EUGANEAN TRACHYTE IN THE MONUMENTAL BUILT ENVIRONMENT: 
ARCHAEOOMETRIC DISCRIMINATING CRITERIA AND WEATHERING ANALYSIS

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Cycle: XXIX

Abstract

Euganean trachyte has been widely used in northern and central Italy as building stone in archaeological and historical heritage, especially from the Roman times. The numerous historical quarries and widespread use of this material bring several problems in recognizing its provenance quarry, which could provide clues about ancient trades, quarrying and sources of stone supply. Recent studies demonstrate that the discrimination criteria proposed in literature are partially unreliable. The present research reviews these criteria and indicates new ones, based on the distinctive associations of mineralogical, textural and microchemical characteristics of the stone. In a second phase, the research will focus on the weathering analysis of Euganean trachyte exposed to different air quality and climate conditions: field-exposure tests and short-term monitoring of quarry samples will be performed, together with the analysis of on-site monumental stone.

Introduction

The Euganean Hills are the most important quarry district in Italy for the extraction of trachyte, a sub-volcanic rock dated to the lower Oligocene (De Pieri et al., 1983; Zantedeschi 1994) and widely exploited since the 7th century BC in more than seventy open-pit quarries. This stone has been historically used in northern and central Italy as building material in numerous monuments and infrastructures, as well as in common construction and artifacts, especially starting from the Roman times, thanks to its high durability and excellent technical properties (Renzulli et al., 1999, 2002a, 2002b; Capedri et al., 2000, 2003; Capedri & Venturelli, 2003, 2005; Antonelli et al., 2004; Santi & Renzulli, 2006; Antonelli & Lazzarini, 2010, 2012; Maritan et al., 2013; Previato et al., 2014).

The present research proposes an archaeometrical study of Euganean trachyte, following two main directions. Firstly, new petrographic and geochemical criteria for identifying the provenance quarry of the stone in archaeological and historical objects will be found. This will provide clues about ancient trades, quarrying and sources of stone supply. The study is needed as the guidelines proposed in literature (Capedri et al., 2000) are partially unreliable (Maritan et al., 2013). Secondly, the weathering of Euganean trachyte in the monumental built environment, exposed to different air quality and climate conditions, will be analyzed; in this regard, comprehensive studies are almost totally lacking (Valluzzi et al., 2005; Lazzarini et al., 2008). During the first PhD year, the research has addressed the first topic.

Experimental approach

An extensive sampling of trachyte was performed in the entire area of the Euganean Hills, on about 40 different outcrops, most of them being historical quarries. Different samples were taken for each site (with a minimum of 2, 86 in total), depending on the size of the quarry or the lithological variability observed, and they were prepared for the following analyses. Thin sections are being characterized through optical microscopy (OM) and scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Smoothed tiles, instead, are being analyzed by means of micro X-ray fluorescence (μ-XRF) at Dipartimento di Scienze della Terra of Università degli Studi di Torino, and the relevant chemical maps processed through image analysis. Finally, bulk XRF analyses were performed, and the data subjected to a preliminary univariate and multivariate analysis, i.e. principal component analysis (PCA) and cluster analysis (CA).

Preliminary results and discussion

Based on the OM examination, the associations of essential femic minerals and accessory minerals cannot be used as a discriminating parameter, as they are randomly distributed, even within a single quarry or lo-
city (hill). Conversely, specific associations of feldspars and their quantitative relationships could be used, although only for particular localities (e.g. Monselice, M. Rustà, Rocca Pendice); indeed, for most of the sites sampled, the feldspar fraction of trachyte is always given by a nearly 1:1 ratio of anorthoclase/plagioclase and secondary amounts of sanidine. Similarly, with regard to texture, in most cases Euganean trachyte is holocrystalline and glomeroporphyric-cumuloporphyric, with hiatal grain size and felty matrix; however, in some sites, it shows cryptocrystalline/glass-bearing domains (e.g. M. Lispida, M. Oliveto), seriate grain size (e.g. M. Merlo, M. Lozzo) or oriented groundmass (e.g. Monselice, M. Cero), which could help in the quarry distinction (Fig. 1). The overall examination of all the samples reveals that OM observations can be useful for discriminating only few sites, whereas some mineralogical and textural characteristics are equally found in numerous different quarries, even very far from each other. The SEM-EDS analyses are focused on particular microstructures, such as zonings, intergrowths, reaction rims etc. The investigations have concerned feldspar phenocrysts so far (Fig. 2), and suggest the possibility to use some overgrowth textures (e.g. corona textures, such as plagioclase with alkali-feldspar rim or anorthoclase mantled by sanidine) as distinctive characteristics among different magmatic bodies.

Fig. 1: Photomicrographs in cross-polarized light of trachyte samples from two of the main Euganean sources of stone in the antiquity, Monselice (left) and M. Merlo (right). Texture differences are evident: trachyte from Monselice has a trachytic-piloxitic groundmass and a hiatal grain size, whereas trachyte from M. Merlo has a seriate and felty texture. In this case, even mineralogical association is different.

Fig. 2: SEM-BSE photomicrograph (left) with related EDS map (right) of a trachyte sample from M. Merlo, showing a plagioclase phenocryst with an alkali-feldspar rim (field size: 571.43 x 457.14 μm).
The μ-XRF analyses are adding information about texture, supporting the OM observations with quantitative results. In particular, the processing of the chemical maps (Fig. 3) is providing very fast measures of phenocrysts/groundmass ratio, grain-size distribution, total area, number, size and shape of phenocrysts of different mineral phases and their quantitative relationships. The global results will hopefully allow discriminating trachyte varieties that are very similar – by naked eye or under the microscope – even belonging to the same magmatic body.

Finally, with regard to the bulk XRF analyses, the results permit to classify Euganean trachyte on geochemical basis: it has an acid to intermediate composition and, according to the total alkali-silica (TAS) diagram, plots mainly in the trachyte field and, partly, in the rhyolite one (Fig. 4). Then, the statistical data treatment is allowing a first grouping of the quarries based on the concentration of major, minor and trace elements, other than the comparison with the reference chemical database from literature (Capedri et al., 2000) – even to test the effectiveness of the different sample-preparation method and of the analysis of additional trace elements. After a preliminary examination of the compositional variation matrix (Buxeda i Garrigós, 1999), no chemical element was excluded from the processing, as none of them showed a concentration clearly affected by alteration processes. Both the univariate and multivariate analysis put into evidence the outliers, i.e. the trachyte samples showing the greatest variability of concentration among the elements measured. Then, the PCA and CA, according to the findings by Capedri et al. (2000), suggested that several chemically-homogeneous groups of quarry sites can be identified (e.g. Monselice, M. Rosso) (Fig. 4); however, within certain localities strong chemical differences can even be outlined, as well as quarries very far from each other can be grouped in the same clusters. In this sense, further data processing is needed, in order to find new quantitative relationships of elements pairs for which the quarries distinctively plot and can be easily differentiated.
**Future research plan**

For the first part of the research, the analyses currently being performed (SEM-EDS and μ-XRF) will be completed and then supported by electron probe microanalysis (EPMA). Subsequently, a microchemical characterization on thin section, through laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), will be carried out at the Department of Earth Sciences of the Memorial University of Newfoundland (Canada). This will provide punctual information on some geochemical parameters such as trace elemental composition of phenocrysts, glass inclusions, accessory minerals etc. This approach has several advantages over the classic one based on bulk XRF (cf. Capedri et al., 2000), as stone alteration possibly does not affect single-crystals composition and high amounts of sample are not needed for statistical representativeness of the bulk composition. The final aim is to suggest a method for provenance identification based on very limited quantities of material, exclusively through determinations on thin section of suitable thickness (45 μm): this is very useful in archaeometry when, for cultural objects, non-destructive or micro-destructive techniques are mandatory.

During the next year, the second part of the research will be first addressed as well. The weathering study of Euganean trachyte will be carried out on both quarry materials and on-site stone exposed to different environmental contexts, in terms of air quality and climate: urban, coastal and rural study areas will be discriminated, in temperate and temperate-cold regions, e.g. northern Italy (historical Veneto cities such as Padova and Venezia) and central Europe (e.g. Germany, where trachyte is used in monumental restorations, Graue et al., 2011). In these sites, trachyte quarry samples will be exposed and monitored for 18 months, performing an alteration analysis every 6 months by means of non-destructive techniques, namely colorimetry, ESEM-EDS, μ-Raman and μ-XRF. In this way, the quantitative modifications caused by environmental aggressiveness and their kinetics will be investigated. The results will be then compared with those from the on-site stone examination, in order to explore the evolution of deterioration for more extended time ranges: Euganean trachyte used in buildings and historical monuments, in the same sites already studied, will be analyzed, by means of SEM-EDS, X-ray powder diffraction (XRPD) and gas chromatography-mass spectrometry (GC-MS). Part of this analytical work will be carried out at the Geo-science Center of the University of Göttingen (Germany).

**References**

ANTONELLI, F., BERNARDINI, F., CAPELDRI, S., LAZZARINI, L., and MONTAGNARI KOKELJ, E. 2004. Archaeometric study of protohistoric grinding tools of volcanic rocks found in the Karst (Italy-Slovenia) and Istria (Croatia). Archaeometry, 46 (4), 537–552.


**SUMMARY OF ACTIVITY IN THIS YEAR**

**Courses, schools and workshops:**

- Workshop “Che cos’è la Microfluorescenza a Raggi-X e dove si impiega?”, Sapienza Università di Roma.
- CMA4CH 2014 “School of multivariate analysis for novices”, Sapienza Università di Roma (planned in December).

**Other:**

- Collaboration arranged with Prof. A. Borghi and Dr. R. Cossio, Dip. Scienze della Terra, Università degli Studi di Torino.
- Collaboration arranged with Prof. J.M. Hanchar, Dept. Earth Sciences, Memorial University of Newfoundland (Canada).
- Collaboration arranged with Prof. S. Siegsmund, Geoscience Center, University of Göttingen (Germany).

- Sep 2014. Visiting student at Dip. Ingegneria Chimica Materiali Ambiente di Sapienza Università di Roma. Analytical tests with a μ-XRF instrument (Bruker M4 Tornado) for chemical mapping of trachyte samples.