TRACHYTE OF THE EUGANEAN HILLS (NE ITALY): PROVENANCE, DECAY AND DURABILITY

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INTRODUCTION

The Euganean Hills (Veneto, northeastern Italy) are the most important quarry district in Italy for the extraction of trachyte used as building and carving stone. Euganean trachyte is a subvolcanic rock with porphyritic texture dated to the lower Oligocene (Milani *et al.*, 1999; Cucato *et al.*, 2011; Bartoli *et al.*, 2015), which has been exploited in tens of quarries all through the centuries, already in Pre-Protohistory and, more intensely, from the Roman age onwards (Buonopane, 1987). This stone has an age-old tradition of usage in cultural heritage, mainly in northern and central Italy, for manufacturing different everyday items, funerary and votive artifacts, as well as for building infrastructure, monuments, and public and private construction. Many applications were linked to the fervent building boom brought by the expansion of the Roman Empire and, later on, Serenissima Repubblica di Venezia (*e.g.*, Renzulli *et al.*, 1999, 2002a, 2002b; Capedri *et al.*, 2003; Capedri & Venturelli, 2003, 2005; Antonelli *et al.*, 2004; Lazzarini *et al.*, 2008; Antonelli & Lazzarini, 2010, 2012).

An archaeometric study of Euganean trachyte is here presented following two main research directions.

The first involves the identification of petrographic and geochemical criteria for determining the provenance quarry of trachyte used in archaeological and historical materials, and their subsequent application to a set of Roman archaeological samples. The numerous quarries and trachyte varieties with very similar characteristics, as well as the widespread use of this stone, complicate the recognition of the original source quarry, which is nonetheless crucial for providing clues about ancient trades and extraction sites. Indeed, previous researches (Maritan *et al.*, 2013) have disclosed the need to find alternative, more complete, and reliable parameters for provenance identification than those available from the archaeometric literature (Zantedeschi & Zanco, 1993; Capedri *et al.*, 2000).

The second research topic addresses the investigation of the decay and durability of Euganean trachyte used as building stone, a subject only occasionally debated so far (Lazzarini *et al.*, 2008; Graue *et al.*, 2011). Here, the results obtained from the mineralogical, microstructural and geochemical analysis of the weathering products of the stone in urban environment are presented. Further indications about the resistance of Euganean trachyte to environmental stresses are also given after a laboratory investigation of the petrophysical and mechanical properties having a critical impact on many deterioration processes.

PROVENANCE

Calibration: petrographic and geochemical tracers

The determination of new provenance tracers for Euganean trachyte was supported by a petrographic and geochemical database obtained from samples collected from 40 quarries in the entire area of the Euganean Hills. The multianalytical investigation of the quarry samples involved optical microscopy, scanning electron microscopy with mapping by energy-dispersive X-ray spectrometry (SEM-EDS), mapping by micro X-ray fluorescence (μ-XRF), X-ray fluorescence (XRF), electron probe micro-analyzer (EPMA), and laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS), supported by techniques of multivariate statistical analysis. The analytical work was carried out at the University of Padova (Italy), except for the μ-XRF and LA-ICPMS analyses, which were performed at the University of Torino (Italy) and Memorial University of Newfoundland (Canada), respectively.

The most useful petrographic provenance tracers principally include quantitative data about mineralogical composition and textural features of phenocrysts and groundmass, determined by image analysis of μ-XRF and SEM-EDS chemical maps, in particular: *i*) abundance and grain size distribution of feldspar phenocrysts (anorthoclase, plagioclase, and sanidine), *ii*) phenocrysts-groundmass ratio, *iii*) content of SiO_2 phases in the groundmass, and *iv*) arrangement and grain size of microlites in the matrix.

On the other hand, the geochemical provenance tracers involve composition of bulk rock and phenocrysts, determined by XRF and LA-ICPMS, respectively. These data were used for building discriminant plots based on chemical concentrations, with quarry clusters serving as future reference for samples of unknown provenance.

In general, differences of petrographic features and bulk-rock composition among trachytes from different Euganean quarries are subtle, so that their precise discrimination may be rather problematic. In addition, the analysis of those properties needs samples to be representative and large enough; this is a major drawback when dealing with archaeological materials, the sampling of which may be restricted to very small portions, in some cases also having altered surfaces. For these reasons, petrographic observations of thin sections or XRF analyses – the most traditional methodologies previously used (Zantedeschi & Zanco, 1993; Capedri *et al.*, 2000) – might not be sufficient to solve provenance problems univocally, even when combining the two techniques. Nevertheless, the novel approach considering quantitative petrographic parameters from image analysis of X-ray elemental maps, in comparison with conventional qualitative examinations, considerably improves the reliability of petrography-based provenance determination (Germinario *et al.*, 2016).

Alternatively, LA-ICPMS analysis at the mineral scale has proven to be a precise, accurate, and highly sensitive method for autonomously recognizing virtually all the Euganean quarry localities, using composition of phenocrysts, especially of biotite and, secondarily, augite, kaersutite, and magnetite. Linear combinations of major- and trace-element concentrations analyzed on these minerals, calculated by a statistical discriminant analysis, were used to build binary and ternary discriminant plots. Biotite is the most informative mineral species, especially considering correlations among the concentrations of Li, Sc, TiO_2, V, MnO, and Co. Quarry clustering achieved with LA-ICPMS is definitely more precise and effective than that based on the XRF data, especially if analyses of different phases are cross-matched. Moreover, the amount of material required for LA-ICPMS is very limited: at best, even few fine-grained crystals of a single diagnostic phase might be sufficient, and this is a great advantage in the study of cultural heritage, when non-destructive or micro-destructive techniques are mandatory. Finally, although LA-ICPMS may work as a stand-alone technique, one could choose to couple a petrographic examination; in this case a single thin section of suitable thickness (40-50 μm) would be needed.

Application: Roman infrastructure in northern Italy

The provenance markers described above were tested in a provenance study of Euganean trachyte used in Roman public infrastructure in Veneto (mostly built from the 1st century BCE to the 1st century CE), which was sampled in roads, bridges, and forum squares in six former Roman cities. This study was done in collaboration with the Department of Cultural Heritage of the University of Padova (Zara, 2016).

LA-ICPMS analysis of major- and trace-element composition of phenocrysts, performed on thin section, was supported by traditional XRF analysis of bulk rock and examination of petrographic features under the optical microscope. The analytical work was carried out at the University of Padova, except for the LA-ICPMS analyses, performed at the Georg-August-University of Göttingen (Germany).

The LA-ICPMS results, especially those obtained on mafic minerals (the sole biotite composition provides most of the information required), lead to a precise, univocal and autonomous identification of the quarry localities where Euganean trachyte was extracted by the Romans. It is possible to distinguish even the archaeological samples sharing very similar mineralogical, textural and bulk-chemical characteristics, but extracted in different sites. On the other hand, the above-mentioned drawbacks of microscopic observations on thin section and XRF analyses arose again, leading to uncertain provenance determinations.

This study also gives interesting archaeological information, about the quarries that were active in the Roman times, the extent and development of their exploitation, the frequency of use of the materials extracted therein, and the commercial and economic dynamics involving their supply for public works. Moreover, indications are given with regard to the territorial organization of the Roman settlements in Veneto, their areas of political influence, and ownership and competition of quarries. A connection can be found between specific quarry localities and the Roman settlements in which trachytes extracted therein were preferentially used. This allows arguing a separate management of the Euganean quarries by the most important cities nearby.

Finally, this study provides broad insights into ancient trades in northern Italy during the Roman age. The main trade lines for the circulation of raw and finished quarry materials can be discussed considering the localization of the Euganean district in relation to the main transport routes and destination centers, the convenience of different means of transport, and the amounts of trachyte required for public works. Most trades were organized by ship transports taking advantage of the many rivers and channels of the Venetian Plain (especially those flowing very close to the Euganean quarries), the nearby Po River, and the Adriatic Sea.

DECAY AND DURABILITY

Weathering in urban environment

Considering the historical importance of Euganean trachyte as building material and the current needs for its most effective safeguard, its response to environmental stresses was examined in urban environment, where concentration of stoneworks is relatively high and their conservation threat more significant.

A set of trachyte samples was collected on the Renaissance city walls of Padova (16^{th} century), for analyzing weathering crusts and patinas, *i.e.*, their mineralogical and microstructural characteristics, and major- and trace-element chemical composition, by optical microscopy, SEM and EDS mapping, X-ray powder diffraction (XRPD), and LA-ICPMS. The analytical work was carried out at the Georg-August-University of Göttingen.

Trachyte alteration can be placed in direct correlation with quantitative environmental parameters, in particular concerning air quality and anthropic pollution sources. The crusts and patinas on the exposed surfaces are rich in heavy metals (*e.g.*, Pb, As, Cr, Cd, Sb) and carbonaceous masses, mainly deriving from particulate matter emitted in Padova due to fuel use in road transport and domestic combustion (ARPAV, 2015). A secondary source of particulate matter is represented by short- and medium-range industrial emissions, *i.e.*, in Padova and in the industrial area of Venezia-Porto Marghera, one of the biggest coastal industrial zones in Europe, 30 km far.

The pollutants are entrapped in a crystalline matrix usually rich in calcite or iron, present as oxides/hydroxides or in amorphous state, also including minor amounts of quartz, dolomite, and other components (metallic and alumosilicon particles, chlorides, etc.). The high concentration of carbonates cannot be traced back to host rock composition. The only plausible and consistent source is identified in neighboring lime and Mg-lime mortars used in the walls of Padova for joining trachyte blocks. In fact, calcium carbonate may be dissolved by acid solutions and reprecipitate due to pH increases (Dolgaleva *et al.*, 2005). Local pH fluctuations, also occurring seasonally, may favor mechanisms of cycling dissolution, short-range mobilization, and recrystallization of calcium carbonate from mortars.

With regard to intrinsic alteration processes, the enrichment in iron of the weathering crusts and patinas is dependent on the leaching of this element from iron-bearing minerals of trachyte, and its migration to surface, where it forms brown-reddish layers. Microscopic examinations disclosed an enrichment in fine-grained iron oxides and hydroxides and amorphous iron in the proximity of biotite phenocrysts and, secondarily, magnetite and ilmenite.

Other less common alteration types detected comprise powdery deposits and gypsum crusts. The thickest, most homogeneous and well-developed crusts, rich in either calcite or gypsum, partially shield the host rock from further pollutant absorption.

From this study, it arises that most of the alteration products of Euganean trachyte are due to exogenous processes, whereas the stone itself does not have particular compositional features prone to trigger major dangerous mechanisms of decay. Generally, composition of the weathering crusts and patinas proves to be an informative marker for the relevant environmental conditions and their evolution, and chemical stability of the rock-forming minerals of the stone and neighboring mortars.

Petrophysical and mechanical properties

In order to further explore the properties affecting the weathering behavior of Euganean trachyte, quarry samples from the most representative extraction localities were subjected to a comprehensive petrophysical and mechanical characterization, involving: density, porosity, water absorption, capillary water uptake, hygroscopic water adsorption and desorption, hydric and hygric dilatation, water vapor diffusion, thermal expansion and residual strains, resistance to salt attack and abrasion resistance. The measurements were mostly done at the Georg-August-University of Göttingen and, partly, at the University of Padova and at the University of Kassel (Germany). Particular emphasis was placed on the characterization of porosimetric properties, by mercury intrusion porosimetry and image analysis of μ-XRF and SEM-EDS X-ray maps, which allowed getting information about a pore size range extended from nanometric to millimetric scale.

The different varieties of Euganean trachyte exhibit a relatively wide array of technical performances, which are almost completely dependent on the diverse porosimetric characteristics. This applies, in particular, to the water-related properties, indicating which modes of water transport and retention preferentially take place and at which rate. High porosity is not necessarily an indicator of bad durability, since the interaction with bulk, capillary or hygroscopic water can be regardless limited by a poorly interconnected pore network. On the other hand, pore size controls the favored interaction with water in either liquid or vapor state; while macropores are involved in liquid water flow, capillary pores are especially responsible for processes of capillary water suction, and micropores mainly for water vapor condensation (Klopfer, 1985; Steiger *et al.*, 2014). Therefore, a deep investigation of pore size, size distribution, shape and degree of interconnection, other than pore volume, turns out to be essential for correctly predicting the weathering behavior of different varieties of Euganean trachyte.

Clues are given about the decay processes that would develop in presence of water or aqueous solutions, in particular cyclic crystallization/dissolution of soluble salts from ground water, rainfall or hygroscopic condensation, during drying-wetting cycles. In this regard, the experiments of salt crystallization outlined diverse deterioration patterns, related to the different porosimetric properties, mechanical strength, textural characteristics, and presence of discontinuities, such as scaling, peeling, blistering, differential erosion (on phenocrysts or groundmass), microcracking, powdering, etc.

The improved knowledge of the technical properties of Euganean trachyte also allows arguing the possible criteria followed by clients, quarrymen, and stonecutters for properly choosing the quarries to exploit in the antiquity, especially during the Roman age. Finally, additional elements for aiding quality assessment of Euganean trachyte by conservators-restorers and building companies and identifying the best performing materials are provided by a comparison with the physico-mechanical properties of the most important trachytes currently or historically extracted in other European countries (Germany, Czech Republic, France, Portugal, and Spain). Euganean trachyte can be defined one of, or the best quality trachyte, having performances even better than those of many tuffs, sandstones, and limestones commercially available and used as dimension stones.

FINAL REMARKS

The outcomes of this multidirectional research on trachyte of the Euganean Hills deliver comprehensive information about the most frequently debated topics in petroarchaeometry, *i.e.*, understanding stone provenance of archaeological and historical materials and examining the cause-effect relationships of their decay.

The study dealing with the calibration and application of provenance tracers paves the way for a more accurate investigation of the social, cultural and commercial dynamics around ancient materials made of

Euganean trachyte. It suggests an effective and precise way to determine the source quarries, highlighting a significant advance in comparison to the criteria previously pointed out in the literature. Finally, it gives several elements to be used for further petrological researches on this rock.

On the other hand, the study on the decay features and durability of Euganean trachyte allows comprehending the link between its widespread use and its properties, also giving indications about its vulnerability in the modern environment. Therefore, its long-time name of excellent and durable material can be debated with objective quantitative data.

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