IL NUOVO CIMENTO Vol. 30 C, N. 1 Gennaio-Febbraio 2007
DOI 10.1393/ncc/i2006-10038-6

Fingerprinting white marbles of archaeometric interest by means of combined SANS and USANS(*)

R. Triolo([1]), F. Lo Celso([1]), V. Benfante([1]), C. Gorgoni([2]), J. Barker([3]), P. Butler([3]) and I. Ruffo([4])

([1]) *Dipartimento di Chimica Fisica, Università di Palermo - Palermo, Italy*
([2]) *Dipartimento di Scienza della Terra, Università di Modena e Reggio Emilia Modena, Italy*
([3]) *NCNR, NIST - Gaithersburg (MD), USA*
([4]) *I.T.C. "L. Sturzo" - Bagheria, Italy*

(ricevuto il 31 Ottobre 2006; pubblicato online il 9 Febbraio 2007)

Summary. — We have performed a series of USANS and SANS measurements on a selected group of marble samples characterized by similar chemical composition but wide range of known metamorphic conditions. With these samples we start the building up of a data base in an attempt to correlate metamorphism and mesoscopic structure of white marbles. Experimental data have been analysed in terms of a hierarchical model. The present data highlight the importance of the structure at meso scale in identifying the provenance of the marble samples. A remarkable simple relation between the model parameters and the metamorphic degree has been found. This curve might represent a master curve to allow fingerprinting of white marbles. Also, two coloured marbles from Villa Adriana (Tivoli, Italy) have been investigated by means of the same techniques. Results obtained follow the general trend found for the white marbles.

PACS 91.60.-x – Physical properties of rocks and minerals.
PACS 61.12.-q – Neutron diffraction and scattering.
PACS 61.12.Ex – Neutron scattering (including small-angle scattering).
PACS 61.43.Hv – Fractals; macroscopic aggregates (including diffusion-limited aggregates).
PACS 61.90.+d – Other topics in structure of solids and liquids; crystallography.

1. – Introduction

Among the natural composites of archaeological interest, there is a wide variety of stones used in buildings, monuments, statues and other objects of archaeological or cultural-heritage interest. White marble is one of the most common stones used for these purposes; in the Mediterranean basin there are about ten main marble supply

(*) Paper presented at the Workshop "RICH—Research Infrastructures for Cultural Heritage", Trieste, December 12-13, 2005.

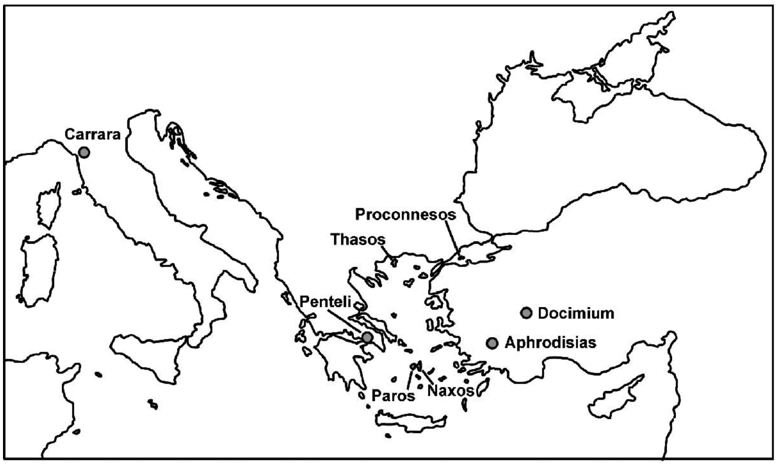

Fig. 1. – The Mediterranean basin and the location of the most important marble supply areas of the past: Carrara, Penteli, Paros, Naxos, Thasos, Proconnesos (Marmara), Aphrodisias and Docimium (Afyon).

districts of antiquity together with many less important ones (fig. 1). Among others, Gorgoni *et al.* have pointed out the importance to archaeologists and art historians of the identification of ancient marbles [1]. The provenance of stone objects is of key importance to archaeology in so far as artistic, technological or commercial exchange patterns may be studied and correlated to historical events and social contacts between cultures. Authentication of works of art in museums is also of great concern, particularly as a number of rather expensive fakes have been acquired by museums from dubious sources [2]. As different white marbles are very similar, there is no single method sufficiently reliable for recognising them. Both petrographic and isotopic general sets of reference data have been produced [3] and improved [1] by including diagnostic parameters of great importance for fingerprinting purposes. However, it looks like the emphasis has been on the microscopic and/or on the macroscopic structure of white marbles, possibly neglecting the intermediate range, *i.e.* the mesoscopic structure. As the mesoscopic structure is the results of the effect of the metamorphic parameters, and as the temperature is the most important parameter determining the metamorphic evolution of a given marble, we thought that it would be important to study a set of marbles coming from the same geographical area, and whose metamorphic history was well documented. In this respect we found the work by Rye *et al.* [4] on the island of Naxos of fundamental importance for the careful mapping of the metamorphic conditions.

2. – Description of the samples analysed

The starting motivation for our study has been the desire to investigate the relationships between the genetic (metamorphic) conditions and the mesoscopic structural features which might make marbles samples unique. The combination of Small Angle Neutron Scattering (SANS) and Ultra Small Angle Neutron Scattering (USANS) allows to obtain unique information in this respect [5]. This is particularly important since, as indicated above, the macroscopic characteristics alone (those that can be resolved by

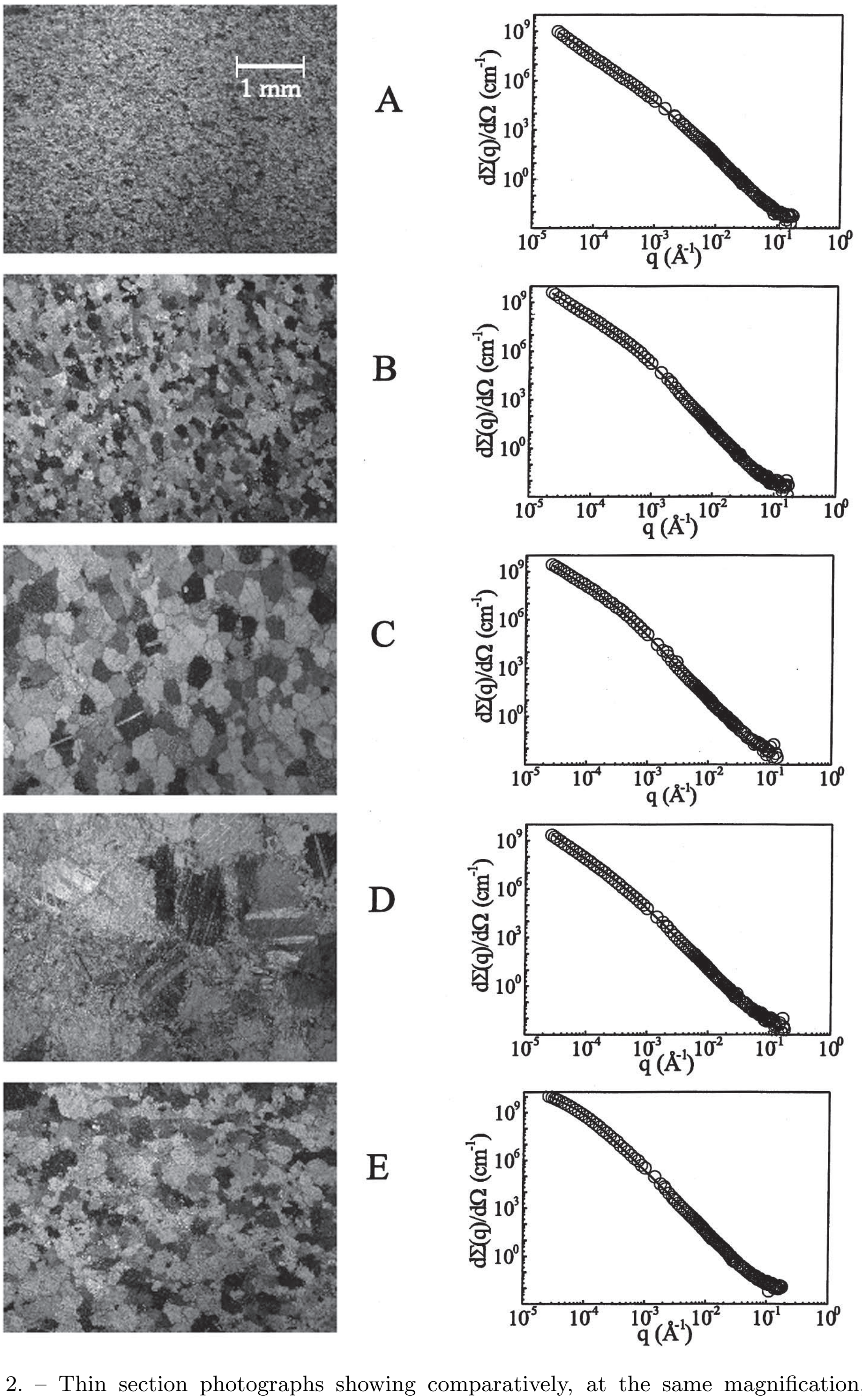

Fig. 2. – Thin section photographs showing comparatively, at the same magnification, the macrostructural characteristics (*i.e.* fabric) of the marble samples (polarized light, crossed Nicols). Aside the corresponding neutron scattering cross-sections. Data taken from ref. [7].

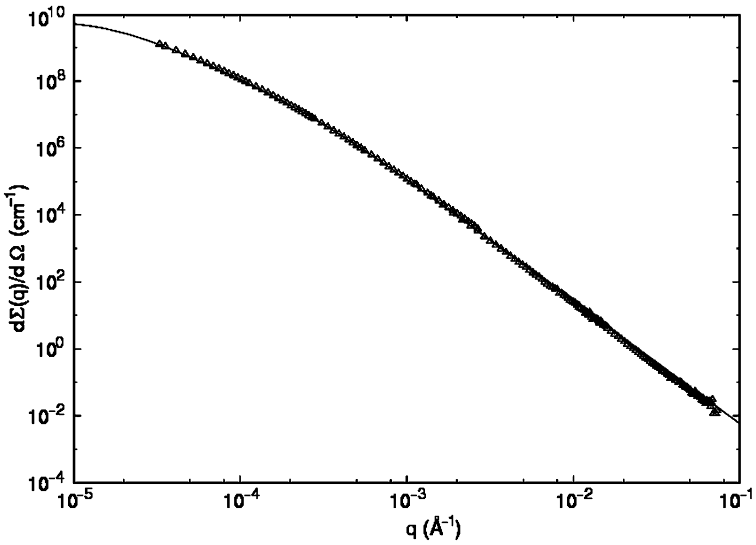

Fig. 3. – Neutron scattering cross-sections (experimental and computed) for a sample of Naxos Island (high metamorphic degree).

using a common optical microscope for mineralogy in transmitted, polarised light) do not always give a reliable diagnostic response. On the other hand, recent researches [6], carried out at the nanoscopic level (*i.e.* by Rietveld-XRD) and thus referring to the basic atomic aggregation (above defined as micro structure), have shown that the micro-structural parameters of the calcite cell (length of the a, b, and c-axes; cell volume, etc.) are influenced by chemical (*i.e.* content of Ca-substituting elements, and in particular Mg) more than metamorphic conditions. It is clear that, in order to be able to trace the provenance of a marble, it is imperative to build a data base containing a large variety of marbles characterized by different meso-structures. We are currently building this data base, and the data shown in this paper is just a small example of how the idea of correlating the meso-structure of a given marble to its thermal metamorphic history might indeed work well. For this reason here we compare a small set of samples collected in different places of the Greeck island Naxos to a set of five samples (see fig. 2) which we have previously characterized [7] and which span a large range of metamorphic conditions. Details on this five marbles may be found in ref. [7]. Two polychromic marbles from Villa Adriana have been studied in comparison with the white marbles. The island of Naxos has been selected as its metamorphic history has been carefully mapped [4]. In particular, the four Naxos samples selected span a range of metamorphic degrees (thermal range in °C) between low (100 °C–200 °C) and medium (300 °C–400 °C). The above maximum temperatures have been estimated by using the information available in the literature [8-13], based on different mineralogical and/or geochemical Geothermometers. These derive from the study of one or more of the following: a) some trace minerals (silicates, etc.) acting as thermal markers; b) the solid solution of magnesite into the calcite lattice (Mg substituting for Ca), etc., which are in turn dependent on the crystallization temperature; c) the fluid inclusions remained trapped into a number of crystals, and any eventual coating minerals; d) the isotopic fractionations concerning different mineral pairs (and nuclides): carbonate-carbonate (oxygen and carbon),

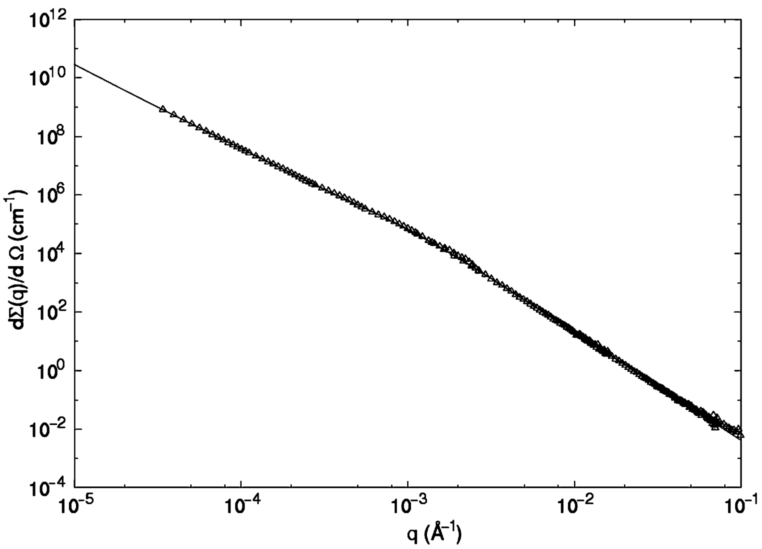

Fig. 4. – Neutron scattering cross-sections (experimental and computed) for a sample of Villa Adriana (medium metamorphic degree).

carbonate-silicate or carbonate-oxide (oxygen), etc. In the absence of specific geothermometric investigations, the metamorphic temperature involved in the formation of a marble can be roughly estimated according to a number of petrographic and geological indications, with special reference to: e) the study of the other associated rocks (silicatic, etc.) forming the metamorphic series of interest, and its general geological setting; f) the simple observation of the marble in thin section (grain size, kind of aggregation, etc.).

3. – Theoretical background

When a beam of radiation (for example neutrons) illuminates a volume V in which scattering centers (*i.e.* atoms and/or their aggregates) are distributed in real space (r) according to a distribution law $\rho(r)$, scattering events take place and a scattered beam will be generated, whose coherent elastic differential scattering cross-section (often simply called scattering intensity) is related to the structure (distribution law $\rho(r)$), to the composition of the sample and to the scattering variable q ($q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and is λ the wavelength of the incident radiation). The form of this relationship depends on the degree of complexity of the structure present in the sample. For example, while scattering data from two-phase systems are in principle easily interpretable, multiphase systems are not so easy to deal with. Geological materials are in general complex multiphase systems. However, a fortunate situation arises when marbles are investigated by means of neutron scattering. In this case the system, even if strictly multi-phase, can be treated as a two-phase system as most of the scattering originates from the contrast between the inorganic components and the voids. Therefore, in what follows we shall always treat our data as belonging to a two-phase system. In the late eighties there has been a strong interest to describe the scattering from natural systems in terms of fractal structures (mass and/or surface fractals). However, these attempts met considerable limitations regarding the interpretation of data because most of the

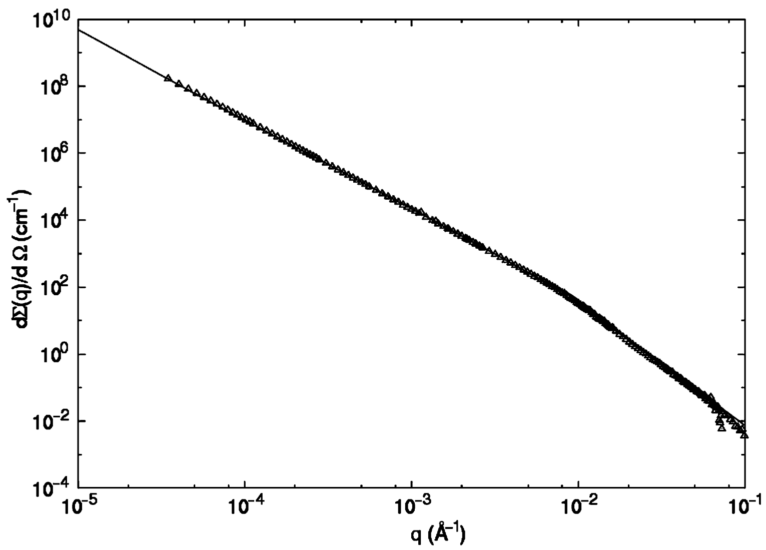

Fig. 5. – Neutron scattering cross-sections (experimental and computed) for a sample of Naxos Island (low metamorphic degree).

power law exponents found were in a range of uncertain attribution, and also because the q range in which data could be obtained was too limited (often less than 1.5 decades). On the other hand, the possibility of extending the range of q towards lower values by using double crystal instruments was precluded by the high wing intensity. Only recently the problem has been circumvented [5] and now cameras able to perform in almost

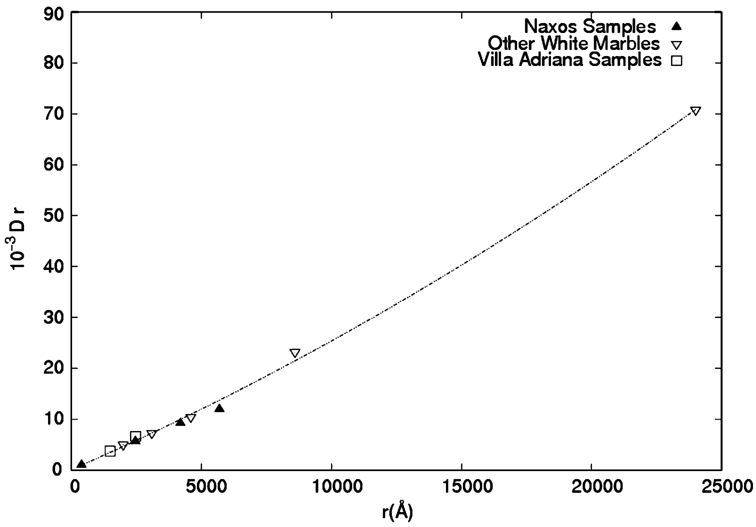

Fig. 6. – Dr *vs.* r plot for the five samples taken from ref. [7] and the new samples reported here.

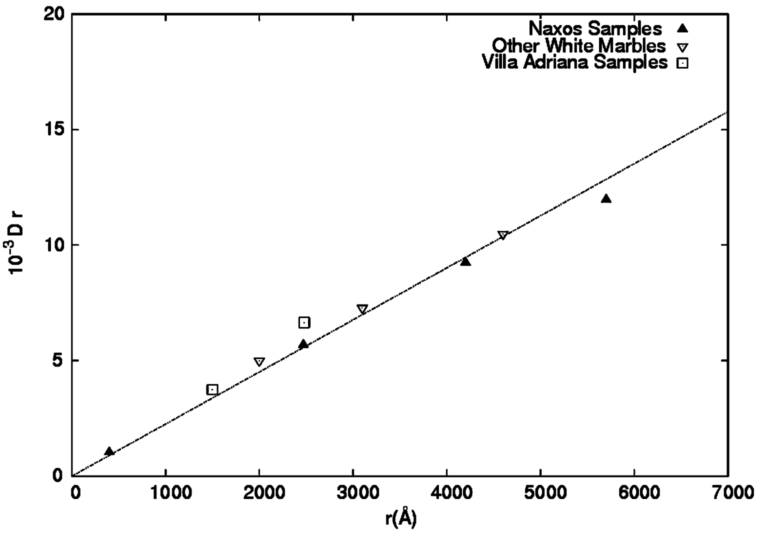

Fig. 7. – Dr *vs.* r plot for the samples of fig. 6 characterized by low and medium metamorphic degree (r less than about 7000 Å).

ideal conditions can be constructed. As a consequence [7], when a neutron scattering experiment is performed on a marble sample, the elastic coherent differential scattering cross-section can be expressed in terms of a hierarchical model which takes into account the existence of a network of fractal aggregates of size R formed by monodispersed solid primary particles of radius r [14]. Figure 2 shows schematically such a model. Eventually, at very low q the intensity is high and with tendency to level off; in other words, neutrons are probing length scales at which the system does no longer show any inhomogeneities and therefore it cannot be resolved. For larger values of q ($q > 1/R$) the scattering intensity drops because clusters of particles of radius R are being resolved; indeed it follows a power law characterized by the exponent D which is related to the fractal dimension or the branching of the aggregate. Going towards even larger q values it is possible to evaluate the radius r of the primary particles and, if their surface has fractal characteristics, the intensity follows a power law with exponent $6 - D_s$ [15] typical of a surface fractal. D_s is indeed related to the dimensionality of the interfacial region of the primary particles and its value must be between 2 and 3 ($D_s = 2$ is for smooth particles following the Porod law $I \propto q^{-4}$). The scattering intensity is expressed as follows:

$$I(q) \propto P(q, r, D_s) S(q, r, D, R), \tag{1}$$

where

$$P(q, r, D_s) = \left(1 + \frac{\sqrt{2}}{3} q^2 r^2\right)^{\frac{D_s - 6}{2}}$$

and

$$S(q, r, D, R) = 1 + \frac{D\Gamma(D-1)}{qr^D} \left(1 + \frac{1}{qR^2}\right)^{\frac{1-D}{2}} \sin[(D-1)\arctan(qR)],$$

TABLE I.

Naxos samples	r (Å)	D_s	D
Nax05	5700	2.30	2.10
Nax16	4200	2.28	2.20
Nax19	2470	2.10	2.30
Nax25	400	2.30	2.58
Other white marbles	r (Å)	D_s	D
Musso	2000	2.45	2.50
Carrara I	3100	2.00	2.35
Carrara II	4600	2.00	2.28
Elba	8600	2.33	2.70
Campiglia	24000	2.25	2.95
Marbles from Villa ADRIANA	r (Å)	D_s	D
Vamp1	1500	2.12	2.50
Vamp3	2480	2.30	2.68

$P(q, r, D_s)$ being the form factor referring to the single primary particle and $S(q, r, D, R)$ the structure factor that reflects the degree of order of primary particles along the aggregates.

4. – Experimental

SANS measurements were performed on the NG3 instrument at the NIST center for neutron research (NCNR), in Gaithersburg, Maryland, USA, covering the range of momentum transfer from $0.001\,\text{Å}^{-1} < q < 0.2\,\text{Å}^{-1}$ with a neutron wavelength $\lambda = 8.1\,\text{Å}$. Samples studied were thin sections (about 1 mm) and therefore multiple scattering was absent. No appreciable neutron activation of the samples was found after the experiment. By using standard procedures, the SANS data were corrected for instrumental background scattering and normalized to absolute scattering cross-section per unit volume ($\text{cm}^{-1}\,\text{sr}^{-1}$) by measuring the incident beam intensity, sample transmission and thickness [16]. USANS experiments were done on Bonse-Hart–type double-crystal diffractometer on BT5 at the NCNR, covering the range of momentum transfer from $2 \times 10^{-5}\,\text{Å}^{-1} < q < 5 \times 10^{-3}\,\text{Å}^{-1}$ [17]. The neutron wavelength was 2.4 Å. The USANS data were slit-desmeared using an iterative technique [18]. By combining the slit-desmeared USANS data with the SANS data, nearly four decades in q, and therefore pore sizes, are probed.

5. – Results and conclusion

The combined (SANS-USANS) sets of data have been fitted to eq. (1). In principle fitting parameters are r, D_s, D and R. However, quite often R is greater than the resolution of the data (*i.e.* no indication of leveling off at low values of q). In these cases, in the fitting procedure, R can be fixed to a value high enough not to produce any effect in the measurable range of q ($R > 2\pi/q_{\min}$, $q_{\min}$ being the lowest value of q experimentally achievable). Figures 3, 4 and 5 show examples of the quality of the fits for a low metamorphic degree sample, a medium metamorphic degree sample and for a high metamorphic degree sample, respectively. Results of the analysis of all the scattering data are reported in table I. Results are shown in fig. 6. A well-defined trend is clearly visible. More importantly, the position of the different samples in the graph area is clearly related to the degree of metamorphism. For example sample Nax25 characterized by a low metamorphic degree has a rather low Dr value, while sample Campiglia, characterized by a high metamorphic degree has a rather high Dr value. Figure 7 shows the same data on a different scale to highlight the correlation between marbles characterized by a low metamorphic degree. It can be seen that the correlation is remarkable, although one cannot exclude that other sources of metamorphism (regional and/or chemical) might be responsible for the structural characteristics of the marbles. An extended database will therefore be necessary for uniquely trace the source of a marble. For this reason data collection on about 120 samples is currently in process.

REFERENCES

[1] Gorgoni C., Lazzarini L., Pallante P. and Turi B., *Interdisciplinary studies on ancient stones*, edited by Herrmann jr. J. J., Herz N. and Newman R. (Archetype Publications London) 2002, pp. 115-131.

[2] See, for example, `www.archaeology.org/0501/etc/conversations.html`, `www.fakesinmuseums.com`, `http://www.museum-security.org/forgeries.htm`.

[3] Moens L., Roos P., De Rudder J., De Paepe P., Van Hende J. and Waelkens M., in *Classical marble: geochemistry, technology, trade*, edited by Herz N. and Waelkens M., *Nato ASI series E*, Vol. **153** (1988), pp. 243–50.

[4] Rye R. O, Schuilling R. D., Rye D. M. and Jensen J. B. H., *Geochimica et Cosmochimica Acta*, **40** (1976) 1031.

[5] Agamalian M. M., Wignall G. D. and Triolo R., *J. Appl. Cryst.*, **30** (1997) 345.

[6] Viani A. *et al.*, *Neues Jahrbuch fur Mineralogie*, **7** (2001) 311.

[7] Triolo R., Lo Celso F., Gorgoni C., Pallante P., Schwahn D. and Baron M., *J. Neutron Res.*, **14** (2006) 59.

[8] Pisa A. D., Franceschelli M., Leoni L. and Meccheri M., *Neues Jahrbuch fur Mineralogie*, **151** (1985) 197.

[9] Cortecci G., Leone G. and Pochini A., *Miner. Petrogr. Acta*, **37** (1994) 51.

[10] Pertusanti P., Raggi G., Duranti C. R. S. and Palmeri R., *Mem. Soc. Geol. It.*, **49** (1993) 297.

[11] Leoni L. and Tamponi M., *Neues Jahrbuch fur Mineralogie*, **4** (1991) 145.

[12] Diella V., Spalla M. and Tunesi A., *J. Metam. Geol.*, **10** (1992) 203.

[13] Siletto G., Spalla M., Tunesi A., Nardo M. and Soldo L., *Mem. Soc. Geol. It.*, **10** (1990) 93.

[14] Emmerling A., Petricevic R., Wang P., Scheller H., Beck A. and Fricke J., *J. Non-Cryst. Sol.*, **185** (1994) 240.

[15] Teixeira J., *J. Appl. Cryst.*, **21** (1988) 781.

[16] Glinka C. J., Barker J. G., Hammouda B., Krueger S., Moyer J. J. and Orts W. J., *J. Appl. Cryst.*, **31** (1998) 430.
[17] Barker J. G., Glinka C. J., Moyer J. J., Kim M. H., Drews A. R. and Agamalian M., *J. Appl. Cryst.*, **38** (2005) 1004.
[18] Lake J., *Acta Cryst.*, **23** (1967) 191.