TECHNIQUES TO DETERMINE THE PROVENANCE OF LIMESTONE USED IN NEOLITHIC ARCHITECTURE OF MALTA

LINO BIANCO

Faculty for the Built Environment, University of Malta, Msida MSD 2080, Malta,
E-mail: lino.bianco@um.edu.mt

Received July 7, 2016

Abstract. The scope of this paper is to put a case for lithological mapping of the limestone used in the Neolithic architecture of Malta to establish, through a comparative analysis, the provenance of the building fabric utilised in the erection of such monumental buildings. In this study, rock samples from the same lithology were assessed through destructive and non-destructive physico-mechanical, textural, chemical and mineralogical analytical techniques, to determine the principal characteristics of the limestone.

Key words: limestone, non-destructive techniques, ultrasonic pulse velocity, thin sections, SEM, X-ray fluorescence, X-ray diffraction, Neolithic architecture, Malta.

1. INTRODUCTION

Limestone has been used as a building stone since time immemorial. Abundant archaeological evidence proves that, in antiquity, builders differentiated between the Oligo-Miocene carbonate sedimentary limestone formations of the Maltese archipelago. No written records exist but their Neolithic architecture is a primary source of their skills. These builders were aware of the variability in the quality of the limestone and differentiated between the harder, more durable Coralline Limestone Formations and the softer, less durable Globigerina Limestone Formation [1]. The lower formation of the soft and porous Globigerina Limestone has been extensively used in the Neolithic megalithic temple architecture of the islands [2]. These temples are outstanding for their originality, complexity and striking massive proportions. They are the oldest existing free standing architectural structures in world civilisation and are UNESCO World Heritage sites [3]. Dated to circa a millennium prior to the Great Pyramid of Giza, they are indeed a feat in building engineering.

Establishing the provenance of the limestone used in the erection of such buildings is imperative. Recent research [4–6] reinforces the significance of locating the source of the limestone used in cultural heritage. It is critical to undertake a petrographical study of the stone utilised in its erection. Such a study has a lead function in establishing the provenance, an important consideration in durability assessment [7]. The restoration and conservation of such heritage entail that one evaluates the original fabric for its eventual preservation.

In the case of the Neolithic architecture of Malta, the locations of the sites from where the limestone was extracted are not known. Although no evidence of the original quarries is available, and given the size and weight of the megaliths and the topography of the islands, it is reasonable to assume that the source was close to where the respective monuments stand.

There are destructive and non-destructive analytical techniques to evaluate the composition of the limestone. These are useful tools to establish the principal physico-mechanical, textural, chemical and mineralogical properties of a given building stone. The destructive ones are invasive and applicable to freshly quarried limestone but not for historical material. Non-destructive, less invasive tests are useful to establish the diagnostic characteristics of the limestone used. Having unparalleled sustainability advantages [8] over destructive and invasive methods, these techniques are allowed in contemporary scientific restoration practice [9] as intrusion is minimal with optimal respect for the physical integrity of the original building fabric. Applying these analytical techniques on freshly quarried limestone and on flaked fragments from the built-heritage fabric, one can identify the alike limestone resources, so imperative in any restoration and/or conservation intervention on a given monument.

2. RESEARCH METHODS

Two analytical techniques for limestone evaluation are available: destructive (and invasive) and non-destructive (and non-invasive). These are used to determine the physical (uniaxial compressive strength and ultrasonic pulse velocity), textural (petrography and scanning electron microscopy), chemical (loss-on-ignition and X-ray fluorescence) and mineralogical (acid insoluble residue and X-ray diffraction) composition of a given limestone. Quarrymen distinguish between first and second quality Lower Globigerina Limestone [10]. Thus, 3 first quality (S1 to S3) and 3 second quality (S4 to S6) rock samples from a quarry which extracts this limestone, the industrial mineral in which the extensive, impressive architecture of the Knights of St John of Jerusalem is erected [11], were analysed to establish their respective principle petrophysical characterisation. The samples were identified by Bertu Agius, the quarry owner. Prehistoric and historic architectural structures are present all over the islands but their density is highest in areas where Lower

Globigerina Limestone outcrops. The first comprehensive study on the factors controlling the quality of the Lower Globigerina Limestone building stone of Malta, undertaken at the University of Leicester, was funded by the Office of the Prime Minister (of Malta) [12]. First quality limestone is more durable than second quality but quarrymen tend to interchange durability with compressive strength. The second quality limestone is richer in non-carbonate content, mainly quartz fragments followed by K-feldspar and clays [12].

2.1. PHYSICAL ANALYTICAL TECHNIQUES

2.1.1. Uniaxial compressive strength

Uniaxial compressive strength (UCS) test was undertaken on limestone in oven-dried (temperature $105^{+}/-5^{o}$C) and saturated state (fully submerged for 4 hours) using an Avery-Denison model. Samples measuring 100×100×100 mm were prepared; the direction of the bedding plane was noted. The results obtained when crushed at a constant loading rate set at 0.15 N/mm^2 applied perpendicular to the bedding plan, varied between 21.8 N/mm^2 and 30.2 N/mm^2 and between 12.9 N/mm^2 and 15.4 N/mm^2 for oven-dried and saturated samples respectively (Table 1). The presence of water led to a significant reduction in the compressive strength.

2.1.2. Ultrasonic pulse velocity

Ultrasonic pulse velocity (UPV) test was performed on oven-dried ($105^{+}/-5\ ^{o}$C) samples only. Velocities were measured using a PUNDIT (Portable Ultrasonic Non-Destructive Indicating Testing) model.

Results obtained for the UPV do not differentiate between first and second quality samples. Variations of the results are similar to the readings from the uniaxial compressive strength test. Correlation exists between UPV and UCS [13]. The standard classification for UPV was used [14]. Given that the ultrasonic velocities are between 2.5 km/s and 3.5 km/s, the velocity recorded is low. Values derived for wet samples are lower [13].

Table 1

Physical and mechanical properties of limestone samples

	S1	S2	S3	S4	S5	S6
UCS (N/mm^2) (oven-dried)	29.85	30.18	29.90	28.83	25.30	21.82
UCS (N/mm^2) (saturated)	14.58	15.42	14.63	12.89	15.26	15.09
UPV (km/s)	02.99	03.06	03.01	02.91	02.98	02.91

2.2. TEXTURAL PROPERTIES

2.2.1. Petrography

Thin sections analysis was undertaken to investigate the cementing fabric, porosity and permeability. Samples analysed consisted of fine grained, well-sorted, porous intrabiosparitic wackestone (Fig. 1). Intra- and inter-particle pores, the former (maximum diameter 375 μm) more frequent than the latter (maximum diameter 250 μm), are present. Porosity along grain boundaries is predominant. Most allochems are cemented by fine grained sparry calcite which imperfectly fills the inter-particle voids.

Planktonic and bentonic foraminifera constitute most of the sediment. Globigerina grains (maximum diameter 50 μm) and rare echinoid fragments are present. Undamaged microfossils have frequently unfilled chambers. Quartz grains (average 15 μm) are dispersed through the fabric, occasional elongated or rounded (maximum 20 μm). Glauconite and some iron oxide(s) are also present as is staining due to breakdown of iron-rich minerals.

2.2.2. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to get high-resolution imaging of the texture, cement fabric and microphotograph pores. A Hitachi S-520 equipped with an energy-dispersive analyzer for semi-quantitative chemical analysis of the area under focus was used.

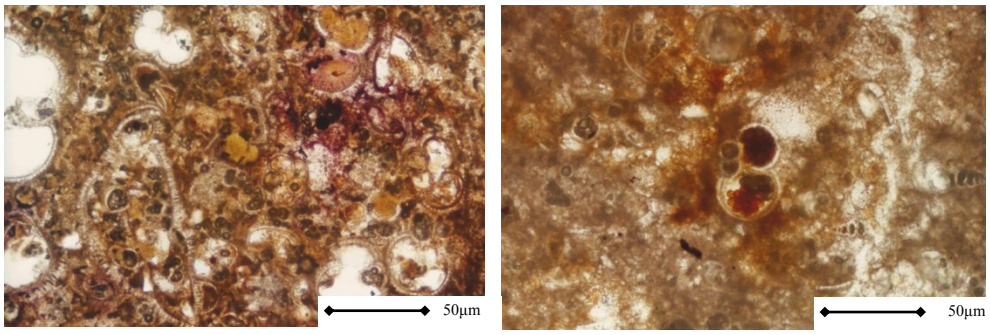

Fig. 1 – Thin section (crossed nicols) of Lower Globigerina Limestone showing the porous planktonic foraminiferal wackestone mainly consisting of globigerina grains and echinoid fragments.

To avoid contamination, fragments (measuring 5×5×5 mm) were freshly cut from the sample retained after thin section preparation. Samples were handled by disposable gloves and tongs to evade contact with skin oil which might out-gas in the scanning electron microscope vacuum system and hence lead to a poor quality image. A film of conductive silver paint was introduced to ensure electrical contact

between the sample and the stub and a thin gold coating was applied to the sample to secure a clear image.

The images derived show the pore structure, the physical-mechanical interlocking and the fine grained cement (Fig. 2).

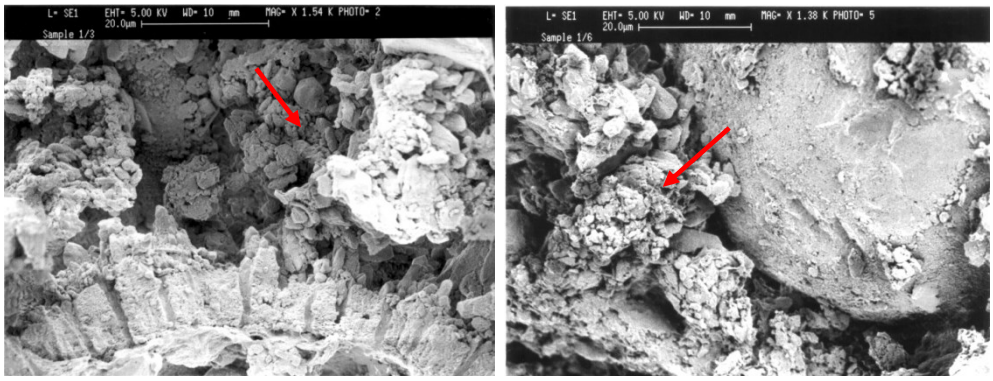

Fig. 2 – Scanning electron images showing the pore structure and the physical-mechanical interlocking and the fine grained sparry calcite cement.

2.3. CHEMICAL PROPERTIES

2.3.1. Loss-on-ignition

Loss-on-ignition (LOI) is a measure of the loss in weight percent of an ignited sample due to the release of CO_2, water and other volatiles. All samples had loss-on-ignition content less than 44%, the theoretical value for pure $CaCO_3$. The second quality limestone is marginal (circa 2%) lower.

2.3.2. X-ray fluorescence

X-ray fluorescence (XRF) was used to determine the bulk chemistry. Fusion beads are optimal in determining the major oxides present. Instead, pressed powder pellets were used. Making use of an ARL 8420^+ XRF spectrometer, pellets were analysed for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O_3, K_2O, and P_2O_5. Thus, the respective chemistries of the samples could be compared (Table 2).

$CaCO_3$ and loss-on-ignition are consistent. The lower the $CaCO_3$ content the higher is the SiO_2 content. The variation of Al_2O_3 and K_2O is similar to SiO_2. The content of these compounds increase with decreasing quality as does Fe_2O_3 and P_2O_5. Variation in TiO_2 is present. MgO is similar to first and second quality whilst traces of MnO and Na_2O are present in both. With respect to the bulk chemistry, S1 is more akin to second quality whilst S6 is similar to first quality limestone.

Table 2

XRF analysis of limestone samples

Oxides	S1	S2	S3	S4	S5	S6
SiO_2	07.954	06.767	05.516	09.695	11.985	06.329
TiO_2	00.184	00.151	00.122	00.221	00.258	00.107
Al_2O_3	01.288	01.062	00.806	01.388	01.615	00.856
Fe_2O_3	00.739	00.595	00.498	01.038	00.978	00.649
MnO	00.032	00.033	00.035	00.036	00.033	00.034
MgO	01.176	01.142	01.113	01.140	01.157	01.137
CaO	49.389	49.668	50.044	48.165	46.651	49.671
Na_2O_3	00.037	00.042	00.025	00.057	00.090	00.058
K_2O	00.425	00.356	00.278	00.512	00.634	00.332
P_2O_5	00.220	00.211	00.204	00.300	00.258	00.310

2.4. MINERALOGICAL PROPERTIES

2.4.1. Acid insoluble residue

The acid insoluble residue (IR) was used to determine quantitatively the non-carbonate fraction present in the samples. Furthermore, x-ray diffraction analysis was performed on the non-carbonate fraction in order to determine the mineralogical composition of the residue.

Second quality stone has a higher insoluble residue content. Non-carbonate impurities are higher in such beds. In all samples, the mineralogy of the insoluble residue is quartz and K-feldspar. Kaolinite and illite are occasionally present.

2.4.2. X-ray diffraction

X-ray diffraction (XRD) was used to determine the bulk mineralogy of the whole rock samples and the mineralogy of the clay fractions. A Philips PW1729 X-ray generator was used. Clay minerals were prepared using oriented mount technique to enhance the d001 peaks [15]. Non-carbonate constituents are easily identified, being relatively in larger proportion, when analysing the filter paper used to determine the IR.

The various types of XRD traces are given in (Fig. 3). First and second quality limestone have similar mineralogy. The main minerals are calcite and quartz. The mineralogy of the insoluble residue is quartz and K-feldspar; kaolinite and illite are occasionally present. These, together with smectite, are confirmed through the mineralogy of the clay fraction.

3. DISCUSSION

The data obtained corroborated with a previous paper published in this journal [16]. The destructive and non-destructive analytical techniques are, independently, not conclusive. The information derived from UCS, petrographical thin sections, loss-on-ignition and from determination of IR is not sufficient to evaluate the limestone analysed in its entirety. UPV, SEM, XRF and XRD do not each provide adequate data to assess the parameters of the limestone in their totality. These analytical methods are important in the assessment of cultural heritage building material as obtaining samples from such fabric is critical.

Applying XRD data, the principal non-carbonate oxides contained in the limestone used in Neolithic architecture as identified through XRF, specifically SiO_2, Al_2O_3, Fe_2O_3, and K_2O, are attributed to quartz, clays, and K-feldspar and some iron oxide mineral(s). XRD did not detect the presence of glauconite, a mineral identified through the petrographic studies of thin sections.

Techniques such as UPV, SEM, XRF and XRD are indicative of the limestone used in a given Neolithic monument. For UPV, which is neither destructive nor intrusive, no sample is required as test is undertaken in-situ on the building stones of the monument. In SEM, XRD and XRF, one can make use of flaked fragments from the building fabric. Having analytical results of such fragments and comparing them with an array of laboratory results undertaken on freshly quarried samples, one can establish the provenance of the limestone. Applied to the entire islands which support several such monuments, one may lithologically maps the sources of the limestone used by the builders.

Isopachyte maps of members of the Globigerina Limestone Formation are available [17-18]. Given that variations are present within the Lower Globigerina Limestone Member, it is imperative that the unique petrophysical characteristics of the limestone used in a given heritage structure is appropriately identified together with its present in-use condition of the fabric. These are important considerations for an informed decision on the preservation and/or conservation intervention required, whether replacement or consolidation of the existing. Using a medical analogy, micro-structural analysis provided by SEM and XRD, and supplemented by XRF, provide the geological DNA of the limestone used by the Neolithic builders. Applied as an integrated approach, these analytical testing regimes are useful for diagnosing the fabric's pathology at micro-fabric level, essential to opt for the appropriate therapy required. Effective diagnosis of the present conditions of the limestone in a given monument is fundamental to establish any intervention for its preservation and/or conservation [19].

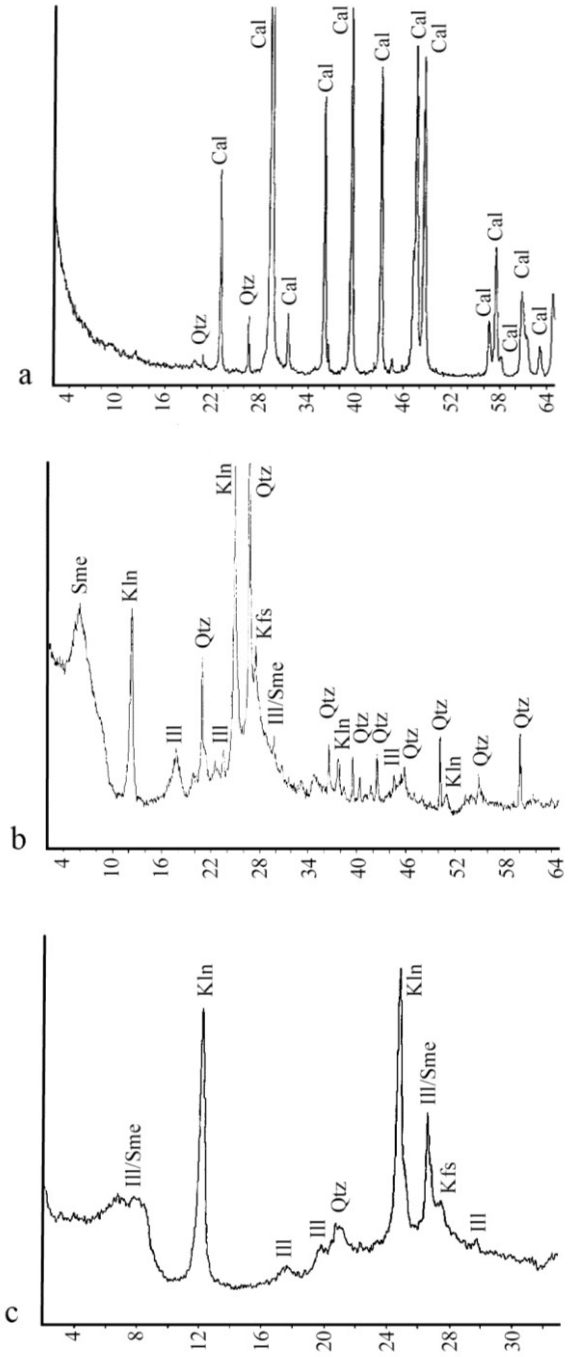

Fig. 3 – XRD trace patterns for sample S1: a) whole rock, b) insoluble residue and c) clay fraction.

4. CONCLUSION

Diagnostic studies are useful to establish the provenance of limestone used in a cultural heritage monument [19–20]. Through physical-petrographical-chemical-mineralogical analyses, the characteristics of the location of the original parent rock from which the archaeological built heritage was constructed can be identified. The original location can be deducted through comparative analysis of in-situ limestone properties used in Neolithic architecture and laboratory analysis of flakes of such limestone with an array of freshly quarries limestone. Once the provenance has been established, identical authentic quarried limestone can be tested for possible preservation and/or conservation interventions such as application of water repellents or the introduction of consolidants to strengthen weakened fabric and/or decrease the rate of surface loss through binding the loosened grains resulting from dissolved intra-particle cement.

Physical, petrographical, chemical and mineralogical analyses are useful for an integrated, holistic approach to natural limestone selection, a critical factor to identify sources either for stone replacement in Neolithic architecture or determine the preservation and/or conservation interventions required. They establish existing limestone resources compatible with the fabric used in a given monument. The notion of time is irrelevant. The Lower Globigerina Limestone is young according to the geological time scale; in terms of this scale, archaeological time is absolute present.

Acknowledgements. The author wishes to thank Dr Hugh Martyn Pedley and the late Professor Anselm Dunham for their advice during the course of my research at the University of Leicester which research was funded by the Oil Exploration Division, Office of the Prime Minister, Malta. Thanks is also due to Alessandra Bianco for her support during the course of preparing this publication.

REFERENCES

1. L. Bianco, *Geocultural activity in seventeenth and eighteenth century Malta*, GeoJournal, **48**, *4*, 337-340 (1999).
2. J.D. Evans, *The Prehistoric Antiquities of the Maltese Islands*, University of London/Athlone Press, London, 1971.
3. UNESCO, *World Heritage List: Megalithic Temples of Malta*. http://whc.unesco.org/en/list/132. Accessed on 30.03.2016.
4. C. Uhlir, K. Schaller and M. Unterwurzacher, *Historic Quarries: Case Studies*, H. G. Bock, W. Jäger and M.J. Winckler (editors) Scientific Computing and Cultural Heritage: Contributions in Computational Humanities, Springer, Heidelberg, 245-253 (2013).
5. R. Navarro, J. Sánchez-Valverde and J.M. Baltuille, *The Natural Stone in the Historic Buildings of the City of Granada (Southern Spain). Features as a Possible Candidate for the Designation of Global Heritage Stone Province*, Engineering Geology for Society and Territory, **5**, 229-232 (2015).

6. E. Torrero, D. Sanz, M.N. Arroyo and V. Navarro, *The Cathedral of Santa Maria (Cuenca, Spain): Principal stone characterization and conservation status*, International Journal of Conservation Science, **6**, *4*, 625-632 (2015).
7. R. Dreesen, M. Dusar, *Historical building stones in the province of Limburg (NE Belgium): role of petrography in provenance and durability assessment*, Materials Characterization, **53**, *2-4*, 273-287 (2004).
8. A. Moropoulou, K.C. Labropoulos, E.T. Delegou, M. Karoglou and A. Bakolas, *Non-destructive techniques as a tool for the protection of built cultural heritage*, Construction and Building Materials, **48**, 1222-1239 (2013).
9. ICOMOS, International charter for the conservation and restoration of monuments and sites, 1965 (the Venice Charter 1964).
10. L. Bianco, *The Industrial Minerals of the Maltese Islands*, Hyphen, **7**, *3*, 111-118 (1995).
11. J. Quentin Hughes, *The Building of Malta during the period of the Knights of St John of Jerusalem*, Alec Tiranti, London, 1967.
12. L. Bianco, *Some Factors Controlling the Quality of Lower Globigerina Building Stone of Malta*, Unpublished M.Sc. dissertation, University of Leicester, Leicester, 1993.
13. E. Vasanelli, D. Colangiuli, A. Calia, M. Sileo and M.A. Aiello, *Ultrasonic pulse velocity for the evaluation of physical and mechanical properties of a highly porous building limestone*, Ultrasonics, **60,** 33-40 (2015).
14. Anon, *Classification of rocks and soils for engineering geological mapping. Part I – Rock and soil materials*, Bulletin of International Association of Engineering Geology, **19**, 364-371 (1979).
15. J. I. Drever, *The Preparation of Oriented clay Mineral Specimens for X-ray Diffraction Analysis by a Filter-Membrane Peel Technique*. American Mineralogist, **58**, 553-554 (1973).
16. A.-A. Balog, N. Cobirzan and L. Barbu-Tudoran, *Evaluation of Limestone with non-invasive analytical methods,* Romanian Journal of Physics, **59**, *5–6*, 601-607 (2014).
17. H.M. Pedley, *The Oligo-Miocene sediments of the Maltese Islands*, Ph.D. Thesis, University of Hull, Hull, 1974.
18. H.M. Pedley, M.R. House and B. Waugh, *The geology of Malta and Gozo*. Proceedings of the Geologists' Association, **87**, *3*, 325-341 (1976).
19. A. Torok, R. Prikryl, *Current methods and future trends in testing, durability analyses and provenance studies of natural stones used in historical monuments*, Engineering Geology, **115**, *3-4*, 139-142 (2010).
20. R. Fort, M. Alvarez de Buergo, E.M. Perez-Monserrat and M.J. Varas, *Characterisation of monzogranitic batholiths as a supply source for heritage construction in the northwest of Madrid*. Engineering Geology, **115**, *3-4*, 149-157 (2010).