Gázquez *et al.*, 2014). In general, detrital layers form on up-facing layer surfaces where debris can accumulate. Down-facing layers (as in stalactites) are composed of debris-free elongate calcite crystals, since gravity would cause the detachment of detrital particles from calcite growth surface (Kolesar & Riggs, 2007). The massive presence of detrital layers can be in general ascribed to high recharge periods characterized by turbulent events (*e.g.* intense precipitations) or more rarely to episodic flooding of cave passages (Lascu & Feinberg, 2011).

The mineralogical characterization of *Busca Onyx* detrital layers was performed on samples collected in C1-C4 quarry sites. Samples collected in C5 quarry site do not show proper detrital layers, but in few cases, some isolated grain of inorganic impurity is embedded between calcite layers.

Identification of mineral species composing the detrital assemblage was carried out through SEM-EDS and μ-Raman spectroscopy. Muscovite, quartz, kaolinite, hematite, and rutile constitute around 90% of the mineralogical species detected in the detrital fraction of each sample. These minerals are well represented in the lithotypes of the southern sector of Dora Maira Massif (such as micaschist, quartzite, and gneiss). Detrital particles were classified as autochthonous or allochthonous whether they derive from the depositional environment (host rock or precipitated in situ) or outside it. Generally, the size of mineral particles is comprised between few μm and hundreds of μm. The grains are poorly sorted, ranging from clays (< 2 μm) to fine sands (63-250 μm) with rare presence of millimetric gravel. The most represented size is silt (2-63 μm). Most particles show rounded and smooth boundaries because of transport processes and few individuals preserve their original morphology.

Considered the average grain size, sorting and provenance of detrital grains, clastic sediments embedded in *Busca Onyx* layers can be described with *backswamp* and *channel* facies models according to White (2007). In fact, the characteristics of mineral particles suggest that these sediments are mostly stream-transported.

Backswamp facies comprises the weathering residue of the bedrock filtering into the conduit system from the overlying soil. Autochthonous sediments present in *Busca Onyx* detrital layers can be ascribed to this facies, which constitutes the majority of clasts. The size of particles ranges between clay and fine silt (smaller than 8 μm). Bigger individuals (*channel* facies) have been sorted by bedload transport along the conduits. They are most present in thicker detrital bands and consist of beds of silts and sands. The varying particle size may represent different flow regimes, attributable to different episodes (*e.g.*, floods, heavy rain, etc.).

In addition, the causes of color of *Busca Onyx* layers were investigated. Marcenaro (2008) in his work attributed the reddish brown coloration of *Busca Onyx* to the presence of clay minerals and/or of iron compounds. This statement is resulted to be only partially true as demonstrated by the elemental maps acquired by means of μ-XRF.

The maps were performed for those elements that can be typically found in minerals composing detrital layers, and data relative to Si, Al and Fe had proven to be sufficient to accurately to identify detrital layers and to give an idea of their distribution. Si, Al and Fe are present and concentrated in certain brown layers, whereas some other brown layers do not show evidence of detrital minerals embedded in them. Elemental maps were acquired for several samples and examining the elemental distributions in layers that macroscopically ranged from light orange to brown, it is proved that some colored layers do not due their color to mineral inclusions (either clays neither iron oxides or iron hydroxides). Considering also that these specific layers give a UV fluorescence response, the hypothesis of a coloration due to the presence of dissolved organic matter in calcite was done.

Dissolved organic matter (DOM) is documented to be found in speleothems and carbonate concretions, mainly in form of humin (HU), humic acids (HAs) and fulvic acids (FAs), causing a typical tan-brown color.

The presence of calcium salts of humic and fulvic acids is indicated by fluorescence in the blue and yellow range of visible spectrum (Shopov, 2004a, 2004b). Organic content in Busca samples was analytically checked through FT-infrared spectroscopy and all the samples show distinct features related to the presence of DOM, which have been attributed to be the cause of the brownish color of some *Busca Onyx* layers, and the cause of fluorescence of the samples.

Finally, in order to complete the characterization of *Busca Onyx* and of its formation environment, U/Th dating was then carried out on samples from quarry site C3. Considering the results, it is reasonable to suppose that the deposition of calcite layers was already ongoing around 320 kyr ago and prosecuted at least until 57 kyr ago.

CULTURAL ENHANCEMENT OF THE AREA

The information obtained through the characterization project describe a complex geological and environmental system, which is also a precious site for cultural enhancement of the area in which it lies. In fact, one of the outcomes of the project on *Busca Onyx* was the valorization and the geo-touristic enhancement of the quarry area. After the last years of activity of the quarry, the site was abandoned and its existence and location were nearly forgotten by the local population. Considering the peculiar morphology of the quarry, which could be very suggestive for excursionists, it is worth to enhance and develop its touristic potential.

In 2015, the Department of Earth Science of the University of Turin and the Municipality of Busca committed in a project that entails the valorization of the quarry area and its preparation for touristic fruition. The cooperation of academic researchers and municipal administrators principally had two objectives on a medium-long term. The first is the valorization of the area through a deepened scientific study of both the quarry and the extracted material; the second is the touristic fruition of the quarry area through the creation of a geo-touristic itinerary. The first steps of the valorization process were the diffusion of the achieved results through lectures and seminars for the public. In addition, the results of the study were collected in a didactic book on *Busca Onyx* and its quarry (Marengo & Costa, 2016).

Furthermore, in order to prepare the site for touristic fruition, it had been necessary to consider its conservation problematics. The main problem for the conservation of the quarry landscape is the vegetal colonization boosted by the wet climate and by the fertile soil. Spontaneous trees and shrubs grow inside the canyons partially obstructing the access and the passage in the trenches. Vines inflict the major damage and climbing plant roots carve millimetric paths in the rock surface, enhancing weathering and erasing superficial features (both natural and artificial). The presence of lichens is also massive and dangerous for the cohesion of the superficial layers of rock. In 2016, the area was organized and partially cleared from the vegetation to allow the first guided tours through the site. Panels with data obtained from the multidisciplinary characterization of the rock and of the quarry are displayed *in situ* in order to make tourist aware of the geological and environmental features of the area along with safeguard and conservation problematics.

FURTHER STUDIES

This PhD thesis opened the possibility of conducting further researches on a great amount of calcite-alabaster samples, which have been collected during the project. Undoubtedly, the most interesting issue may be a complete paleoenvironmental and paleoclimatic reconstruction of Busca area. This should be accomplished with an extended dating and isotopic campaign. A climatic reconstruction would be of interest because at present there are few data for southern Piedmont.

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