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Cappadocian ignimbrite cave churches: stone degradation and conservation strategies

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Abstract

The focus of this research is to investigate the minero-petrographic features and the conservation aspects of the stone materials from some rock-hewn churches in Cappadocia region (Turkey) in order to choose the most appropriate consolidating systems to improve the resistance against the weathering and degradation phenomena of this unique world heritage site. In this study, specimens from the Tokalı church in the Göreme's Open Air Museum, and from the Forty Martyrs Church in Şahinefendi were analysed by optical microscopy and X-ray diffraction in order to examine the properties of the rock and especially how well preserved it is. The ignimbrite samples show a porphyritic structure with vitrophyric groundmass and crystalloclastic-vitrophyric texture. The presence of smectite and illite caused serious damage to the rock structure such as cracks, decohesion, exfoliation, and disaggregation phenomena.

The consolidation tests were performed on the ignimbrite specimens, sized according to the standard procedure, by using three commercial silica-based products: NanoEstel, Estel 1000, and Estel 1100. The consolidant penetration was investigated by titanium labelling procedure followed by scanning electron microscopy-energy dispersive spectroscopy analysis. Colour measurements were used to study the possible chromatic changes due to the treatments. The capillary test was performed to evaluate the amount of water absorbed by the stone surfaces before and after the consolidating treatments. Lastly, the surface cohesion due to the consolidation was investigated by using the peeling test carried out on untreated and treated samples.The consolidating tests showed that the solvent-based products (Estel 1000, Estel 1100) exhibit a better distribution than the aqueous suspensions (NanoEstel). Nevertheless NanoEstel gives better results in the capillary absorption test, suggesting that this product has the ability to leave the stone porous structure substantially unaltered.

Key words: Cappadocia; ignimbrite; consolidation; degradation.

Introduction

The diagnostic analysis of the degradation and alteration processes of the monuments in stone has acquired a high importance for their restoration and maintenance. Such studies require analysis of the materials used and an accurate characterization of the degradation products with the aim of evaluating the effects of the degradation (Bulakh et al., 2005; Barone et al., 2008a, 2008b; Belfiore et al., 2012).

Different typologies of protective and consolidant products, such as acrylic and siloxane polymers, perfluoroethers and fluorinated polyolefins, and nano-structured materials (Appolonia et al., 1995; Alessandrini et al., 2000; Ruffolo et al., 2010; La Russa et al., 2011, 2012) have been tested on the stone materials with the aim of improving the physical properties of the rocks. However, many conservation materials used in the past for specific interventions have proved to be inappropriate because of their poor affinity with the substrate, leading to increasing stone deterioration after their application (Moropoulou et al., 2003).

In this context, an important case study is represented by the monuments in Cappadocia region, situated in Central Anatolia, Turkey (Andaloro, 2008, 2009a). In this area including the provinces of Nevşehir, Kayseri, and Niğde provinces, there is a considerable number of historical rock-hewn settlements carved into the outcropping ignimbrite changed into earth pillars by weathering phenomena and commonly called "fairy chimneys". The historical and modern rock structures in the Cappadocia region can be divided into two main categories: a) cliff or semi-underground structures, and b) underground structures (Aydan et al., 1999).

The rock-hewn churches contain invaluable wall paintings, which provide touristic attraction as well. Weathering, erosion, and human activities threaten the future of the fairy chimneys. Studies aimed at the conservation of these historical monuments necessitate the understanding of both natural and man-made processes (Topal and Doyuran, 1998). One of the important factors impacting on the decay of historical building materials is the climatic conditions where the buildings are located. Climatic factors such as high humidity, high rainfall, and low temperature in addition to seasonal changes and drastic fluctuations in day-time and night-time temperatures accelerate the deterioration of building materials (Topal and Doyuran, 1998; Topal, 2002).

For this reason, the physical, mineralogical, geo-engineering, and geo-mechanical properties of this region's rock units have been widely investigated (e.g. Topal and Doyuran, 1997, 1998; Aydan et al., 1999, 2007; Ito et al., 1999; Seiki et al., 1999; Ulusay et al., 1999; Watanabe et al., 1999; Aydan and Ulusay, 2003; Kasmer et al., 2007; Tunusluoglu and Zorlu, 2009). This study is focused on the diagnostic analysis of two rupestrian churches, namely the complex of the Tokalı (Göreme) and the Church of the Forty

Martyrs in Şahinefendi, where, despite the conservation measures carried out in the past on the external walls, stony materials are still suffering severe degradation processes.

The complex of the Tokalı is an extraordinary monument inside the Open Air Museum in the Göreme valley. In 1985 this area, constituted by a vast monastic complex composed of scores of refectory monasteries placed side by side, each with its own fantastic church, was declared a UNESCO World Heritage site. The Forty Martyrs Church, located 18 km to the south of Ürgüp, is part of a large rocky settlement consisting of about 100 caves carved over the centuries and used for various purposes.

Polarized optical microscopy and X-ray diffraction (XRD) analysis were carried out in order to define both the main textural-mineralogical features and degradation and alteration products. Furthermore, three consolidant products have been tested on ignimbrite samples to study the interactions and compatibility between applied products and substrate, particularly to evaluate the re-aggregation features provided by each treatment. These findings provided useful information for detecting the most suitable products to improve the material physical properties of the stone so as to preserve these extraordinary and striking structures.

Geological and environmental setting

In order to be aware of the essential characteristics of the investigated samples a brief description of the geological and environmental framework in the studied area may be useful.

Convergence of the Afro-Arabian continent toward the Eurasian plate (Figure 1a) resulted in intense magmatic activity within the Anatolian collage in Neogene times (Innocenti et al., 1982; Dhont et al., 1998; Piper et al., 2002; Le Pennec et al., 2005). The Central Anatolian Volcanic Province (CAVP) is located in the centre of Turkey and extends 300 km along a NE–SW direction over a wide area (32500 km^2), where ignimbrites cover 20000 km^2 (Koralay et al., 2007) (Figure 1a). These rocks are very representative in the Nevşehir Plateau, a large tabular structure within CAVP between the tectonic depressions of the Tuz Gölü to the west and Sultansazliği to the east and between the Kirşehir massif to the north and the Taurus mountains to the south (Le Pennec et al., 2005) (Figure 1a). Ürgüp Formation (Pasquarè et al., 1968) represents the most important and widest stratigraphic unit inside the plateau; this unit lies on a Pre-Neogenic basement composed of ophiolitic and plutonic rocks (syenite, monzonite, gabbro, pyroxenite) as well as fluvial deposits (alternations of mudstone and conglomerates) (Temel et al., 1998). Ürgüp Formation comprises two levels of lava flows and nine Upper Miocene to Pliocene welded to non-welded rhyolitic ignimbrites interbedded with pumice-fall deposits, pyroclastic surge, and continental deposits including fluvial sediments (Koralay et al., 2011) and calcareous-marly beds of lacustrine environment. In particular, Le Pennec et al. (1994) names the ignimbrites considering the sites where these deposits are exposed better, for example Kavak, Zelve, Sarimaden Tepe, Cemilköy, Tahar, Gördeles, Sofular, Kızılkaya, and Valibaba Tepe.

The Kavak ignimbrite builds up the area around the Tokali church in Göreme, whereas the Cemilköy ignimbrite builds up the area around Şahinefendi (Figure 1b). Kavak ignimbrite consists of ash-fall and flow deposits interbedded with volcanic–clastic sediments. It is well exposed in Kavak village. This unit covers an area of 2600 km^2, having a volume of 80 km^3. Its thickness is between 10 and 150 m. Kr-Ar dating gives ages of 8.6-11.2 Ma (Innocenti et al., 1975; Temel, 1992), making it the oldest ignimbrite of Ürgüp Formation. The ignimbrite sequence reaches a thickness of 95 m at Göreme.

The Cemilköy ignimbrite consists of ash flow deposits that are well exposed at Cemilköy village. Le Pennec et al. (1994) estimated its volume to be 300 km^3 and its outcrop area 8600 km^2. It is one of the most important of the non-welded ignimbrites, with a maximum thickness of 110 m at Cemilköy and 20 m at the study area of Şahinefendi.

Regarding the environmental features, this area shows the typical characteristic of continental climate, which is dominant in central Anatolia. Summers are hot and dry; winters are cold with moderate snowfalls, while springs are rainy. The average minimum temperatures reach -7.3 °C in January, whereas the maximum temperatures amount to 30.5 °C in July and August. (Türkeş and Akgündüz, 2011). The maximum precipitations that range between 156.6 mm and 126 mm caused by cyclonic anomaly circulation just over Turkey in spring (April or May) is of primary importance in terms of gully erosion, sheet flood effect, precipitation of iron-oxide, and formation of clay minerals by chemical weathering on rock surfaces (Topal and Doyuran, 1998; Türkeş and Akgündüz, 2011). The effects of running water and rock weathering (i.e. differential disaggregation, decohesion, exfoliation, detachment) are also increased by the occurrence of intensive rainfall events called "Kırkikindi yağmurları" (Türkeş and Akgündüz, 2011).

Rock hewn churches

The complex of Tokalı in Göreme is characterized by several painted churches in a landscape of impressive beauty. The Tokalı consists of two churches, the old and the new one, carved into the Kavak ignimbrite (Figure 2 a,b) and decorated in two phases in the course of the tenth century (Wharton Epstein, 1986). The Old Tokalı is constituted by an ample *naos*, the main room of the church, covered by a barrel vault. The walls of the church exhibit an extensive pictorial cycle, dated back to the first quarter of the tenth century, with scenes of the life of Christ and of Saint John the Baptist (De Jerphanion, 1942). The new church consists of a wide transversal "naos", covered with a barrel vault, and a sanctuary with three *apses*, separated by the principal body of the church through a system of arcades. The walls of the new church are completely covered by extraordinary paintings dated back to the mid-tenth century. These wall paintings, made under the patronage of the Phocas family, who were closely related to the imperial court of Constantinople

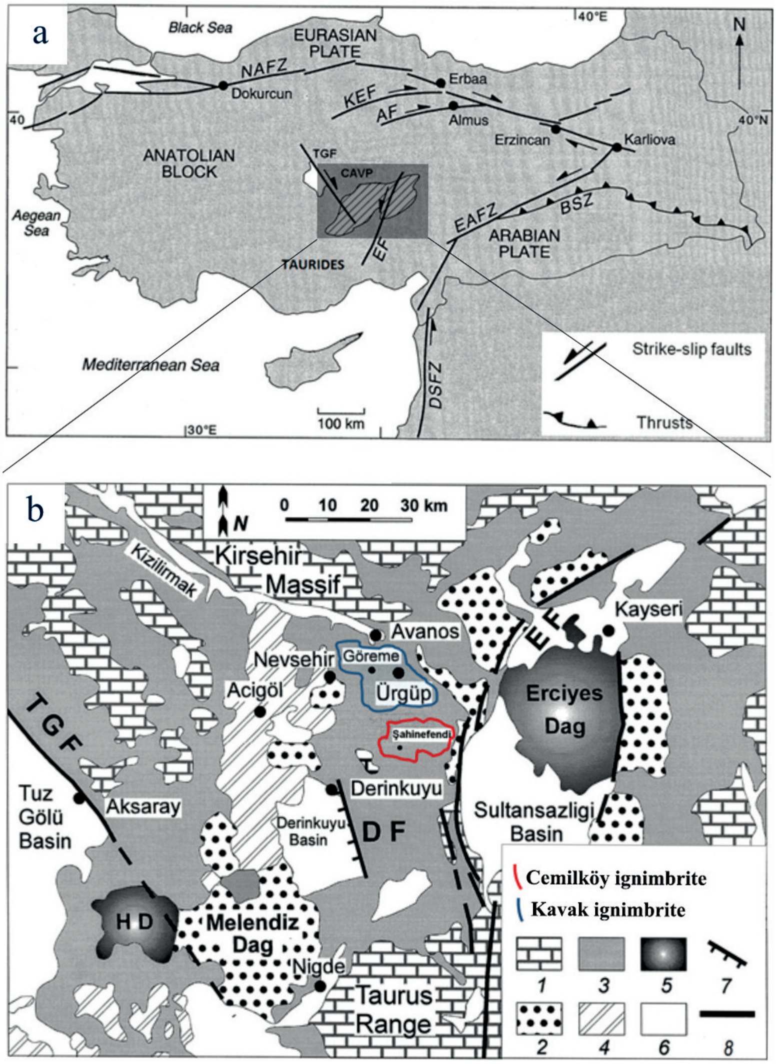

Figure 1. a) Important tectonic features in Turkey and the situation of the Central Anatolian Volcanic Province (CAVP) location. Abbreviations: AF = Almus Fault Zone; BSZ = Bitlis-Zagros Suture Zone; DSFZ = Dead Sea Fault Zone; EAFZ = East Anatolian Fault Zone; EF = Ecemiş Fault Zone; KEF = Kirikkale–Erbaa Fault Zone; NAFZ = North Anatolian Fault Zone; TGF = Tuz Gölü Fault Zone (modified from Piper et al., 2002). The darker frame highlight the Cappadocia area. b) Geological sketch map of the studied area (Temel et al., 1998). (1) Pre-Neogenic Basement rocks; (2) Major Miocene-Pliocene volcanic complexes (stratovolcanoes and monogenetic centres; basalts to rhyoliths); (3) Ignimbrites and contemporaneous continental sediments. Blue and red lines define the outcropping areas of Kavak and Cemilköy ignimbrites, respectively; (4) Mainly monogenetic Quaternary volcanism (maars, domes, lavas flows, and cinder cones, basalts to rhyolites); (5) Large Quaternary volcanoes; (6) Quaternary alluvium; (7) Derinkuyu Quaternary normal fault (DF); (8) Major Neogene to quaternary strike-slip faults: Tuz Gölü Fault Zone (TGF) and Ecemiş Fault Zone (EF); HD = Hasandağ.

Figure 2. External and internal views of: Tokalı church (a, b), and Şahinefendi Forty Martyrs church (c, d).

(Andaloro, 2011a), undoubtedly represent the highest quality level attained in Cappadocia with regard to the wall decorations.

The Forty Martyrs church in Şahinefendi (Figure 2 c,d) is excavated into the Cemilköy ignimbrite. It is located in the southern slopes of the hill named Orta Tepe. The interior of the church has two parallel aisles covered by barrel vaults. The original pillars were lost and they were substituted during the architectural restoration carried out by the Archaeological Museum of Nevşehir in 1997 (Andaloro, 2009b, 2010, 2011b). Concerning the Forty Martyrs' church, a conservation work was performed more recently (Andaloro, 2012; Pelosi et al., 2013), revealing a stone conservation issue, which is also related to the paintings' conservation (Pelosi et al., 2010).

Sampling and macroscopic observations

The examined materials consist of nine ignimbritic specimens (Table 1) from both Göreme area and Şahinefendi. According to local directives, the sampling phases were supervised by a Turkish officer, limiting the choice of sampling areas; however the most representative zones were chosen. Samples were collected from the same level of the geological formation where the cave-churches were carved. In particular, Göreme specimens come from four areas in the Open Air Museum near to Tokalı's complex,

Table 1. Sampling sites and sample description.

Sample ID	Sampling Area	Alteration/degradation forms
T1	Open Air Museum; Outcrop	Exfoliation and Crumbling
T2	Open Air Museum; Outcrop	Exfoliation and Disintegration
T3	Open Air Museum; Outcrop	Absent (fresh sample)
T4	Open Air Museum; Tokalı church	Absent (fresh sample)
S1	Şahinefendi; outcrop next to the Forty Martyrs church	Detachment
S2	Şahinefendi; outcrop next to the Forty Martyrs church	Absent (fresh sample)
S3	Şahinefendi; Forty Martyrs church	Absent (fresh sample)
S4	Şahinefendi; Forty Martyrs church	Argillification and disintegration
S5	Şahinefendi; Forty Martyrs church	Soiling

whereas five points were selected in Şahinefendi around the Forty Martyrs' church.

Precisely, the specimens sampled in Göreme area are T1 and T2 (sized ~ 10 × 10 × 5 cm) from the surface of the rock, and T3 and T4 (sized ~ 70 × 20 × 20 cm), which are representative of the stone bulk. Göreme ignimbrite is unsorted, mostly cream-white, and sometimes pinkish and yellowish coloured (Figure 3b); in particular the chromatic variations are localized mainly along joint systems and on the levels more exposed to meteoric water leaching.

The samples taken from Şahinefendi are S1, S2, and S3 (sized ~ 40 × 20 × 20 cm), representing the bulk of the rock, and S4 and S5 (sized ~ 15 × 10 × 3 cm), consisting mainly of the stone surface. Macroscopically, Şahinefendi ignimbrite appears unsorted and pale grey, with very local pinkish and reddish colouration around biotite lamellae, gabbro, andesite, and pyroxenite fragments (rock fragments sized ~ 5 mm to 1 cm).

Concerning ignimbrites, it is possible to recognize different degradation and alteration processes. The most common forms are chromatic changes (Figure 3b), exfoliations (Figure 3 a,b), lichen colonization (Figure 3a), cracking, disintegration, detachments (Figure 3c), and soiling + scaling phenomena (Figure 3d).

Analytical methods

In order to characterize the stone materials and alteration and degradation products, several analytical techniques were applied to the

Figure 3. Sampling locations and related degradation forms for: a) sample T2 (lichen colonization and exfoliation); b) sample T1 (exfoliation and reddish colouring); c) sample S1 (detachment); d) sample S5 (scaling and soiling).

samples. Optical microscopy observations were performed on the thin sections using a Zeiss Axiolab microscope in order to study the microscopic features.

The mineralogical composition of both whole samples and clay-sized fractions (< 2 μm) was obtained by XRD using a D8 Advance Bruker diffractometer with CuKα radiation. Spectra were gathered in the range 3-65° 2θ for the bulk samples and 3-35° 2θ for the clayey fractions. Measuring conditions were set at 40 kV voltage, 30 mA current, 0.02° 2θ step size, and 3.0 sec step time. For the whole rock analysis, samples were carefully powdered by hand grinding in an agate mortar to produce an average particle size smaller than 10 μm. The powder was then side-loaded into a glass sample holder to obtain a randomly oriented specimen, thus minimizing preferred orientations. The clay-sized fraction was prepared by gentle crushing in a ceramic mortar, suspension by a mixer, dispersion in an ultrasonic bath, and then centrifugation in distilled water. The < 2 μm fraction was then piped and dried at room temperature on glass slides to produce a thin oriented layer. Ethylene-glycol-solvated and 180° C-heated slides were also prepared.

Ignimbrite specimens, were taken from nearby outcrops and cut (size 5 × 5 × 2 cm) for the consolidation tests. Three commercial consolidating products were used: NanoEstel, Estel 1000, and Estel 1100. The choice of these products was suggested by their chemical nature, since they are mainly constituted by silica, a material with a strong affinity for the stone.

NanoEstel is an aqueous suspension of silica nanoparticles having an average size of 30 nm, Estel 1000 is composed of TEOS (tetraethyl orthosilicate) diluted in white spirit (a mixture of aliphatic hydrocarbons having a boiling point of 145-250 °C), and Estel 1100 is composed of tetraethyl orthosilicate and oligomers of polydimethylsiloxane diluted in white spirit. All products have a SiO_2 content of 30 wt%. Approximately 300 g/m^2 of consolidating materials were applied on the rock surface with a brush. Consolidation product was applied both undiluted (30 wt% SiO_2) and diluted, with water in the case of NanoEstel and white spirit in the case of Estel 1000 and Estel 1100 (20 wt% and 10 wt% SiO_2).

Evaluation of the consolidant penetration depth was carried out using a labelling procedure: 5 wt% of TTIP (titanium isopropoxide) was added to Estel 1000 and Estel 1100, while 5 wt% of TiO_2 nanoparticles (average particle size 30 nm) was added to NanoEstel. It is reasonable to assume a comparable behaviour between labelling agents and consolidants. In the untreated sample, there is not any detectable amount of titanium. This method allowed us to evaluate the penetration by measuring the amount of titanium by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis. For this purpose an FEI Quanta 200F Philips SEM coupled with EDS was used. All analyses were carried out using an acceleration voltage of 20 kV and under low vacuum conditions (10^{-3} mbar pressure).

Colourimetric tests were carried out using a CM-2600d Konica Minolta spectrophotometer to identify chromatic variations induced by the treatments. Chromatic values are expressed according to the CIE (Commission Internationale d'Eclairage) L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and -a* green), and b* the yellow/blue coordinate (+b* indicating yellow and -b* blue) (ISO 11664-4, 2008). According to Baga et al. (2012) measurements were carried out using a 8.0 mm-diameter viewing aperture, specular component excluded (SCE), UV 0%, Illuminant D65 and 10° observer angle. Ten measurements on each sample have been carried out.

In order to evaluate the amount of water absorbed by a stone specimen per surface unit (Qi) over time before and after a treatment (UNI EN 15801, 2010), the capillary test was performed. Qi is defined as: $Qi = (m_t - m_0)/S$, where S is the area of the base of the sample, m_t is the sample weight measured during the test, and m_0 is the sample weight at the beginning of the experiment.

In order to assess the superficial cohesion induced by consolidation treatment, peeling tests were performed on untreated and treated samples. A peeling test is defined as a method to quantify the adhesion of a surface or near-to-surface layer to a substrate. Following Drdàcky et al. (2012), a pressure-sensitive tape having a size of 4 × 3 cm^2 was applied to the investigated area and then pulled off. The amount of material detached from the surface after peeling off the tape was measured. The test was repeated ten times on the same area. It is generally assumed that this amount reflects the cohesion characteristics of the substrate (Drdàcky et al., 2012). Therefore, the peeling test is used to evaluate the surface degradation or consolidation effects after restoration procedures.

Results

Petrographic and mineralogical analysis

Göreme products show a porphyritic structure with vitrophyric groundmass and crystalloclastic-vitrophyric texture. The estimated composition is visually estimated as follows: 45 vol.% glass, 54 vol.% crystals, and 1 vol.% lithic fragments. Plagioclase and quartz phenocrysts represent the most common minerals within the samples. Plagioclase is euhedral with tabular shape and size ranging between 2 and 0.01 mm. Plagioclase phenocrysts show marked zoning and resorption textures at both the core and the rim (Figure 4a), with development of strong sieve-textures in some instances. Some of the crystals are affected by inclusions of glass and opaque oxides. Quartz phenocrysts are anhedral and destabilized with development of embayments (Figure 4b) and the presence of glass inclusions. Their size varies between 2 and 0.05 mm. Biotite exhibits euhedral shape and dimensions of about 1 mm. Pumice dimensions reach the maximum size of ca. 3 mm. Two main shapes were observed: sub-rounded

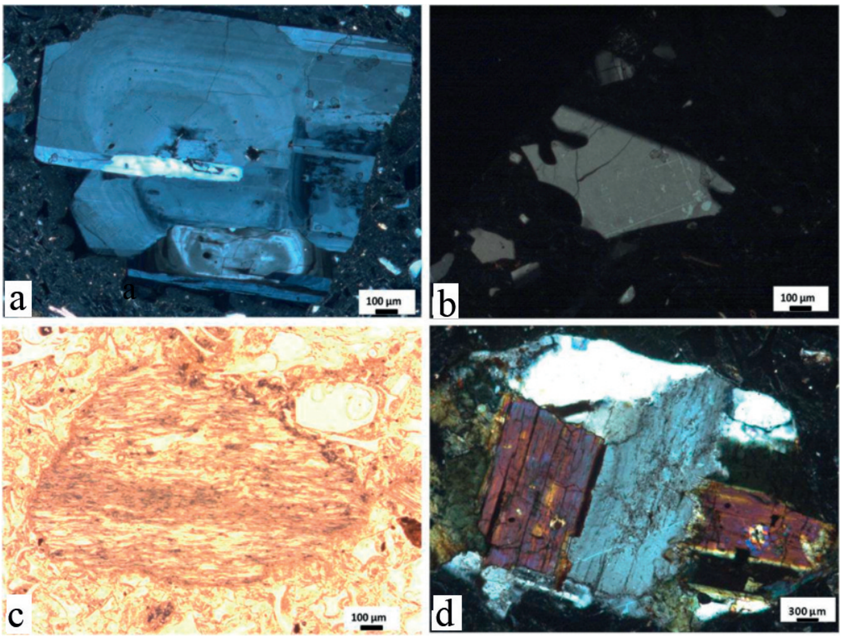

Figure 4. Microphotographs of Göreme (a-b) and Şahinefendi samples (c-d). Göreme ignimbrites are characterized by a porphyritic structure with vitrophyric groundmass and crystalloclastic-vitrophyric texture. Photos show: a) a tabular zoned plagioclase with resorption texture at both core and rim and size around 2 cm, from sample T3 (crossed polarized light.); b) an anhedral crystal of quartz (500 µm in size) with development of embayments, from sample T4 (crossed polarized light). Şahinefendi ignimbrites show a porphyritic structure with vitrophyric groundmass and vitrophyric texture. Photos show details of: c) a pumice (about 600 µm in size), with slaty fabric, strongly flattened with elongated vesicles, and evidences of platy and cuspate glass shards in the groundmass around the pumice (sample S1, plane polarized light; d) gabbro fragment in sample S2, about 1 cm in size, constituted by clinopyroxene and plagioclase (crossed polarized light).

with sub-spherical vesicles and flame-shaped with elongated vesicles. Plagioclase crystals were observed in some pumices. Lithic fragments display sub-rounded shape with a diameter of about 1.5 mm. They are constituted by plagioclase and quartz or by microlithic fragments in vitrophyric groundmass.

Secondary processes are markedly evident within the samples, which produced pores filled by authigenic calcite together with newly-formed iron oxides and clayey fraction in the glassy groundmass and in the lithic fragments..

Investigations of the Şahinefendi samples reveal a porphyritic structure with vitrophyric groundmass and vitrophyric texture, with the following estimated proportions among the constituents: glass 70%, crystals 20%, and lithic fragments 10%. The crystal component is defined by quartz (7 vol.%) and plagioclase (10 vol.%) with subordinate amounts of biotite (2 vol.%) and opaque oxides (1 vol.%). Quartz phenocrysts are angular and anhedral, with some crystals embayed; undulose extinction is absent. Grain sizes vary in diameter from 0.05 mm to 1 mm. Plagioclase, which exhibits evident optical zoning, is commonly tabular in shape and ranges in length, along the apparent c-axis, from 0.01 to 1.5 mm. Only some phenocrysts are partially resorbed or display micrometre-sized glass inclusions. Biotite is usually euhedral and varies from 0.09 mm to 0.7 mm in size. Within samples from Şahinefendi, the pumices are from 5 mm to about 1 cm in diameter with slaty fabric, that is, strongly flattened with elongated vesicles (Le Pennec et al., 1994) (Figure 4c). Platy, cuspate, and Y-shaped glass shards are present. Lithic fragments are generally sub-rounded and range from 0.85 to 3 mm in diameter. Andesite, gabbro (Figure 4d), and pyroxenite fragments are also present. Finally, other fragments with porphyritic structure, chiefly constituted by plagioclase, have been observed, and are often affected by oxidation and increases in the clay fraction.

In samples from Göreme, the XRD spectra of the whole rock analysis revealed the presence of plagioclase as the most abundant phase, followed by quartz, biotite, clay minerals, and only small amounts of calcite and magnetite. The analysis of the oriented-specimens for the clay-sized fraction (< 2 μm) evidenced that the composition is dominated by smectite and, in minor quantity, illite.

Bulk analyses of Şahinefendi samples showed that plagioclase and quartz are the predominant phases, while biotite, hematite, and clay minerals are subordinate. Traces of amphiboles, probably deriving from the lithic fragments (gabbro and andesite), were also detected, along with small amounts of gypsum (only in samples S4 and S5), which is probably ascribable to anthropogenic activities in the area. The < 2 μm fraction consists exclusively of smectite. The results are summarized in Table 2. Relative abundances of phases were estimated on the basis of the intensity of reflections in the diffraction patterns.

Consolidation tests

In order to provide some indication as to the most suitable consolidation treatment, three products were tested on the Göreme samples (NanoEstel, Estel 1000, Estel 1100).

The penetration capability of the products

Table 2. Mineralogical composition of the whole-rock and of the < 2 μm fraction detected by XRD.

Samples	Complete rock								< 2 μm		
	Pl	Qtz	Bt	Amph	Gp	Mag	Hem	Cal	CM	Sm	Ill
T1	++	+++	+	-	-	+	-	-	++	++	-
T2	++++	++	++	-	-	+	-	-	+	+	+
T3	++++	++	+	-	-	-	-	+	+	+	+
T4	++++	++	+	-	-	+	-	+	+	+	+
S1	++++	++	+	+	-	-	-	-	+	+	-
S2	++++	+	+	+	-	-	+	-	+	+	-
S3	++++	++	+	+	-	-	+	-	+	+	-
S4	++	+++	+	+	++	-	+	-	++	++	-
S5	+++	++	+	+	++	-	-	-	++	++	-

Pl = plagioclase; Qtz = quartz; Bt = biotite; Amph = amphibole; Gp = gypsum; Mag = magnetite; Hem = hematite; Cal = calcite; CM = total clay minerals; Sm = smectite; Ill = illite. ++++ = very abundant; +++ = abundant; ++ = common; + = scarce; - = not detected

within the bulk samples was investigated by the SEM–EDS technique. In particular, EDS microanalysis was carried out on cross-sections in order to reveal in depth the distribution of Ti due to the use of titanium-containing compounds as labelling agents added to the tested products (Figure 5). It is evident that the product shows decreasing of titanium concentration (Ti %m/m) content from the surface to the bulk. For Estel 1000 and Estel 1100 treatments, titanium content decreases dramatically after 200 μm of depth, although traces of Ti are detectable up to 1000 μm. On the contrary NanoEstel seems to penetrate less; in fact Ti cannot be detected at more than 600 μm.

Treated ignimbrite surfaces were investigated in order to assess the colour variations with respect to untreated samples. The colour change, expressed as ΔE (ISO 11664-4, 2008), was calculated using the following relation:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (1)$$

where ΔL*, Δa*, and Δb* represent the differences between the values of each chromatic coordinate in the treated samples and in the untreated ones, respectively.

The importance of this parameter is linked to aesthetic reasons. ΔE values recorded after the coating application are reported in Table 3.

Capillary absorption experiments were carried out on both untreated and treated samples. Qi versus $t^{1/2}$ values (reported as square root of seconds) were plotted according to UNI 10859 (2001), as shown in Figure 6. The curve profiles can be roughly clustered into three groups corresponding to each product. Estel 1100 treatments show a greater decrease in water absorption, although after 400 $s^{1/2}$ the specimens reach Qi values similar to those of the other treatments.

The results of the peeling tests performed on treated and untreated samples are reported in Figure 7. Measurements show a decrease in the amount of material released (rm) from the surface after each repetition. The equation describing the sequence of weights of the removed material rm(n),

$$m(n) = A + B\ eCn \qquad (2)$$

was suggested by Ferron (2007), where n is the repetition number, A the value of rm after infinite repetitions, and C the rate of decrease in rm, while A+B represents the value of rm at n = 0. Equation (2) has been fitted on the experimental data and the results are summarized in Table 4. R^2 values reveal that the data are strongly affected by noise, due to the intrinsic precision of the method (Drdàcky et al., 2012). Lower values of rm (n = 1) parameters were observed in the treated samples, suggesting evidence of the consolidation effect provided by the applied products. It worth to note that there are more reliable tests to detect the increase of straightness provided by treatments, such as uniaxial compression test, that require large amount of samples. In our case, such quantities were not available, for this reason the peeling test, despite its poor repeatability, has been chosen for the small amount of sample required.

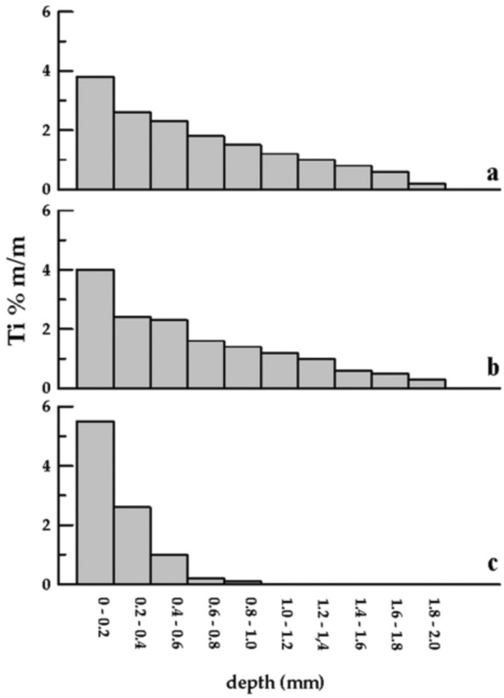

Figure 5. Ti distribution from the surface to the stone bulk for Estel 1000 (a), Estel 1100 (b), and NanoEstel (c). Ti content reflects the consolidant penetration depth.

Discussion

From a minero-petrographic point of view, both ignimbrites (Göreme and Şahinefendi) show the same porphyritic structure with vitrophyric groundmass and crystalloclastic to vitrophyric texture, although the Şahinefendi samples contain a larger glass fraction and different types of lithic fragments with respect to

Table 3. Colour variations after consolidant application at different dilutions (wt%).

Product used for treatment	wt%	ΔL*	Δa*	Δb*	ΔE*
NanoEstel	10	-3.00	1.10	0.91	3.62 ± 2.82
	20	-0.55	0.02	-0.41	0.85 ± 0.23
	30	-0.09	-0.47	-2.70	3.10 ± 2.33
Estel 1000	10	-1.37	0.78	0.70	1.81 ± 1.44
	20	-1.21	0.44	-0.02	1.45 ± 0.43
	30	-5.57	0.60	0.66	5.70 ± 2.34
Estel 1100	10	-4.72	0.93	1.12	5.02 ± 2.31
	20	-2.84	0.63	0.65	3.02 ± 2.45
	30	-4.42	0.73	0.75	4.56 ± 3.23

those from Göreme. The neoformation of clay minerals (e.g. smectite and/or illite) and iron oxides (e.g. haematite or magnetite), recognized in both lithotypes, results from alteration processes of volcanic glass and mafic fragments (Turkmenoglu et al., 1991). In this regard, it is worth noting that the presence of clay minerals can cause discolouration (Topal and Doyuran,

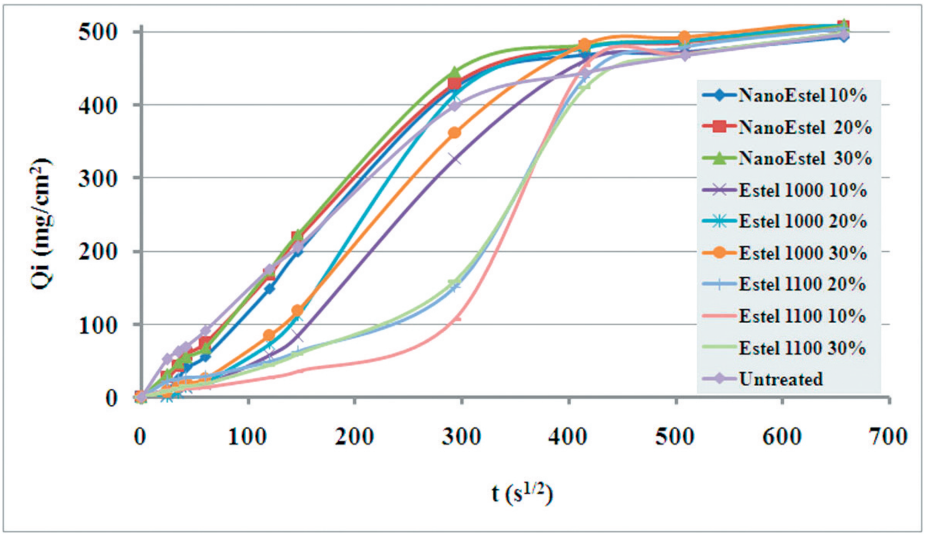

Figure 6. Capillary water absorption of treated and untreated specimens (x-values are expressed as the square root of seconds). Experiments had been carried out up to 5 days (~ 657 s0.5).

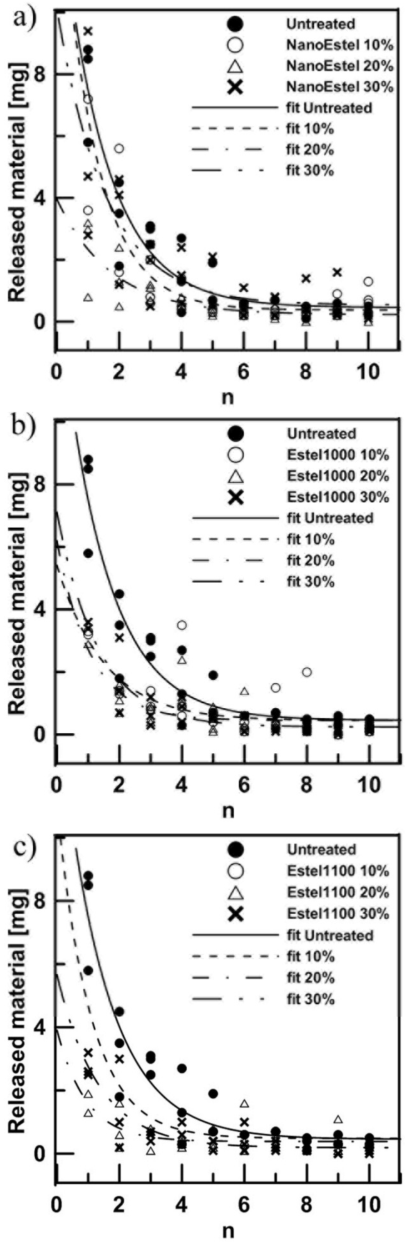

Figure 7. Results of peeling tests performed on a) NanoEstel-, b) Estel 1000-, and c) Estel 1100-treated samples. A set of three measurements had been carried out for each treatment; curve calculation had been performed by taking into account all data.

1998). Furthermore, smectites, which are expandable clay minerals, can produce serious damages to the rock structure, such as tension cracks, due to the swelling of minerals in contact with water (Topal and Doyuran, 1998).

Due to their strong tendency to degrade, it is evident that specific treatments are needed for conservation purposes of the examined stone monuments. The choice of consolidation products here selected for the experimentation was based on the chemical compatibility between stone and product, being all three tested consolidant composed by silica. Results of experimental tests, performed after the application of products on stone specimens, allowed drawing some important considerations, which are summarized as follows.

Colorimetric measurements revealed that all treatments induce low variations; in particular, NanoEstel causes just negligible colour modifications after treatment, while, in some cases, Estel 1000 and Estel 1100 induce ΔE values close to 5 (Table 3).

The assessment of penetration capability of products pointed out that the solvent-based ones (Estel 1000 and Estel 1100) show a better penetration than the aqueous suspension (NanoEstel) (Figure 5). This difference is mainly due to the better wettability of the white spirit with respect to water; furthermore, in spite of the nano-sized silica particles, NanoEstel displays a worst penetration than TEOS, probably due to the liquid feature of this latter.

The capillary water absorption test (Figure 6) revealed the hydrophobic feature of Estel 1110, due to the polydimethylsiloxane polymer, a

Table 4. Summary of peeling test fitting parameters at different dilutions (wt%).

Product used for treatment	wt%	A (mg)	B (mg)	C	rm (n=1) (mg)	R^2
Untreated	-	0.4536	13.94	-0.6826	7.5	0.89
NanoEstel	10	0.3726	14.92	-0.8691	6.6	0.79
	20	0.2237	3.735	-0.5695	2.3	0.67
	30	0.4374	9.352	-0.6352	5.5	0.65
Estel 1000	10	0.4441	4.967	-0.6578	3.0	0.52
	20	0.4450	5.748	-0.9300	2.7	0.51
	30	0.2439	6.866	-0.7584	3.5	0.82
Estel 1100	10	0.4419	10.53	-0.9219	4.7	0.61
	20	0.3849	3.523	-1.066	1.6	0.51
	30	0.1872	5.477	-0.7580	2.8	0.75

compound that provides a water-repellent feature to the stone. Such a hydrophobic effect has positive implications for what concerns the conservation of examined stone monuments, since avoiding the contact between water and expandable-lattice clay minerals (i.e. smectite), the latter cannot expand. Nevertheless, it must be taken into account the possibility to lead to scaling (Figure 3d) that takes place when the surface of stones has very different physical properties with respect to the bulk. Treatments with Estel 1000 lead to a slight decrease in the water uptake, while in the case of NanoEstel, the behaviour is quite similar to that of untreated samples, suggesting that this product has the ability to leave the porous structure of stone substantially unaltered.

Peeling tests pointed out that the consolidants applied at 30% concentration exhibit a worst performance than the more diluted ones (Table 4). This can be misleading, because in the case of samples treated with the 30% product, a certain amount of consolidant remained on the surface and did not penetrate into the porous structure of the stone. This behaviour must be taken into consideration when evaluating the consolidant penetration. The most suitable dilution seems to be 20%; furthermore, the best results were obtained with Estel 1100, while NanoEstel seems to behave slightly better than Estel 1000. However, Estel 1100 contains organic groups and its use should be limited to indoor environments, since an outdoor exposition could induce oxidation processes.

Conclusions

This study focused on the diagnostic characterization of stone materials from the complex of Tokali in Göreme and the Church of the Forty Martyrs at Şahinefendi (Turkey). From a minero-petrographic point of view, both ignimbrites show the same porphyritic structure with vitrophyric groundmass and crystalloclastic -vitrophyric texture, although the Şahinefendi samples contain a larger glass fraction and different types of lithic fragments with respect to those from Göreme. Clay minerals (smectite and illite) were detected in all of the investigated samples, and their presence can be the cause of the observed serious damage to the rock structure such as cracks, decohesion, exfoliation, and disaggregation phenomena.

In order to improve the material cohesion and resistance against weathering phenomena, three consolidant products were tested. As regards the penetration capability, the solvent-based products (Estel 1000 and Estel 1100) showed a better penetration than the aqueous suspension (NanoEstel). The most suitable concentration for all products seems to be 20%. Although in terms of cohesions Estel 1100 achieved the best results, its use should be limited to indoor environments since it contains organic groups so that an outdoor exposition could induce oxidation processes. Furthermore, a strong gradient of physical characteristics between bulk and stone surface induced by a water repellent treatment, can be lead to soiling degradation phenomena. NanoEstel achieved better results in the capillary absorption test, suggesting that the product has the ability to leave the stone porous structure substantially unaltered.

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