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PETROGRAPHIC AND MINERALOGICAL CHARACTERIZATION OF VOLCANIC ROCKS AND SURFACE-DEPOSITIONS ON ROMANESQUE MONUMENTS

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ABSTRACT

The stone used on the monuments, especially if they come from ancient times (e.g. medieval period), when exposed to the atmosphere, they are frequently affected by weathering and bio-deterioration processes. Thus, these latter produce various chemical and mineralogical transformations of substrate at the interface with the atmospheric agents as function of intrinsic compositional and physical characteristics of the material. Moreover, if there also are ancient treatments on the surface of geomaterials, the investigation field is further complicated. This research aims to analyse the surfaces of different volcanic lithology (basalts, andesite, pyroclastic rocks) used in the medieval Romanesque churches of Sardinia (XI-XIV cent.) having high historical-architectural and cultural relevance. By mineralogical and petrographic analysis (OM) and other different analytical methods (XRPD, colorimetry) the investigations addressed to define: i) petrographic features of volcanic rocks substrate; ii) chemical and mineralogical composition of coatings/crusts and any salt fano- and cryptoefflorescence; iii) compositional and microstratigraphic characterization of ancient treatments (*i.e.*, Ca-oxalate films) on the surface of facades; iv) chromatic modifications of surface with respect to the substrate due to the alteration processes.

The results show the incidence of several factors in the alteration process, as function of the occurred time, petrophysical features and composition of geomaterials, their position in the monument structure, exposition to the weathering processes, microclimatic characteristics, environmental conditions.

KEYWORDS: Alteration, Sardinia, Oligo-Miocenic, Plio-Quaternary, Ca-oxalate, petrography, Romanesque, Medieval

1. INTRODUCTION

Among the research activities on Cultural Heritage, the study of decay and the characterization of the external rocks / environment interface are of enormous importance.

The stone alteration depends on the intrinsic petrographic and mineralogical characteristics of rocks and the conditions of environment where the monument is located. Thus, the chromatic aspect of the rocks taking at the interface with the atmosphere is usually different from what of unaltered (fresh) rock substrate. Generally, this difference is due to weathering and bio-deterioration processes, which involve physical and / or chemical modifications of the rock, or deposition of organic and inorganic substances on the surface (e.g. atmospheric particles).

The weathering processes occur in various forms, depending also on the physical characteristics of the rock (porosity accessible to fluids, internal matrix cohesion, degree of welding or compactness, etc.). Alteration especially affects the medium-highly porous rocks (e.g. carbonatic rocks, pyroclastic and ignimbrite volcanics, etc.) and ancient mortars frequently used on the Cultural Heritage for their easy workability (Antonelli et al. 2014a; Columbu et al., 2014a, 2014b, 2015a, 2015b, 2017, 2018a, 2018b, 2018c, 2018d; Columbu, 2017, 2018 in press; Lezzerini et al., 2016, 2018a, 2018; Ramacciotti et al., 2018). Earlier investigations on weathered rocks and remedies have been quoted (Sabatino et al., 2016; El Derby et al., 2016; Samanian et al., 2012; Manoudis et al., 2017).

The decay process can involve only the outer surface of the stone, thus involving a very small portion of material (< 2 mm), or it can get deeper, reaching in some cases some centimeters. In first case, the surface formations derive from physical-chemical processes due to the pollution, weathering or to specific alterative phenomena (i.e., formation of calcium oxalate films). Most researchers agree that the Ca-oxalate-films are the result of man-made ancient treatments on the surfaces of the monuments.

In this research, the geomaterial surface alteration processes used in the construction of some Sardinian medieval Romanesque churches (XI-XIV sec.) with high historical-cultural relevance have been studied. They are (from north to south Sardinia, Figs. 1, 2): St. Maria (Tergu) SS. Trinità di Saccargia (Codrongianos), St. Maria del Regno (Ardara), San Nicola (Ottana), San Gregorio (Solarussa), San Geminiano (Samassi).

These churches are some significant examples of medieval Sardinian Romanesque architecture that represents a building phase almost intact in Sardinia. This Cultural Heritage has strongly interacts with the landscape where the churches are located, also because of the lead role assigned to construction materials, with the almost total absence of Romanesque churches made in clay bricks and then plastered (once finished) and the consequent free use of stones.

Several volcanic stones with different compositional and petrophysical features (i.e., pyroclastics, basaltic rocks, etc.) were sampled from selected monuments and analysed. These rocks, belonging to the Cenozoic Sardinian magmatism occurred in Sardinia, are widely used as construction stones together other materials in historical times in Sardinia, from Punic-Roman to Romanesque (Columbu et al., 2014b, 2017a, 2017b; Columbu, 2017; Columbu and Garau, 2017; Columbu and Verdiani, 2012, 2014; Macciotta et al., 2001; Miriello et al., 2015; Verdiani and Columbu, 2010). This is generally due to their easier availability in the territory and especially to their better workability compared to silicate igneous or metamorphic rocks (Antonelli et al., 2014b; Bertorino et al., 2002; Columbu et al., 2014a; Columbu et al., 2015a). The volcanic rocks used to the churches of St. Maria, San Nicola and San Geminiano belong to the first Late Eocene-Miocene phase of Cenozoic volcanism. The volcanics of the Saccargia, St. Maria del Regno, San Gregorio churches belong to the second Late Miocene-Pleistocene phase.

The research intends to analyse the composition of altered surfaces of these geomaterials by use of different analytical methodologies (OM, XRPD) to define the compositional characteristics of the solid phases present in the stone surface, but also the micro-stratigraphic aspects of different film levels.

Different following case studies were considered: i) simple chromatic alteration of stone-surface, ii) alteration of rock with formation of coatings that compositionally are also linked to the stone substrate, iii) chemical/physical processes with the formation of compounds which have no connection with the substrate, iv) deposition/formation of crystalline phases or amorphous substances related to the ancient treatment of stone (e.g., Ca-oxalate films) or recent restore interventions.

In this last case, the research focused on the microstructure of these films, investigating how their composition can be related to the organic component present in treatments applied to surfaces with protective and/or chromatic properties (Droghini et al., 2005, 2009a, 2009b, 2010; Giamello et al., 2005a, 2005b; Giamello and Scala, 2009; Sabatini et al., 2000). Except for a form of alteration of the substrate, the films have historical memory value linked to the evolution of the artifact and the finishing techniques, a value that, combined with the protective features outlined against the substrate, paves the way for the theme of the preservation of the films themselves.

2. HISTORY AND ARCHITECTURE OF ROMANESQUE MONUMENTS

In Sardinia, in the central part of the Mediterranean Sea, the introduction of the Romanesque architecture (from the 11th to the 13th centuries) assumed very specific and original aspects, reinterpreting the church subject according to a mingling of elements with the use of the local geomaterials, with the evident effort to replace the elements made of marble and similar stones with the use of local stones, and rereading the structure of the church according to the particular materials offered on the major island of the Mare Nostrum.

The story of the Romanesque churches in Sardinia is concentrated in a range of almost three centuries: from the second half of the 11th century to the second half of the 13th century. Most of these monuments arrived in our time in good conditions. The robust construction and a correct employed of the stones allowed to preserve these constructions.

Each monument of those selected in this research shows any particular historical or architectural or cultural characteristic.

The Santissima Trinità of Saccargia Basilica (Codrongianos; Figs. 1, 2) is the most famous Romanesque monument in the architectural landscape of Sardinia, so that it became one of the symbols of the island's Middle Ages. It was completed in 1116 A.D. (Coroneo, 1993). Originally, as nowadays, the structure forms a Tau cross drawing, with NW-SE orientation axis, and a transept overlooked by three apses faced toward SE. The walls were built up using ashlars of whitish sedimentary (i.e. limestones, marls) and black volcanic lithologies (i.e. basaltic rocks), in alternating rows as "Opera Bicroma", very appreciated and frequently used in medieval period, according to the technique of the Pisan-Pistoian workers, operating in Giudicato Turritano at the end of 11th century (Sechi, 1992).

The church of St. Maria del Regno (St. Mary of the Kingdom) in Ardara (Figs. 1, 2), consisting of basalts and other subordinately pyroclastic products, is one of the key monuments of Sardinian Romanesque. Its importance is twofold, both from a historical point of view, because it is the best-preserved and best-documented royal-chapel of the four Sardinian kingdoms (Usai, 2011), both from a purely historical and artistic point of view, since it is one of the incunabula of Romanesque architecture in Sardinia, together with the basilica of San Gavino in Porto Torres.

The San Nicola Cathedral in Ottana (Figs. 1, 2) is one of the most important Sardinian Romanesque monuments of 12th century. It was built in two stages, possibly by two different worker-teams, during the age of the Giudici, and it had the role of cathedral of the Ottana diocese. The church, featuring a T-cross plan called a *croce commissa* shows a Pisan-Romanesque style. Its importance stems from its excellent state of preservation, the absence of superfluous and major changes that might have severely altered the church's appearance and readability. The unified character of the structure is evidenced by the dimensional uniformity of the ashlars (medium size) (Coroneo, 1993).

The San Gregorio church in Solarussa (Figs. 1, 2) is the only religious monument existing in this style and this period in the Arboerese diocese. It dated to the 12th century and it is founded on a pre-existing medieval smaller single-nave church, presumably already dedicated the St. Gregory the Great. It was often mentioned as a domo in the Condaghe of Santa Maria di Bonarcado (Virdis, 2002). The church is indicated by V. Angius (Angius & Casalis, 1833-1856) as an ancient Camaldolese possession. The building is the result of workforce stemming from the construction yard of the Clesia nova in Bonarcado, as it can be inferred from the absolute nakedness of the walls, the sleek profile of the single windows and the relieving arch of the portal opened in the facade, defined in two colors with wedge ashlars (Coroneo, 1993).

At the time of the Giudici the St. Maria del Regno Basilica (Fig. 2) was the place of a Montecassino priory, mentioned in 1122 under the title of "Sancta Maria de Therco". Situated over an area (Fig. 1,) where recent archaeological excavations have revealed traces of a thriving late Byzantine domus, the church features a single nave and a transept, a gabled front and a characteristic deep red bulk counterbalanced by the white arches and the white panels with black inlays in the façade wall surface. In post-medieval times it was built a cover with a barrel vault (probably in the second half of the 19th century, as in many other similar cases dating the same moment) which caused severe static problems to the monument, since nobodyapparently considered the static requirements of the building and the load on the side walls, not large enough to support such a heavy load. The stone vault was later eliminated in favor of a new cover in wooden trusses.

Also known with the dedication to San Geminiano (also called San Gemiliano; Figs. 1, 2), possible corruption of the original Mamilianus (with reference to the homonymous monastery in the Tuscan island of Montecristo), the small, single nave church of Samassi stands today with its gray bulk, resulting from the use of the local freestone, renowned today for its industrial use and known as "Serrenti stone". The formal analysis, given the uncertainty of the surviving documentation, suggests a datation of the church to the second half of the 13th century (Coroneo, 1993). It is worth mentioning the re-use, in the jamb of the front portal, of a small marble pillar deriving from the Middle Byzantine liturgical furnishings (Coroneo, 2000), and another similar fragment reused in the North door, two indicators of a spolium showing a memory-function of the earlier Byzantine age, as it frequently occurs in the churches of southern Sardinia.

3. GEOLOGICAL SETTING

The geological background of Sardinia has been recently reviewed by several authors (e.g., Beccaluva et al., 2011; Carminati et al., 2010, 2012; Lustrino et al., 2009, 2011). Until the Oligocene, Sardinia–Corsica block was part of the southern European paleomargin. After a NE–SW striking rifting stage, mostly developed during the Oligocene, a ~55–60° Early Miocene counter-clockwise rotation separated the Sardinia–Corsica block from Europe (~22–15 Ma; Fig. 2; Carminati et al., 2010, 2012; Gattacceca et al., 2007, and references therein). The rotation of the Sardinia–Corsica block is related to the opening of the Ligurian–Provençal back-arc basin which led, during the Oligocene, to the rifting system between Sardinia-Corsica and Provence (Advokaat et al., 2014; Beccaluva et al., 1989, 2011; Burrus, 1984; Cherchi & Montadert, 1982; Coulon, 1977; Dostal et al., 1982), with formation in Sardinia of the Oligocene-Aquitanian rift called "Fossa Sarda", ~220 km long from north to south of island, and ~40 km wide (Cherchi et al., 2008; Faccenna et al., 2002; Lecca et al., 1997). The origin of the Oligo–Miocene extensional movements recorded in the western Mediterranean basins and the consequently Cenozoic Sardinian magmatism, have been related to the gravitative sinking of subducted oceanic lithosphere of the Tethyan Ocean (Ionian Sea) subducting northwestward since late Eocene, possibly coupled with an asthenospheric east-directed mantle flow (e.g., Alvarez et al., 1974; Beccaluva et al., 1989; Carminati et al., 2012; Gueguen et al., 1998).

Cenozoic magmatism is subdivided in two main following phases (Beccaluva et al., 1989, 2001, 2005a, 2005b, 2011; Lustrino et al., 2011): 1) orogenic magmatic activity developed mostly during Late Eocene–Miocene times (~ 38–15 Ma), where major and trace element indicators, as well as Sr–Nd–Pb–Hf–Os–O isotope, indicate complex petrogenetic processes including subduction-related metasomatism, variable degrees of crustal contamination at shallow depths, fractional crystallization and basic rock partial melting, with tholeiitic, calcalkaline, shoshonitic and ultrapotassic products (Lustrino et al., 2013); 2) anorogenic magmatism occurring during Late Miocene–Quaternary times (~ 12 to ~ 0.1 Ma), geochemically unrelated to active or recent subduction processes (e.g., Lustrino et al., 2007, 2009, 2011) with tholeiitic to Na-alkaline products. These two magmatic phases are diverse magmatic affinity and they are well-constrained in space and time and with regional tectonics (Beccaluva et al., 1989, 2005a, 2005b, 2011; Lustrino et al., 2011). According to Piromallo and Morelli (2003) and Spakman (1990), geophysical data indicate that flattened relics of the Cenozoic Apennine–Maghrebian subduction still exist below Sardinia and the Betic–Calatrava districts in southern Spain.

The orogenic igneous activity starts in Calabona area (N Sardinia, ~38 Myr; Lustrino et al., 2009) with a small microdiorite body. Then, late Eocene–Late Oligocene activity in Sardinia was sporadic, with a peak during the 22–18 Myr time range (Beccaluva et al., 1985; Carminati et al., 2012; Gattacceca et al., 2007; Speranza et al., 2002, and references therein). Rock mostly show a composition from intermediate to acid subalkaline. The products essentially are basaltic andesites, andesites, dacites and rhyolites, mainly resulting from explosive activity with mostly ignimbritic flows, rare mildly alkaline compositions (shoshonites and latites) and very rare basic–ultrabasic exceptions (e.g., basalts and picritic basalts of Montresta and Arcuentu, north-western and south-western Sardinia, respectively; Brotzu et al., 1997; Morra et al., 1997; Downes et al., 2001; Franciosi et al., 2003; Beccaluva et al., 2013). Trace element abundances and isotopic ratios of the less differentiated Late Eocene–Middle Miocene rocks led several authors to propose a derivation from a mantle wedge modified by slab derived fluids (e.g., Conte et al., 2010; Downes et al., 2001; Franciosi et al., 2003; Guarino et al., 2011; Lustrino et al., 2009; Mattioli et al., 2000; Morra et al., 1997).

The anorogenic igneous activity begins in the early Late Miocene and continues until the Pleistocene, with a peak concentrated around Middle–Late Pliocene (Beccaluva et al., 1985; Lustrino et al., 2000, 2004, 2007a, 2007b, and references therein). This magmatism, associated with the extensional tectonic, probably linked to the collapse of the Tyrrhenian area, started at 11.8 Ma in Isola del Toro (SW Sardinia) with an abrupt change in terms of chemistry, petrography and volcanological features compared with the older igneous activity (Lustrino et al., 2007a, 2009). After a quiescence of ~5 Ma, the volcanic activity mainly developed in the time span ~6 to < 0.1 Ma (Beccaluva et al., 1985a, 1989; Lustrino et al., 2007b; Peccerillo and Frezzotti, 2015), starting from the southern sector of Sardinia only (Capo Ferrato, Rio Girone and Guspini; Lustrino et al., 2000, 2007a) and continuing in other Sardinian areas. This volcanism overall produced mafic to silicic subalkaline, transitional to Na-alkaline rocks (sometimes with a K-affinity; Peccerillo and Frezzotti, 2015).

During the second period (~6 to < 0.1 Ma) the volcanic activity has often been fissural type, due to an extensional regimen that has reactivated faults of various orientations (Beccaluva et al., 1985). Volcanic cones (where present) and emission centers are often located along these faults and have given rise to limited lava flows (Logudoro), or extensive expansions (Campeda and Abbasanta plateaux), or domes with different composition (Montiferru (see Fedele et al., 2007) and Mount Arci volcanic complexes).

The erupted products are mainly alkaline basic rocks,with minor subalkaline basalts, and differentiated products along different areas of the island, covering an area of ~2000 km^2 (Beccaluva et al., 2011).

The Capo Ferrato products (5.3-4.9 Ma; Beccaluva et al., 1985) had a transitional character, the intermediate had an alkaline and subalkaline character, while the latter products (Logudoro < 0.5 Ma) had a purely alkaline character. Volcanic effusions have concentrated in particular areas such as Montiferro complexes (3.9 to 1.7 Ma), Mount Arci complex (3.8-2.8 Ma), Orosei Gulf (3.9-2.1 Ma), plateaux of Planargia-Campeda and Abbasanta (3.8-1.7 Ma), plateaux (Giare) comprised between Marmilla and Sarcidano (3.8-1.7 Ma) and finally, more recently, Logudoro (2.9-0.1 Ma) in the northern part of Sardinia (Beccaluva et al., 1985; Peccerillo and Frezzotti, 2015).

The three major volcanic evolutionary series were defined based on different patterns of major and trace elements (Peccerillo, 2005; Peccerillo and Frezzotti, 2015): i) a Na-alkaline serie, strongly undersaturated in silica, ranges from basanite-tephrite to phonolite in composition, with some of the most evolved rocks reaching a peralkaline composition (it only occurs in the volcanic complex of Montiferru, western Sardinia); ii) a moderate alkaline / transitionalserie, undersaturated silica in a non-critical way, with a Na- to mildly K-alkaline affinity, ranging from trachy-basalt to trachyte (with outcrops in several areas of Sardinia, including Mount Arci); iii) a subalkaline silica satured to silica-oversaturated serie (basalt - basaltic andesite - dacite - trachyte - rhyolite) with tholeiitic affinity (it occurs at Mount Arci).

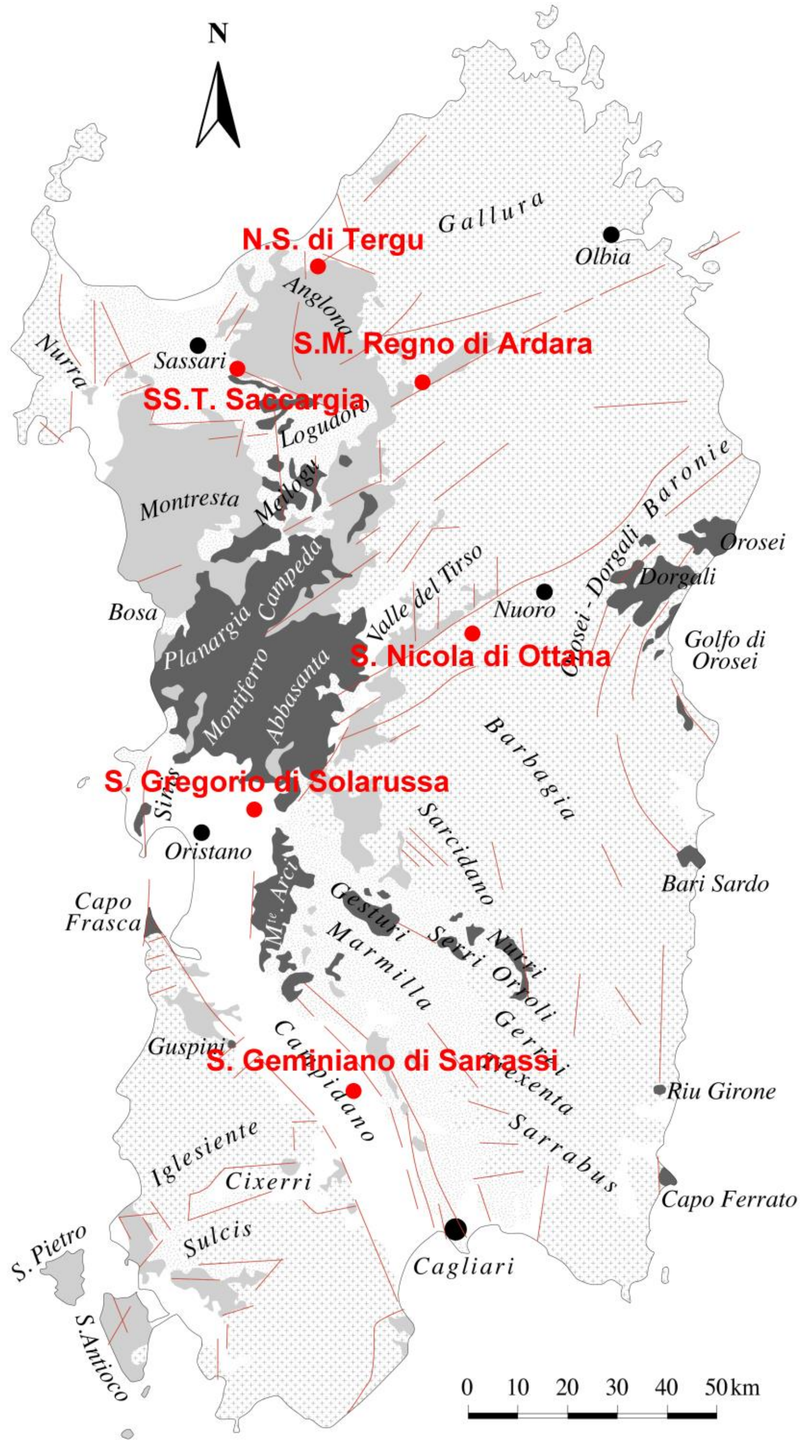

Figure 1. Schematic geological map of Sardinia with the localization of the Oschiri village and sector reported on the sketch map of Fig. 2. Legend of patterns and colours referred to lithologies: white = recent alluvial sediments; light grey = Oligo-Miocene volcanics including the Oschiri ignimbrites; dark grey = Plio-Pleistocene volcanics; stippled grey = Miocene marine sediments; grey crosses = Paleozoic crystalline basement and Mesozoic formations; red continuous and dashed lines = faults (after Columbu, 2017).

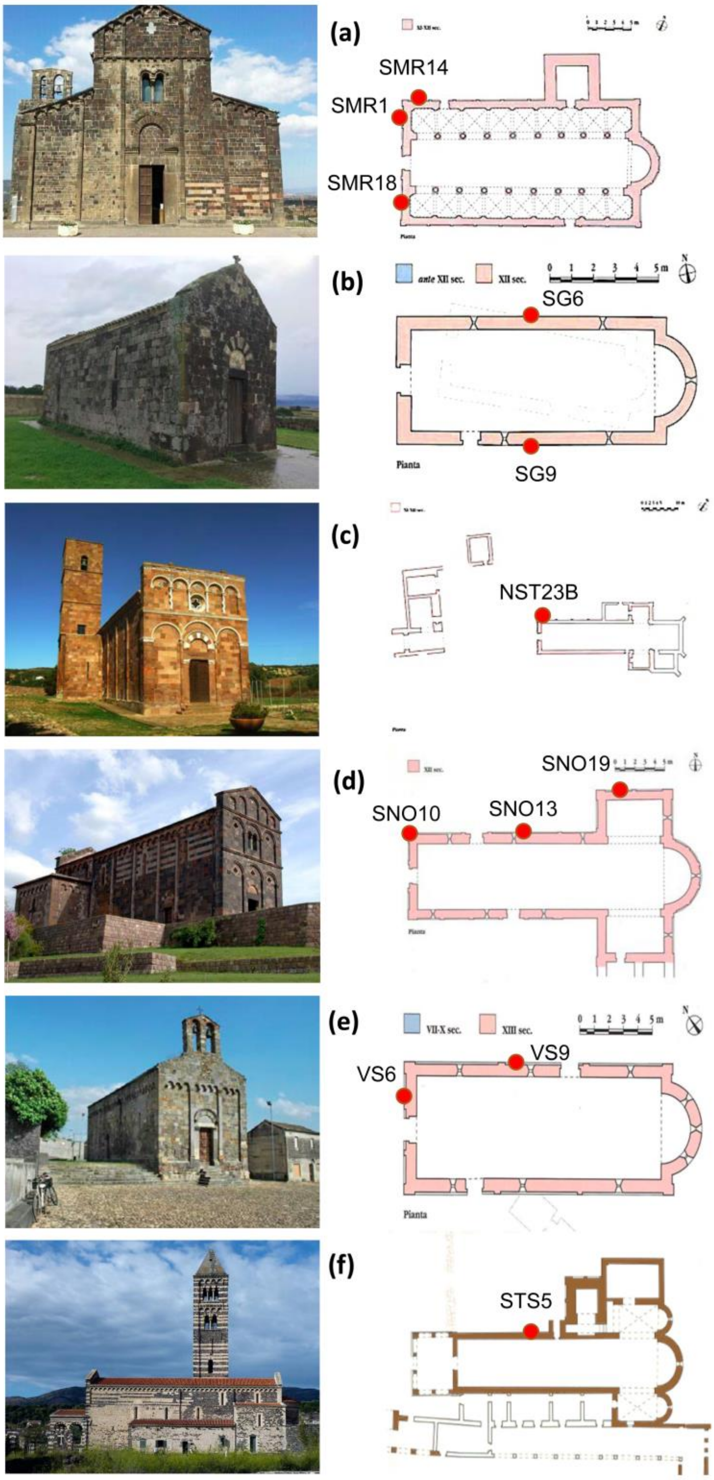

Figure 2. Studied Romanesque-style churches with sampling points of stones in the plans: (a) St. Maria del Regno (Ardara), (b) San Gregorio (Solarussa), (c) St. Maria (Tergu), (d) San Nicola (Ottana), (e) St. Geminiano (Samassi), (f) SS. Trinità di Saccargia (Codrongianos).

4. MATERIAL AND METHODS

4.1. *Sampling and features of volcanic rocks*

12 samples of volcanic rocks have been collected from the medieval churches of Sardinia. Following samples (Table 1; Figs. 3, 4) taken from the monuments have been studied and analysed: 5 samples of basalt rocks belong to the St. Maria del Regno (Fig. 4) and San Gregorio churches (Fig. 4), 1 sample of andesite from SS. Trinità di Saccargia Basilica (Fig. 3), 2 samples of andesitic-dacitic rocks from San Geminiano church (Fig. 3), 3 samples from San Nicola

church (Fig. 3), and 1 sample from rhyolitic rock from St. Maria of Tergu church (Fig. 4). The volcanics used to construct the studied monuments have local origins. The rocks of SS. Saccargia Basilica, St. Maria del Regno and San Gregorio churches belong to the Sardinian Late Miocene-Pleistocene volcanism.

The volcanics of Saccargia Basilica show geochemical characters typical of the Plio-Pleistocenic transitional and sub-alkaline series of north Sardinia volcanism (Beccaluva et al., 1981) with similar petrographic characteristics with those from the Meilogu sub-region (Logudoro). According to the classifications of De La Roche et al. (1980) and Middlemost (1975), the transitional volcanics from monument are mainly classified as K-trachy-andesite, while the subalkaline rocks as trachyte, latite and trachy-andesite (Columbu et al., 2018).

The volcanic rocks used to construct the St. Maria del Regno show different chemical characters, belonging to the alkaline, transitional and subalkaline series. The alkaline products (including the sample SMR 14 analysed in this paper) are mainly classified as trachy-basalt (Columbu et al., in progress). The transitional products (including the samples SMR 1 and SMR 18) are classified as latit-basalt and latit-andesiti with Na-affinity, and trachy-basalts e trachy-andesites with K-affintiy. In the monument there are also subalkaline volcanics with have a latit-andesite and latite composition, SiO_2 about 54%, and alkali-sum of about 7%.

The San Gregorio church, located on central Sardinia, was constructed with transitional and subalkaline andesitic rocks. The transitional products (including the sample SG 9) are mainly classified as lati-andesites (Na), basaltic-andesites (Na), latites (Na), trachy-andesites (K). The subalkaline products (including the analysed sample SG 6) are classified as lati-andesites and andesite with Na-character (Columbu et al., in progress).

The volcanic rocks used to construct the church of San Geminiano, San Nicola and St. Maria of Tergu churches belong to the Late Eocene-Miocene volcanism of Sardinia. The volcanics of San Geminiano, outcropping in the Serrenti area, mainly show a composition from andesitic (to trachy-andesitic) to dacitic. In the *San Nicola* were used local ignimbrites mainly rhyodacitic and rhyolitic in composition. There are a wide variety of stone colours: from blackish to orange-pink. The St. Maria of Tergu was constructed with volcanics belong from outcrops distant about 2 km from the church. with a main rhyolitic composition (Columbu et al., in progress).

It should be noted that not all analysed samples (Columbu et al., in progress) from the monument have characters of unaltered rocks. Thus, it is necessary to consider the possibility of contamination of the samples by binders used in the construction of churches. Several samples therefore show the presence of normative corundum, generally indicative of poor freshness of rock or crustal contamination.

4.2. *Analytical methods*

Each sample taken from the monuments has been studied to define any chemical/physical/mineralogical transformation on the surface of the rock, to define the chromatic alteration of the rock-surface (also by a comparison of colorimetric data measured on the substrate and outer surface), chemical reactivity with the mortar binder of the plasters.

The selected stone materials were studied and analysed by different methods: macroscopic observation (according to the Recommendations NORMAL 1/88), colorimetry, stereomicroscope, polarizing microscope, X-ray powder diffraction (XRPD).

Colorimetric analysis is a fundamental prerequisite in classifying the surface type. It was carried out according to the Italian Cultural Heritage Code UNI EN 15886: 2010; Recommendations NORMAL 43/93, 1993), using a Minolta Chroma Meter CR-200 Colorimeter. It consists of a measuring head connected to a computer equipped with a display and a printer. The measuring space has an area of 8 mm and works with diffused light. Before the measurement is performed, the instrument must be calibrated on a standard reference white and as standard as close as possible to the colour to be measured. The measurement area has been chosen so that it is representative of the material being analysed, avoiding particular areas (e.g. veins, macropores, etc.). The reflection measures are influenced by the surface roughness, so the surface of the sample to be analysed has been smooth and flat. For each measurement point, at least three determinations were made, then expressed the mean value. The colour data were expressed in Table 2 according to the standards of the "Munsell" tables. This system is a colour space used as an international standard to define colours according to Hue, Brightness (Value) and Saturation (Chroma). Colour characterization is done by directly comparing the sample with Removable Tiles belonging to the Munsell Book of Colour. The colour is encoded by indexes, written behind the coloured tile, consisting of a number (2,5-5-7,5-10) and one or two uppercase letters (RYGBP-YR-GY-BG-RP) indicating the tint, followed by two numbers separated by a bar whose first number indicates the brightness and the saturation. The colours of analysed sample surfaces have been expressed also as CIE L* a* b* coordinates (Table 2), frequently used in the chromatic characterization of lithoid materials (e.g., Cultrone and Sebastián, 2009; De Bonis et al., 2017; Di Benedetto et al., 2015). Further more, the measure of change (ΔE) in visual perception of two colours determined on the rock substrate and outer patina has been calculated. The ΔE value has been calculated by CIE 76 formula, according to the International Commission on Illumination - Commission Internationale de l'Eclairge (CIE) recommendations (1976) and to Robertson (1977). Then, to define also the mineralogical composition, texture and microstructure characteristics, petrographic classification of all the samples were studied with optical polarized microscope Leitz Wetzlar on polished thin sections.

Initially, the rock samples taken from the monuments are studied through the stereomicroscope in reflected light, to select the most representative fragments to work for the thin sections. Subsequently, the sample fragments were worked and embedded in colourless epoxy resin to produce thin sections up to thicknesses of 30 microns and to define the mineralogical composition, texture and microstructure characteristics, petrographic classification with optical polarized microscope Leitz Wetzlar. Observations on the polarizing optical microscope of thin sections are also intended to detect the presence of traces of pigments in the horizons of alteration and to reconstruct the microstratigraphy present on the film sample. For each thin section analysis, the description of what was observed was reported, correlated by extensive photographic documentation (Table 2; Figs. 5, 6, 7).

The stone samples from the monuments were analysed by XRPD methods to determine the crystalline phases. XRPD was carried out by using the Philips X'Pert PRO PW 3040 instrument, equipped with solid state detector X'Celerator PW 3015. The applied filament-anticathode potential difference is 40 kV, and the speed of scanning, representing the rotation speed of the detector, is 1.6°/min. The angular range being investigated is always between 2° and 70° (2θ). In total, more than 20 measures were performed.

Each sample, manually grinded in a mortar, was analysed on the outer original stone surface (with brown ochra patina) and on a portion of the "fresh" stone surface that was specially cleaned. Analysis of inner side surface is useful to define the original composition of rocks, while analysis of outer side surface is useful to highlight any compositional difference with the substrate and the presence of alteration film or any ancient treatment used in ancient time to colour or to protect or preserve the stone from the monument.

Table 1. List of samples: STS= SS. Trinità di Saccargia (Codrongianos), VS = St. Geminiano (Samassi), SNO= San Nicola (Ottana), SG = San Gregorio (Solarussa), SMR= St. Maria del Regno (Ardara), St. Maria (Tergu).

Sample	Substrate	Church	Sampling point	Size (mm)	Description
STS5	Trachy-andesite	Santissima Trinità di Saccargia (SS)	West – side of monument	3,5*3	Mortar layer > 4mm thickness. The outer has dark color for alteration phenomena
VS6	Pyroclastite	San Geminiano di Samassi (CA)	Facade of monument	4,5*3	Scratch / crust of gray-beige color alteration
VS9	Pyroclastite	San Geminiano di Samassi (CA)	East – side of monument	2,6*2,3	Crust of gray-beige color alteration
SNO10	Pyroclastite	San Nicola di Ottana (NU)	North – side of monument	1,6*1,8	Brownish-reddish crust
SNO13	Pyroclastite	San Nicola di Ottana (NU)	West – side of monument	1,3*0,7	Iron oxide alteration crust
SNO19	Pyroclastite	San Nicola di Ottana (NU)	North – side of monument	2,7*3	Ocraceous patina
SG6	Basalt	San Gregorio di Solarussa (OR)	North – side of monument	3*1,5	Upper layer with altered substrate, probably due to oxidation phenomena
SG9	Pyroclastite	San Gregorio di Solarussa (OR)	South – side of monument	1,5*3	Ochre color film
SMR1	Basalt	Santa Maria del Regno di Ardara (SS)	West – side of monument	3*4,5	Outer ochre film, clay crust inside
SMR14	Basanite	Santa Maria del Regno di Ardara (SS)	West – side of monument	2,3*2,5	Ochre color alteration crust
SMR18	Basalt	Santa Maria del Regno di Ardara (SS)	West – side of monument	3*2	Rust-colored alteration crust
NST23B	Pyroclastite	Nostra Signora di Tergu (SS)	West – side of monument	4,2*2,5	External ochre-beige film, intermediate layer with efflorescence. The inside side looks healthy

Figure 3. Monument samples (left coloum: external surfaces; in the middle: internal surfaces; rigth: side surfaces): STS = SS. Trinità di Saccargia (Codrongianos), VS = St. Geminiano (Samassi), SNO= San Nicola (Ottana). Note: the STS5 sample reported in the photo is a fragments of plaster originally adherent to the trachy-andesite rock substrate.

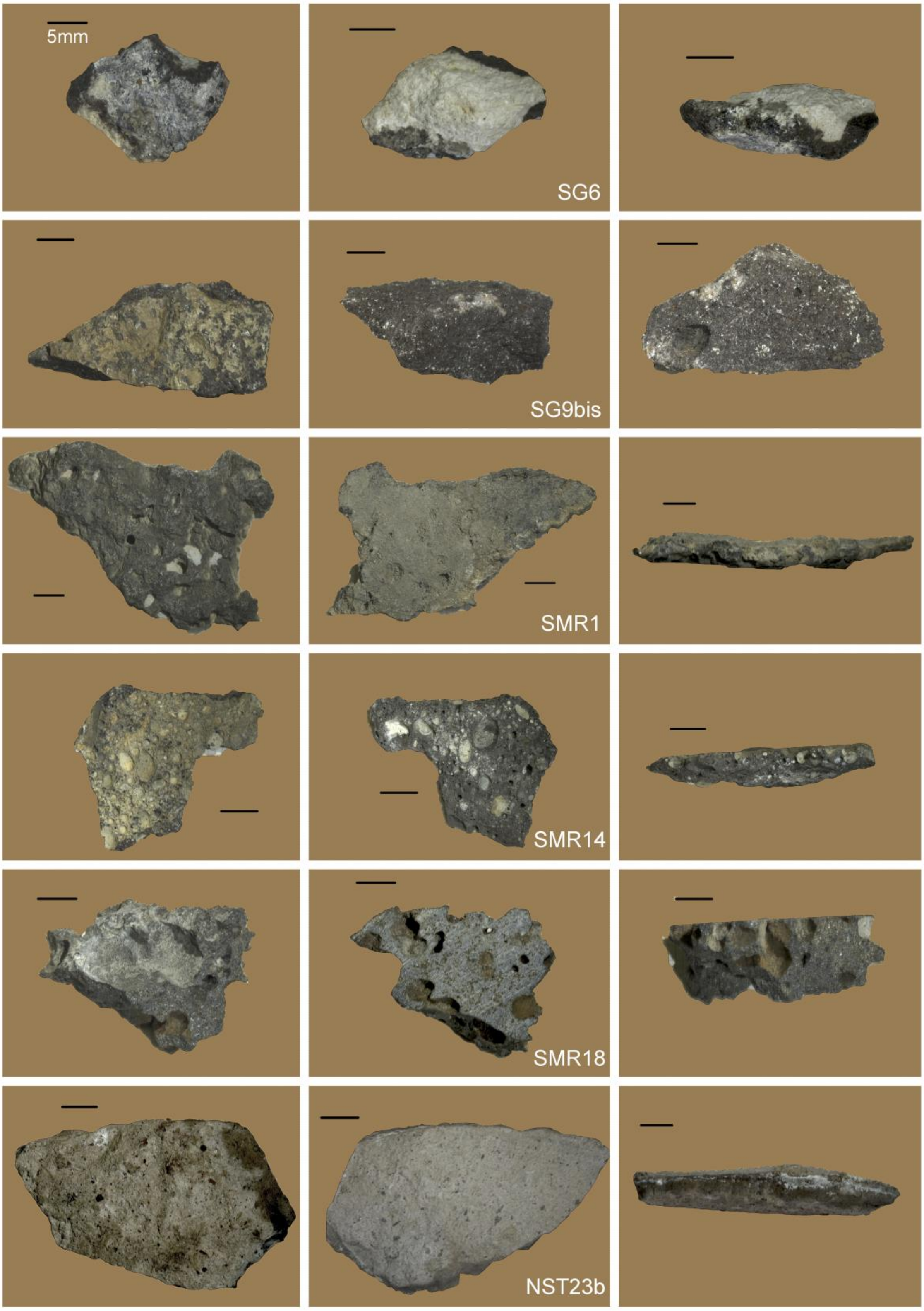

Figure 4. Monument Samples (left coloum: external surfaces; in the middle: internal surfaces; rigth: side surfaces): SG = San Gregorio (Solarussa), SMR= St. Maria del Regno (Ardara), NST = Nostra Signora (Tergu).

5. RESULTS AND DISCUSSION

5.1. Petrographic features of volcanic rocks

The mineralogical-petrographical analysis by OM analysis on the sampled rocks from the six medieval Romanesque churches highlights the presence of six main volcanic lithologies (Figs. 5, 6, 7). Data are reported in Tables 2.

The basalt rocks used to construct the SS. Saccargia Basilica have similar petrographic characteristics with those from the Meilogu sub-region (Logudoro; Columbu et al., 2018).

The analysed sample (i.e., STS 5) belongs to the vacuolar facies. It shows an oligoporphyric structure with rare phenocrysts (~2%) of iddingsitic olivine and plagioclase. The groundmass is holocrystalline with fluidal texture of plagioclase and clinopyroxene microliths. The volcanic samples from the outcrops show similar from the Meilogu sub-region sometimes also include rare allotigen micritic carbonate elements. According to the normative mineralogy (Columbu et al., 2018), the normative amount of corundum (ranging from 0.4 to 3.5%) indicates the presence of alteration processes or contaminations with mortars of monument.

The basalt rocks (samples SMR 1 and SMR 18) from the St. Maria del Regno show similar petrographic features. The structure is weakly porphyric, with a porphiric index (I.P.) about 7-8%, for olivine crystals, more rare clinopyroxene and subordinate plagioclase with rare individuals, but of fair size; it has a high colour index (about 45%). The matrix is pilotassitic for the predominance of glass and there are also plagioclase microliths, clinopyroxene and granules of oxide opaques (with doubtful-generation). In some portions of the section the groundmass is from strongly to totally hyaline. The sample SMR14 is strongly vitreous, finely vesiculated; the phenocrystals, represented by olivine and clinopyroxene, are rare and small in size. The matrix consists of abundant dark blackish, tachilitic glass, in which rare plagioclase and clinopyroxene microliths are immersed. The olivine phenocrystals show extensive red edges of alteration, while in the center, in the relatively healthy nucleus, the principles of alteration highlight the traces of the typical flaking planes according to the forms {010} and {100}.

The basaltic-andesitic rocks (including the SG9 sample) of San Gregorio church are somewhat homogeneous for structural, textural and parageneretic characters, with a not uniformly distributed bubbleiness, slightly flattened according to the flow lines. The samples have a porphyric structures (with I.P. = 10% approximately) for olivine phenocrysts, up to about 2 mm in size, with euhedral habit and only the larger fenocrystals maintain a still healthy core and they are only altered in the edges (in iddingsite). The other phenocrystals are plagioclases with a homogeneous euhedral habit. The groundmass is hypocrystalline and consists of plagioclase and clinopyroxene microliths. Interstitial glass is not abundant. Texture varies from locally intersertal to weakly fluidal, tendentially pilotassitic. Among the opaque minerals is the simultaneous presence of magnetite and ilmenite. The sample SG6 shows a scoria facies, characterized by a high vesicularity. The olivine and plagioclase phenocrysts are less frequent and the glass is abundant in the groundmass in which rare plagioclase and clinopyroxene microliths also appear. The texture is fluidale, more precisely ialopitica, for the abundant presence of glass.

The volcanic rocks used to construct the church of San Geminiano, with a mainly dacitic composition,(e.g., sample VS 6) shows a porphiric structure (I.P. about 15%) for phenocrystals of opaques (Ti-magnetite, magnetite), plagioclase (with composition from andesine to oligoclase), orthopyroxene, rare quartz. The groundmass mainly consists and plagioclase microliths.

The ignimbrites used to construct the *San Nicola* church, mainly rhyodacitic in composition, show a wide variety of colors: from blackish to orange-pink. Microscopic observations by polarizing microscope show isotropic texture, and presence of high amount of lithics, hypoialine groundmass and marked isotropic textures (Fig. 6). The structure is porphiric (I.P. = 18-23%) for opaque phenocrysts, clinopyroxene, amphiboles (i.e., green hornblende), plagioclase and quartz. The colour index ranges from 5 to 7. Among the phenocrysts, the opaque minerals are round-shaped and somewhere altered. The green hornblende shows anhedral gown. The groundmass is hypo-hyaline and consists of opaque crystals (possibly magnetite), K-feldspars, quartz, anhedral microliths of plagioclase and clinopyroxene.

The rhyolitic pyroclastic rocks of St. Maria of Tergu show a porphiric structure for phenocrystals of sanidine and plagioclase with euhedral habit. Groundmass varies from vitrophiric to pseudofluidal where are present plagioclase and opaques, where are also present pumices from subcircular to flattened to strongly flattened (in more welded facies).

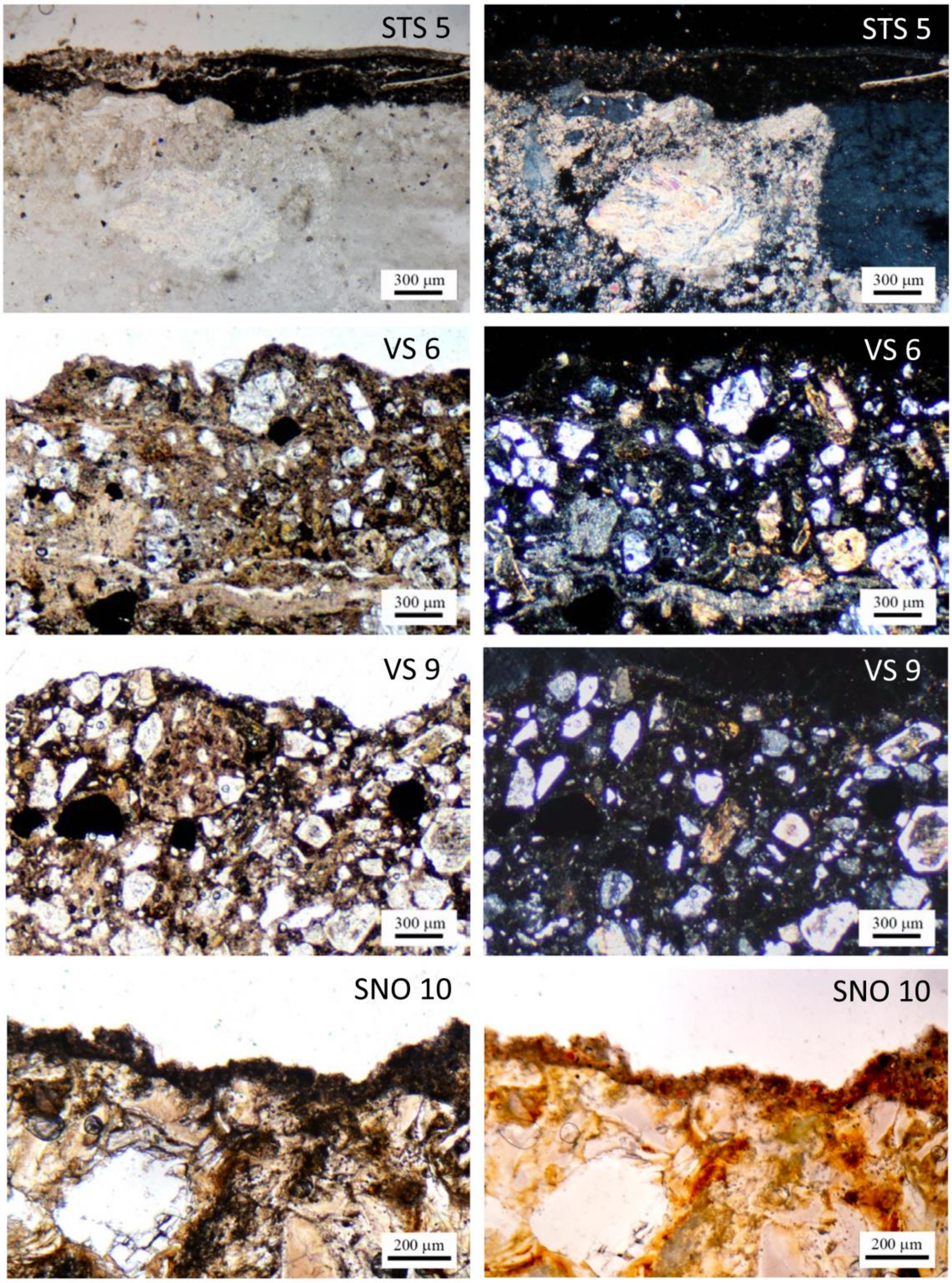

Figure 5. Microscopic features (Left: transmitted plane polarized light - Right: STS5, VS6, VS 9, crossed polarized light ; SNO 10, reflected light darkfield with bright background) of samples taken from the Santissima Trinità di Saccargia Basilica (STS 5), San Geminiano church of Samassi church (VS 6, VS 9) and San Nicola of Ottana Basilica (SNO 10).

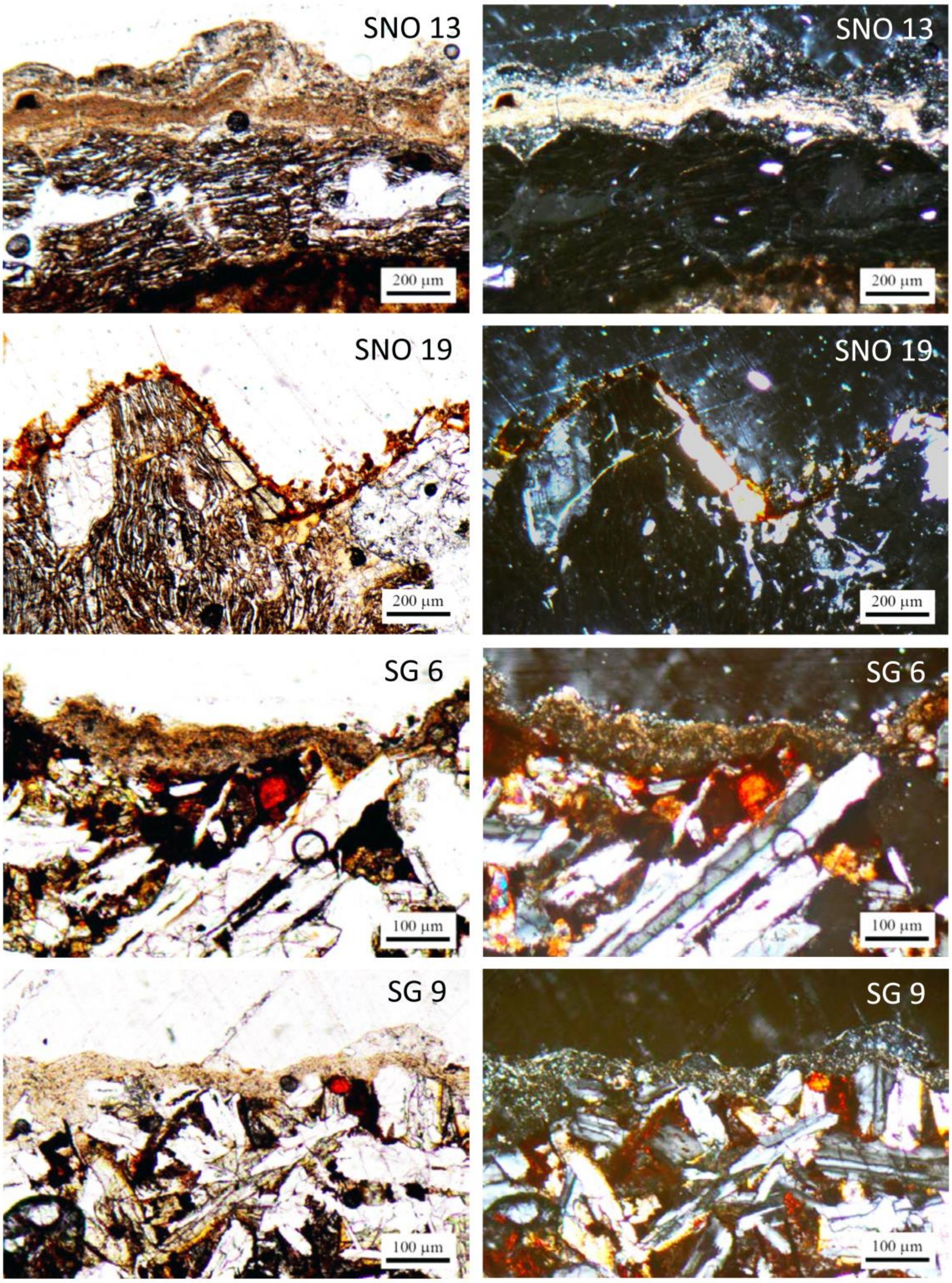

***Figure 6.** Microscopic features (Left: transmitted plane polarized light; Right: crossed polarized light) of samples taken from the San Nicola of Ottana Basilica (SNO 13, SNO 19) and San Gregorio church (SG6, SG 9).*

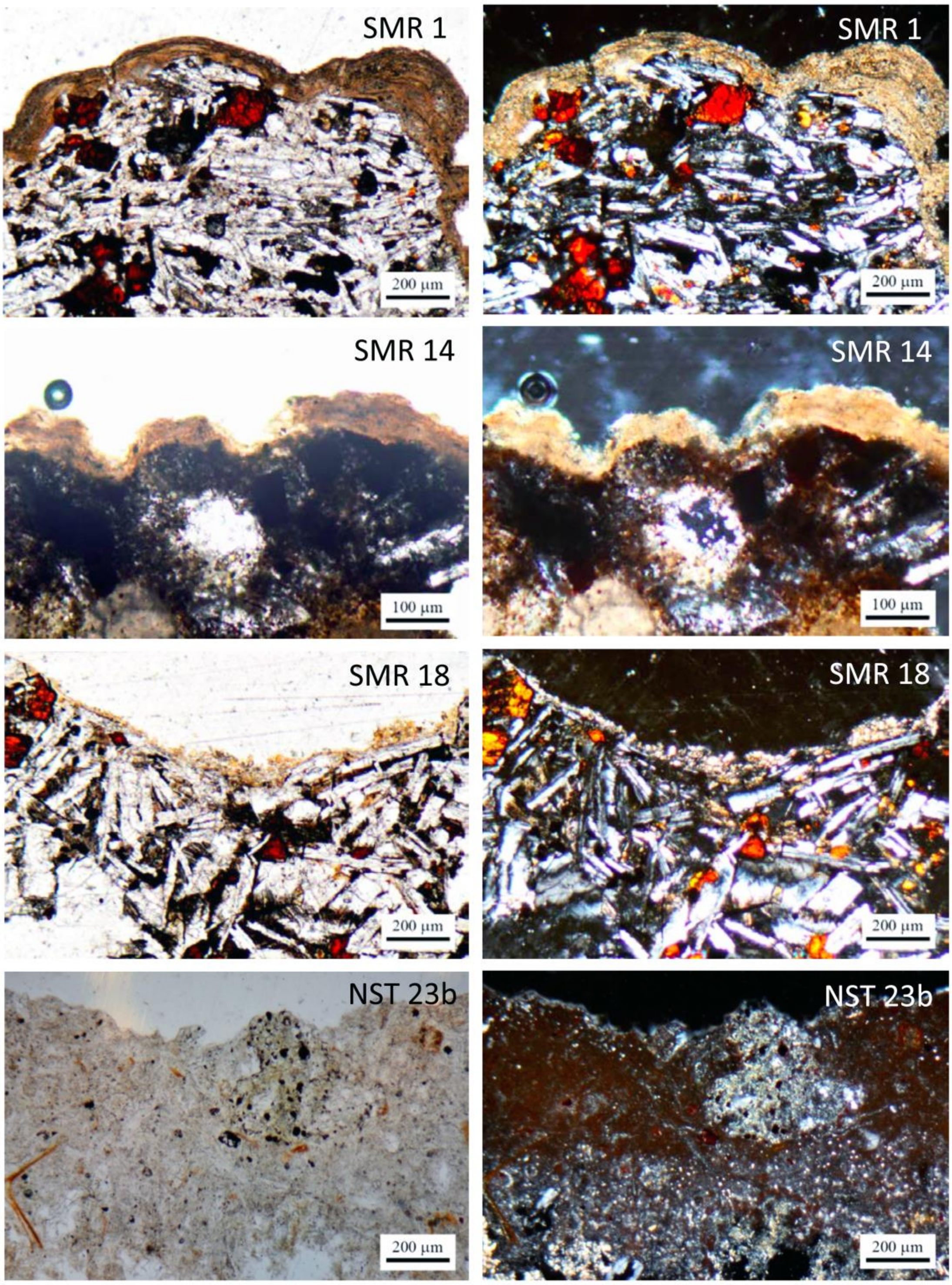

***Figure 7.** Microscopic features (Left: SMR1, SMR 18, transmitted plane polarized light; SMR 14, tppl plus reflected light; NST 23b, reflected light darkfield with bright background - Right: SMR1, SMR 18, polarized light; SMR 14, NST 23b, cp plus reflected light) of samples taken from the St. Maria del Regno of Ardara Basilica and Nostra Signora di Tergu churches.*

5.2. *Composition and micro-stratigraphy of alteration deposition*

Microscopic analysis on the sample STS 5 coming from Saccargia Basilica (Tabs. 1, 2) highlights a complex micro-stratigraphy, with the presence of two ancient mortar layers with different compositions and a third black layer:

1) the *arriccio* plaster layer (originally adherent to the rock substrate; Figs. 3, 5) consisting of lime binder and quartz-sandy aggregate with size frequently lower of 2 mm;

2) the finishing layer (with thickness from 400 to 700 µm, Fig. 5), consisting of a finely calcitic aggregate), pigmented with abundant black-carbon particles; given the greater size of the calcite crystals (from 10 to 80 µm) with respect to the size of binder calcite (frequently < 1 µm), it' is probable that they belong to crushed marble;

3) the third black layer, with variable thickness (from 50 to 400 µm, Fig. 5). The XRPD analysis (Fig. 8) on this black layer shows the mineralogical composition of previous layers observed in microscopic analysis, represented mainly by calcite and quartz, together traces of Ca-oxalate (i.e. weddellite).

Moreover, on the surface of sample there is a thin deposition layer (with size < 80 µm) with the presence of gypsum (and also halite) due to the sulphation processes of plaster binder. (Fig. 5). Due to a completely different composition of *arriccio* layer (characterised by a light colour) and outer black layer, the sample STS5 shows the greater ΔE value (17.4; Table 2) with respect to all other samples.

The samples (VS 6 and VS 9) of dacitic rocks coming from the church of San Geminiano of Samassi (Tabs. 1, 2) show a chromatic alteration of the rock with a change between the substrate and the surface with a ΔE value between 4.1 (sample VS 6) and 8.3 (VS 9; Table 2), typical of the intermediate-acid volcanic rocks. In some case this chromatic change probably is due to the oxidation processes or any chemical/physical transformation on the surface of the volcanic rock (i.e., leaching of silica and alkali, devitrification of glass). Microscopic analysis of micro-stratigraphy on thin section (Fig. 5) shows the presence of ancient residual lime-plaster adherent to the rock substrate. XRPD analysis carried out on this plaster (Fig. 8) shows the presence of quartz (belong to the aggregate), calcite and plagioclase (Table 2). Probably this latter belongs to the rock volcanic substrate.

Two basalt samples from the church of San Gregorio (SG 6, SG9;

2) show yellowish and ochra colours on the surfaces with different characteristics with respect to the black rock substrate, as evidenced by high ΔE values (about 10.21; Table 2). The yellowish surface area of sample SG 6(Fig. 6), consisting of plagioclase, carbonate-hydroxy-apatite (Table 2; Fig. 9), corresponds to a thin layer with a medium thickness of 60 µm, probably lime, in which there are sporadic iron oxides. The ochre surface area of sample SG 9, consisting of quartz, plagioclase and sporadic iron oxides, corresponds to a layer of residual lime plaster with a maximum thickness of 180 µm (Fig. 6).

Three basaltic samples (SMR 1, 14, 18) taken from the Basilica of St. Maria del Regno of Ardara show different case studies. The sample SMR 1 has a lime layer with a thickness between 50 and 250 µm (Fig. 7), containing small granules of iron oxides (and other with black colour). The ochre surface area consists of calcite, quartz, plagioclase, traces of Ti-oxides (i.e., Ti-magnetite) and carbonate-hydroxy-apatite (Table 2; Fig. 10). The mean of ΔE value is 8.7. On the surface of sample SMR 14 there is a thin carbonate layer with thickness from 10 to 100 µm (Fig. 7). The yellowish surface area consists of Ca-oxalate (i.e., whewellite), quartz, gypsum and carbonate-hydroxy-apatite (Fig. 10). The substrate shows good adherence with the lime, due to: i) the presence of micro-vesicles and a wrinkled surface (which improving the mechanical griping of stone with the mortar); ii) a good chemical reactivity between the carbonate-binder and the glassy matrix of this rock (Fig. 7). Sample SMR 18 shows a whitish surface, with presence of residual plaster with plagioclase (Fig. 10) . On the surface of sample there is gypsum precipitation and new re-crystallization with a maximum thickness of layer about of 60 µm (Fig. 7).

The rhyodacitic rocks taken from the San Nicola of Ottana church (samples SNO 10, 13, 19; Tabs. 1, 2) show chromatic alteration processes on the surface (Fig. 3), with different colours: from yellowish to ochra to brown (Table 2). The ΔE value varies from 2.9 (in sample SNO 13) to 5.7 (SNO 19) to 12.7 (SNO 10) where is the maximum contrast between the substrate and the brown patina.

By microscopic analysis, sample SNO 10 (Fig. 5) shows the presence of a deposition layer with thickness of 150 µm, consisting of quartz, plagioclase and traces of talcum, which origin is uncertain, probably belonging to atmospheric or biodeteriogen particles. Sample SNO 13 (Fig. 6) shows a lime layer (with thickness from 60 to 200 µm) on which there is another layer of plaster with abundant atmospheric particles (Fig. 9) and secondary mineral of alteration (i.e. illite, see XRPD data, Table 2). The presence of clay-minerals negatively affects the rock (McGreevy and Smith, 1984; Franzini et al., 2007). In fact, beying negatively charged crystals, clay phases are subjected by osmotic swelling (Sebastian et al., 2008) or, in other cases, they can experience intracristalline swelling due to their hydration (Moore and Reynolds, 1997). In this latter case, the basal spacing of crystals can arrive to about 70% with water or humidity saturation (Colas et al., 2011; Wangler and Scherer, 2008). Thus, on function of physical and mechanical features of rock (e.g., elastic modulus; Jimenez-Gonzalez et al., 2008), the cyclic swelling of clay minerals in the outer portion of rock leads to dimensional variations with exfoliation or flaking of the stone (Berthonneau et al., 2012).

Sample SNO 19 (Fig. 6) shows the presence of thin layer with thickness of 30 µm, made up of iron oxides penetrating inside the substrate fractures (Fig. 9). XRPD analysis (Table 2; Fig. 9) shows the presence of rock mineralogy (e.g., plagioclase). The chemical transformation processes on these volcanics is more concentrated inside fractures and fissures of the rock sub-parallel to the outer facade, where, in advanced alteration degree, clay minerals were found. Due to a lower welding degree and different geochemical and petrographic features with respect to the basalts of other churches, also show physical alteration. However, they show a good physical-mechanical resistance, the decay processes (i.e., exfoliation, flaking) are not frequent.

The pyroclastic rhyolitic sample (NST 23b) coming from the church of St. Maria of Tergu not shows the presence of any crust or deposition layer on the stone (Fig. 7). The surface shows ochre colour and by XRPD analysis, it consists of feldspar (i.e., sanidine), quartz, cristobalite, traces of gypsum and Ca-oxalate (i.e., weddellite), Fig. 10. In these rocks it's very difficult observe any chemical or mineralogical alteration process on the surface because this kind of acid rock shows high porosity (generally > 30%; Columbu et al., in progress), thus it is easily degradable under physical point of view (Columbu et al., 2014) with loss of material on the surface.

Table 2. Colorimetric data, with chromatic change (ΔE) between substrate and surface of samples, paragenesis of rocks by microscopic analysis and results of XRPD analysis of all analysed samples with microstratigraphic description.

Sample	Colorimetric H/V/C coordinates	Colorimetric CIE L* a* b* coordinates	ΔE XIE 76	Paragenesis of rock substrate	XRPD analysis on alteration crust	Microstratigraphy
STS5	Patina: 10yr/5,2/0,2 Substrate: 9,8yr/7,1/1,3	53,62-0,27-1,31 72,58-1,84-8,17	17,44	Ti-magnetite magnetite iddingsitic olivine plagioclase clinopyroxene	Black surface area, corresponds to the layer "c" of the section: calcite, quartz, gypsum (traces) and weddellite (traces)	Pigmented with abundant black carbon lime mortar with sandy aggregate (*intonachino*). The thickness of the layer varies from 50 to 400 µm. Level of sulphation on the surface with variable thickness from a few microns to a maximum of 80 µm.
VS6	Patina: 0,6yr/5,5/082 Substrate: 0,8yr/5,9/1	56,67-3,02-2,65 60,70-3,71-,3,33	4,14	Ti-magnetite magnetite plagioclase orthopyroxene quartz	Gray-beige surface, rock: quartz, albite and calcite (traces)	Substrate: pyroclastite, absence of alteration layer.
VS9	Patina: 9,7yr/5,6/0,2 Substrate: 9,5yr/6,2/1,1	57,68-0,33-1,26 63,70-1,78-6,86	8,35	Ti-magnetite magnetite plagioclase quartz orthopyroxene	Beige surface area, rock: quartz, albite and calcite (traces)	Substrate: pyroclastite, absence of alteration layer
SNO10	Patina: 5,1b/8,3/1,6 Substrate: 9,6b/9,6/2,7	84,26-(-4,86)-(-4,01) 96-(-6,31)-(-8,66)	12,71	magnetite quartz plagioclase sanidine	Brown surface area, rock: quartz, plagioclase and talc (traces)	a) Substrate: rhyodacitic pyroclastite b) average level of 150 µm of atmospheric and rare biodeteriogen particles.
SNO13	Patina: 07,1yr/4,2/0,2 Substrate: 9,0yr/4,3/0,5	43,30-0,58-1,15 44,34-1,05-3,14	2,94	magnetite quartz plagioclase sanidine	Yellowish surface area, rock: plagioclase and illite (traces)	a) Substrate: rhyodacitic pyroclastite b) Lime layer, thickness from 60 to 200 µm. Above this layer there is a level of gypsum with abundant atmospheric particles.
SNO19	Patina: 7,5yr/4,6/0,9 Substrate: 8,1yr/4,1/0,5	47,45-2,45-5,1 42,26-1,30-2,99	5,71	magnetite quartz plagioclase sanidine	Ochraceous surface area, rock: anorthite	a) Substrate: rhyodacitic pyroclastite b) Layer thickness of 30 µm, made up of iron oxides penetrating inside the substractes fratcures.

SG6	Patina: 7,6yr/5,4/1,6 Substrate: 3,1yr/4,5/1,0	55,65-3,85-8,82 46,42-3,71-4,45	10,21	magnetite quartz plagioclase	Yellowish surface area, corresponds to the layer "b" of the section: anorthite, carbonate-hydroxy-apatite	a) Substrate: basalt; b) Layer with a medium thickness of 60 μm, probably lime, with sporadic iron oxides.
SG9	Patina: 7,0yr/4,9/1,8 Substrate: 0,6yr/4,2/0,8	50,55-4,45-9,86 43,30-3,51-2,75	10,20	magnetite quartz plagioclase	Ochre surface area, corresponds to the layer "b" of the section: quartz, albite and gypsum	a) Substrate: basalt b) Layer with a maximum thickness of 180 μm likely to be lime inside which there are sporadic iron oxides.
SMR1	Patina: 9,0yr/4,7/0,8 Substrate: 8,4yr/5,3/1,3	48,49-1,57-4,92 56,64-2,78-7,51	8,63	quartz Ti-magnetite plagioclase	Ochre surface area, corresponds to the layer "b" of the section: calcite, quartz, plagioclase, Ti-oxide (traces) and carbonate-hydroxy-apatite	a) Substrate: basalt; b) Lime layer of thickness between 50 and 250 μm. The layer contains small granules of iron oxides and blacks, probably due to the part of the substrate.
SMR14	Patina: 8,2yr/5,5/2,0 Substrate: 8,6yr/5,3/0,8	56,67-4,11-11,66 54,64-1,74-4,62	7,70	quartz Ti-magnetite plagioclase	Yellowish surface area, corresponds to the layer "b" of the section: whewellite, quartz, gypsum and carbonate-hydroxy-apatite	a) Substrate: basalt with low degree of crystallinity, with small plagioclase crystals and pyroxene; b) carbonate layer thickness of 10 to 100 μm on the exterior edges of the pores.
SMR18	Patina: 9,2yr/5,3/0,7 Substrate: 8,6yr/4,2/0,5	54,64-1,26-4,28 43,30-1,28-2,98	13,40	quartz Ti-magnetite plagioclase	Whitish surface area, corresponds to the layer "b" of the section: plagioclase and gypsum	a) Basalt; b) Precipitation and crystallization (gypsum) on the surface with maximum thickness of 60 μm.
NST23B	Patina: 4,1yr/5,7/1,8 Substrate: 4,2yr/6,8/1,5	58,69-5,47-8,48 69,63-4,27-6,92	11,12	sanidine quartz, plagioclase	Ochre surface area: sanidine, quartz, cristobalite, gypsum (traces) and weddellite (traces)	Substrate: rhyolitic pyroclastite. Absence of alteration layer.

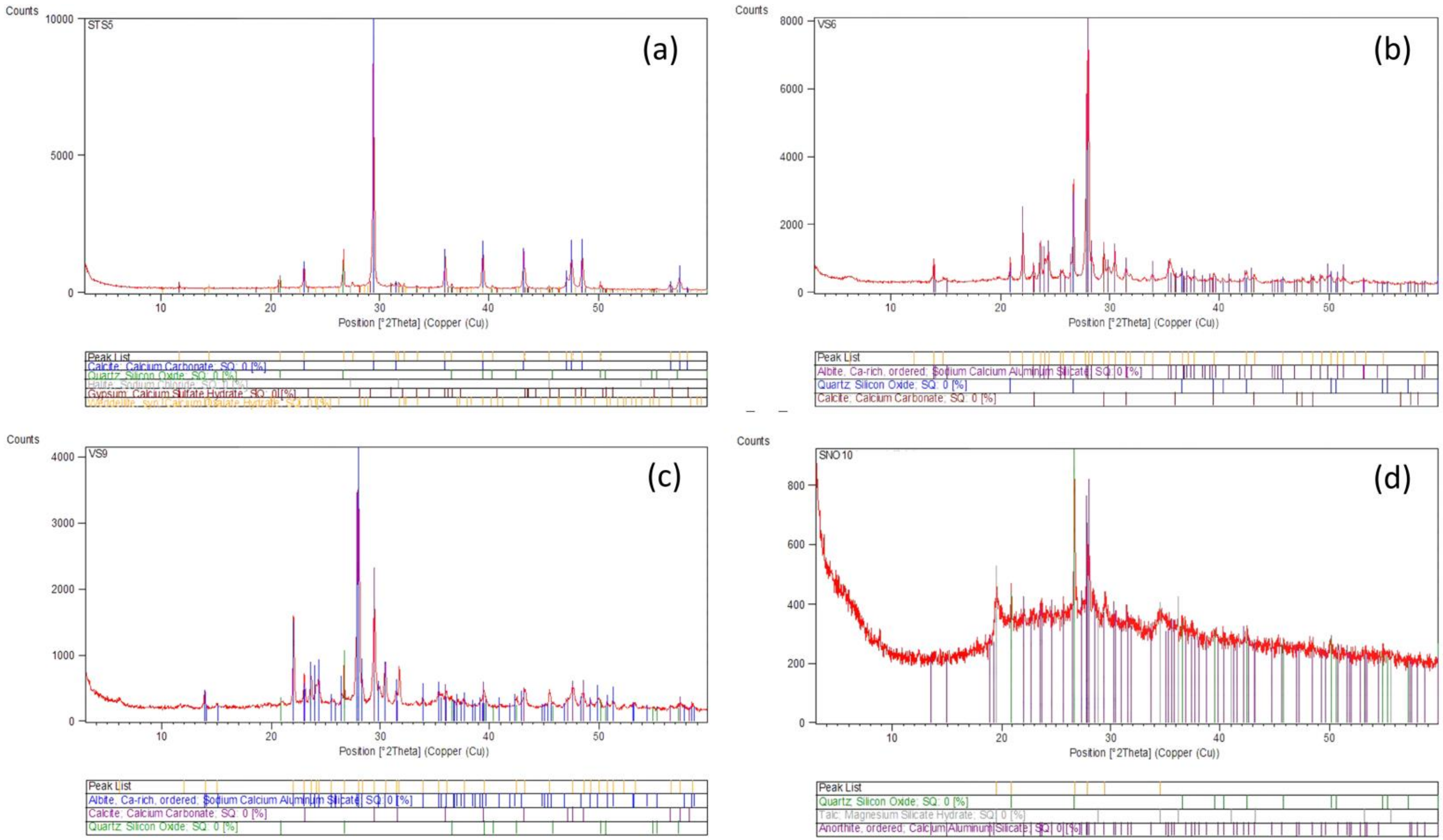

Figure 8. Results of XRPD analysis of samples STS 5 (a), VS 6 (b), VS 9 (c), SNO 10 (d), taken from the Romanesque churches.

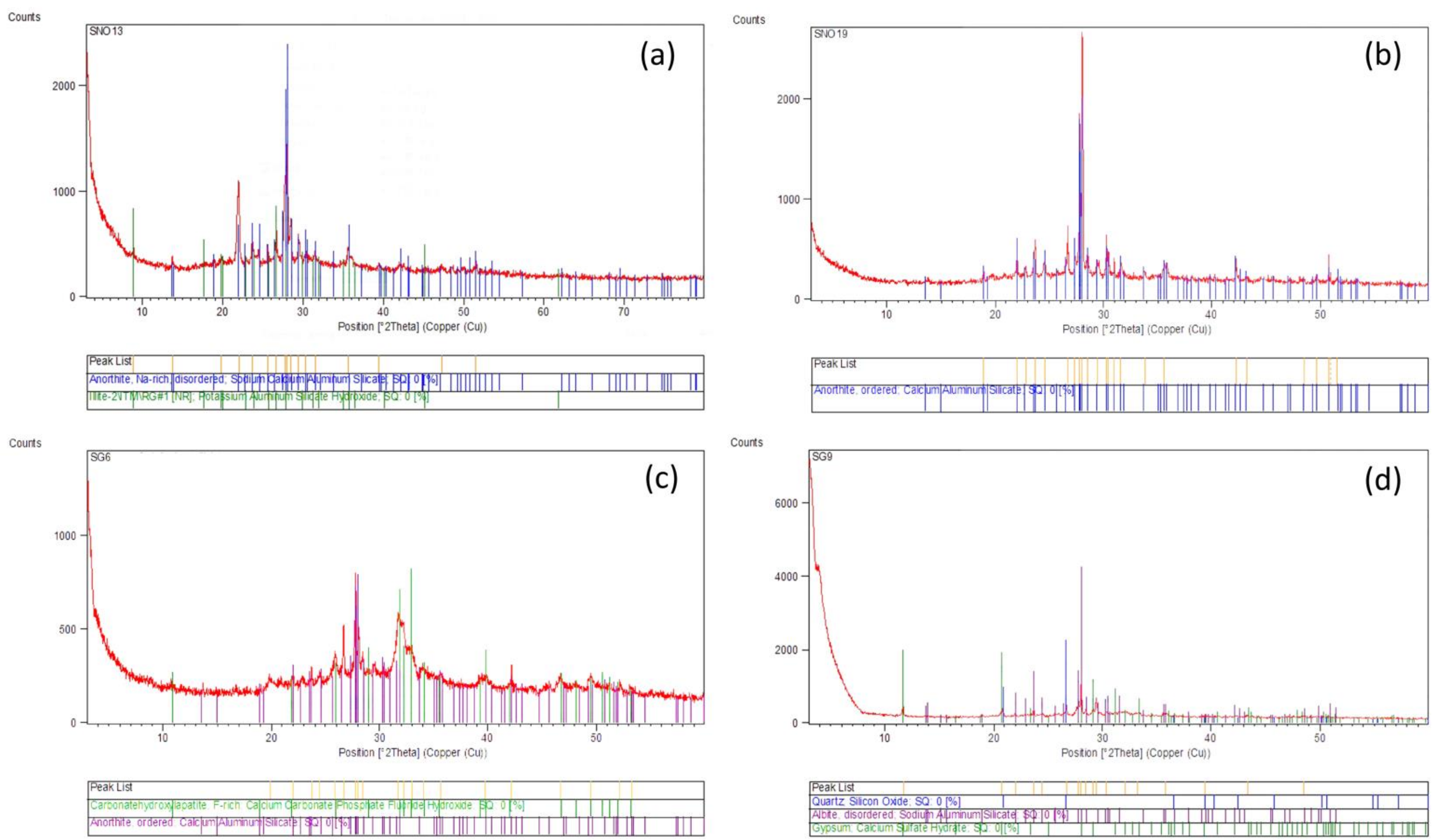

Figure 9. Results of XRPD analysis of samples SNO 13 (a), SNO 19 (b), SG 6 (c), SG 9 (d), taken from the Romanesque churches.

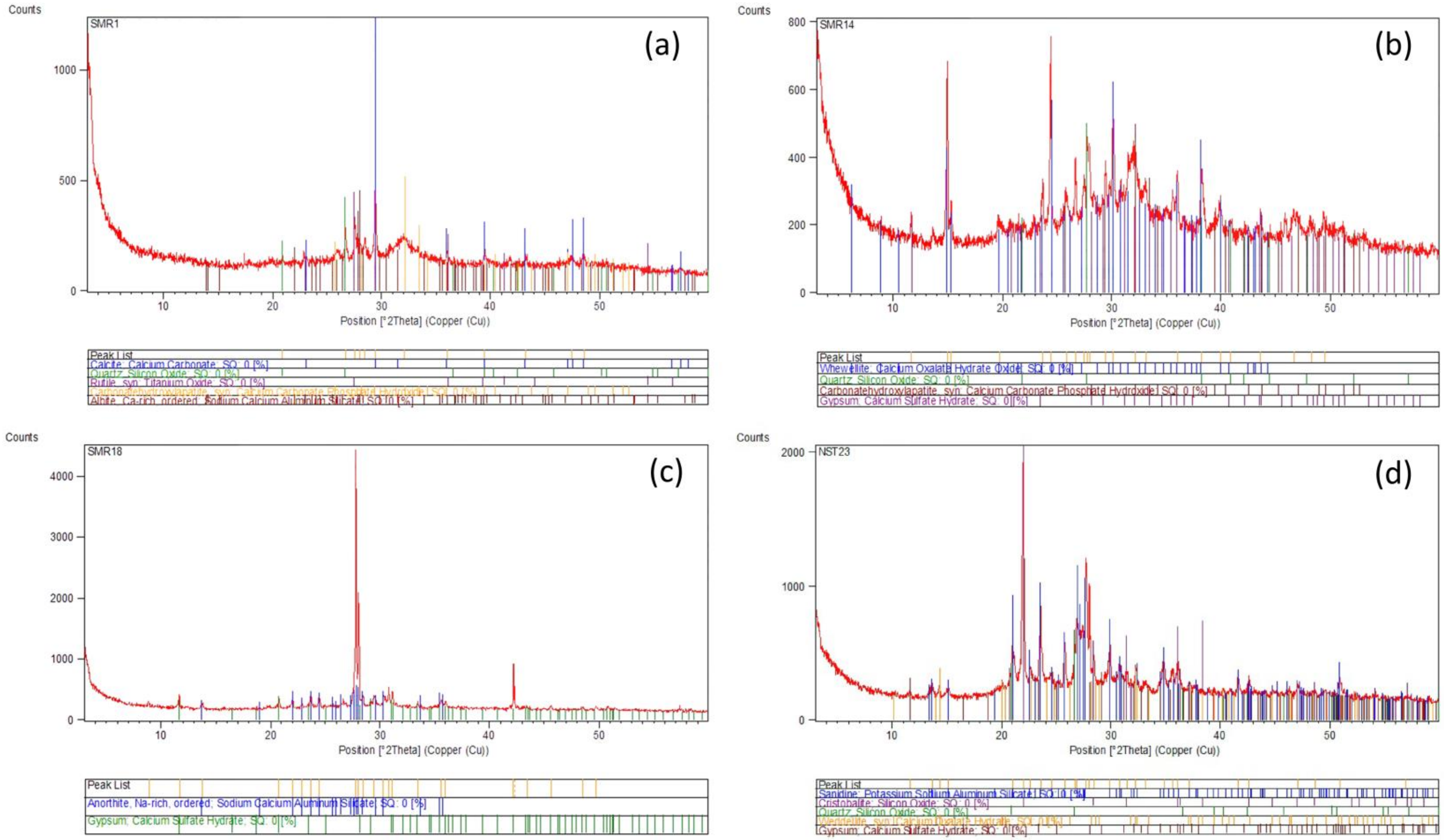

Figure 10. Results of XRPD analysis of samples SMR 1 (a), SMR 14 (b), SMR 18 (c), NST 23b (d), taken from the Romanesque churches.

6. CONCLUSIONS

The research results allowed define the mineral-petrographic characteristics and surface alteration or deposition processes of the volcanic rocks used in the construction of the six analysed medieval Romanesque churches. The volcanic materials, coming from different geological contexts of Sardinia (Logudoro, Abbasanta plateaux, Marghine, Campidano rift). The different analysed rocks belong to the volcanic series of the two main Sardinian magmatic phases: Late Eocene-Miocene and Late Miocene-Pleistocene.

The compositional variability of these rocks (from basalt to andesite, to trachy-andesite, to dacite to rhyodacite, to rhyolite) has allowed us to observe how distinctly develop the processes of alteration and / or deposition of new mineralogical phases on the outer surface of the monuments. Decay processes and surface transformation mechanisms differ according to the compositional features of the rocks.

- Acid volcanics (e.g., rhyolithic pyroclastics of northern Sardinia used on St. Maria of Tergu church), due to a low degree of welding and generally high porosity (> 30%), are more physically-mechanically degradable. The physical processes (e.g., exfoliation, flaking, decohesion), mainly induced by salt crystallization mechanisms and differential hydric dilatation of stone, involve the frequent removal of superficial material portions. Thus, on the external surfaces of these rocks, it is difficult to observe chemical transformations by deposition of new secondary mineralogical phases. However, in some cases, where more protected by weathering, XRPD analyses revealed the presence of original ancient lime-plasters, and possible medieval treatments (with presence of Ca-oxalates).
- Dacitic and rhyodacitic volcanics (e.g., ignimbrites of central and southern Sardiniaused on the San Nicola of Ottana and San Geminiano churches, respectively) show a slightly different behaviour due to their greater compactness and less porosity (12-25%), usually less suffering of physical processes. It is possible to observe traces of chemical-mineral processing processes with the presence of secondary clay minerals (e.g. illite) and gypsum. These phases, along with oxides and hydroxides, are mainly found in the micro-fissures and microfractures induced by exfoliation and flaking, respectively.
- Basic volcanics (basalt, andesite, trachy-andesite and latite), used for the churches of Saccargia, St. Maria del Regno and St. Gregorio, show no chemical or physical alteration, they are very stable rocks to the alteration over time. However, they show the presence of plaster lime residues on the surface, and in some cases also calcium oxalates (e.g., Saccargia church).

Considering that the studied churches refer to all the same historical period, represented by the Romanic style (from 11th to the 14th century), the results show that volcanic building materials were almost always treated with products in medieval time. Probably, lime-based inorganic compounds were finally used, with fine aggregate consisting essentially of fine quartz-feldspar sands, sometimes involuntarily pigmented by carbonaceous residues (probably resulting from the same calcination of limestone to make the lime), and with the use oforganic substances. The latter, through processes of chemical-mineralogical transformation, have led to the formation of Ca-oxalates, which are known to them in literature, relative to their mode of formation, especially in the case of carbonate rocks (sandstone, limestone, marble, etc.).

The presence of the organic and inorganic substances frequently is due to the depositions on the stone surface (*e.g.*, as atmospheric particles) or to the ancient treatments (*i.e.*, weddellite and whevellite). These secondary crystalline phases have been find in other several monuments (*e.g.*, St. Antioco di Bisarcio, San Pantaleo di Dolianova, etc.), independently from the kind of substrate (volcanic rocks, sandstone, marble). In fact, the presence of the Ca-oxalate on the facades of ancient monuments, as noted, is a possible testimony of application of organic substances on the surfaces themselves, with aesthetic reason, to standardize or improve the tone colour of the stone, or conservative reason, to limit the negative effects of weathering.

The presence of oxalates on more alterable rocks (acid rocks) and on physically-mechanically-resistant rocks (basic rocks) used to construct the Romanesque churches indicates that possible treatments have more aesthetic meaning than preservation of materials. Probably had the function of homogenizing the colours, in some cases very variable. The intention of the -designer of the architectural work of wanting to re-decorate decorative motifs is also confirmed by the use of bicroma in the main façades, through the use of stone-coloured materials of different colours (e.g., Saccargia church: dark basalt with white limestone; Tergu church: reddish pyroclastite with whitish limestone, etc.). In these cases mentioned, probably, the treatments focused only on the side and apse walls of the churches.

In the specific case, the discovery of these films in the volcanic rocks of important Romanesque churches in Sardinia, constitutes a first step towards a comprehensive study of these films, also to the understanding of their historical and material significance in terms of use and function.

ACKNOWLEDGEMENTS

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