Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, τομ. XLVII , 2013
Πρακτικά 13ου Διεθνούς Συνεδρίου, Χανιά, Σεπτ. 2013

Bulletin of the Geological Society of Greece, vol. XLVII 2013
Proceedings of the 13th International Congress, Chania, Sept. 2013

ASSESSMENT OF THE QUALITY OF CALCINATION OF MARBLES FROM THASSOS ISLAND USING RAMAN SPECTROSCOPY AND X – RAY DIFFRACTION

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Abstract

The degree of calcination of a dolomitic and a calcitic marble from Thassos Island, was investigated, by combining both Raman spectroscopy (RS) and X-Ray diffraction (XRD) techniques. The samples were prepared in isometric 2 cm cubes and calcined at three different temperatures, 900, 1050 and 1200 ^{0}C for 2 hours in order to produce quick lime. RS was applied at the lime sample's surface and inner (near core) part after gently crushing. XRD was applied on the bulk rock specimens in order to verify the transformation process during heating of the raw material. Quality control of the applied calcination procedure is provided through the hydration of quick lime. The rise in solution temperature suggests the chemical "reactivity" of the produced slaked lime. Raman and XRD results revealed the presence of unburned quantities of calcite and dolomite on samples that were calcined at 900 ^{0}C. Furthermore, temperatures of 1050 and 1200 ^{0}C have shown comparable mineralogical features signifying evenly the conversion of carbonate minerals to their oxide equivalents, proving the completion of the calcination process. Finally, reactivity tests showed that the highest reactivity value of the produced quicklime, for both marbles is observed at the temperature of 1050 ^{0}C.

Key words: *Quicklime, Raman, XRD, Calcination temperature, Reactivity.*

Περίληψη

Στην παρούσα εργασία χρησιμοποιώντας τις τεχνικές της φασματοσκοπίας Raman και της περίθλασης ακτίνων X μελετήσαμε την εξέλιξη της ασβεστοποίησης δύο ανθρακικών πετρωμάτων (δολομιτικό κι ασβεστιτικό μάρμαρο) που προέρχονται από το νησί της Θάσου. Τα δείγματα κόπηκαν σε κύβους μέσης ακμής 2 cm και ασβεστοποιήθηκαν για 2 h σε τρείς διαφορετικές θερμοκρασίες έψησης (900, 1050 και 1200 ^{0}C). Η φασματοσκοπία Raman εφαρμόστηκε στα ασβεστοποιημένα δοκίμια *τόσο στην εξωτερική επιφάνεια όσο και στο εσωτερικό τους μετά από θραύση, με σκοπό την παρατήρηση της εξέλιξης της ασβεστοποίησης από το εξωτερικό προς τον εσωτερικό πυρήνα. Η περίθλαση ακτίνων-Χ σκοπό είχε να επιβεβαιώσει τις παρατηρήσεις της φασματοσκοπίας Raman στο σύνολο του ασβεστοποιημένου υλικού. Υπολογίσαμε τη δραστικότητα των ασβεστοποιημένων δοκιμίων με σκοπό να έχουμε ένα μέτρο της ποιότητας των ψημένων υλικών. Τα αποτελέσματα των φασματοσκοπικών τεχνικών δείχνουν την παρουσία άψητου υλικού (ασβεστίτη και δολομίτη) σε δείγματα που προέρχονται από τη χαμηλότερη θερμοκρασία έψησης των 900 ^{0}C. Στις θερμοκρασίες των 1050 και 1200 ^{0}C διαπιστώθηκε η παρουσία μόνο οξειδίων γεγονός που υποδηλώνει πως η διαδικασία της ασβεστοποίησης έχει ολοκληρωθεί. Από τα αποτελέσματα της δραστικότητας προκύπτει πως οι υψηλότερες τιμές παρουσιάζονται στην θερμοκρασία έψησης των 1050 ^{0}C, που σημαίνει οτι σε αυτή τη θερμοκρασία παράγεται ο ποιοτικότερος ασβέστης.*

Λέξεις κλειδιά: *Άσβηστος ασβέστης, Φασματοσκοπία Raman, Περίθλαση ακτίνων Χ, Θερμοκρασία έψησης, Δραστικότητα.*

1. Introduction

Lime is the most frequently used material in construction application, ever since prehistorical times. Lime refers to calcareous rocks derivatives after calcination, such as quick lime (CaO) and slaked lime ($Ca(OH)_2$). Both forms have several uses and are used in many industries to neutralize acid waste, and as causticisers in the pulp and paper industry, as flux in the steel industry, in road stabilization, in gold recovery and in environmental applications (Triantafyllou & Manoutsoglou, 2004). The most abundant type of calcareous rocks is limestone, marble, travertine, chalk, coquina, tufa, stalactites and stalagmites. Marble is the most common metamorphic rock formed under high pressure and temperature of sedimentary carbonate rocks, most commonly of limestone or of dolomitic rock and is composed of recrystallized carbonate minerals, most commonly calcite and dolomite. Its principal uses are in construction, in interior decoration and in sculpture.

Quicklime production is based on carbonate calcination and of subsequent hydration of quicklime (slaking) through the following reactions:

$CaCO_3\ (s) + \text{heat} \rightarrow CaO\ (s) + CO_2$ (1)

$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2$ (2)

In case of dolomite the following reaction is considered:

$CaMg(CO_3)_2\ (s) + \text{heat} \rightarrow CaO\ (s) + MgO\ (s) + CO_2$ (3)

In this study we compared two quicklimes, a calcium lime and a dolomitic lime, derived from the calcination of carbonate rocks with different composition, a Ca-rich and a Mg-rich marble, respectively. In particular, the studied samples were calcined at 900, 1050 and 1200 ^{0}C and the products were hydrated in order to produce slaked lime (reactivity test). We studied the produced quicklime's in terms of Raman Spectroscopy (RS) and X-ray diffraction (XRD) analyses. The goal of the current study is to use RS and XRD in order to quantify the quality of calcination in terms of conversion of the carbonate minerals (calcite, dolomite) to their calcined equivalents (lime, periclase).

2. Geology of Thassos Marbles

Thassos Island (Figure 1) belongs to the Rhodope Massif, which is located in Northern Greece, between Strimona and Evros rivers. The lithology of Thassos is mainly composed of marble

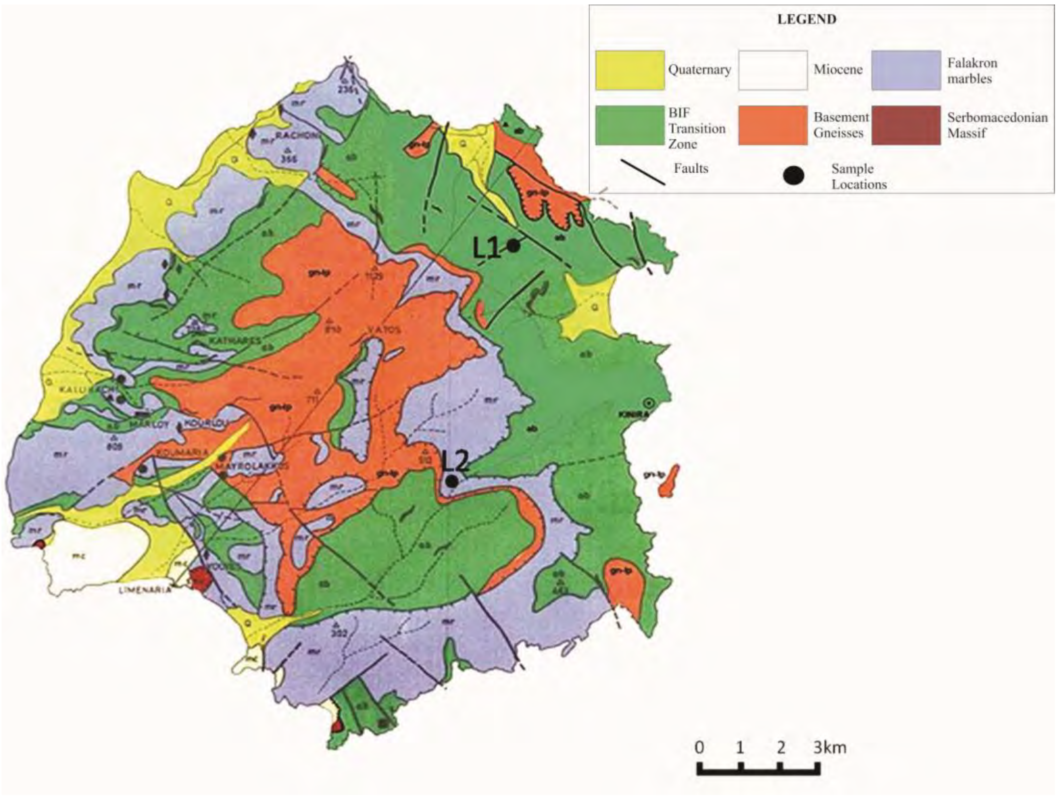

Figure 1 - Modified Geological map of Thassos Island and sampling locations (Source: http://www.geocaching.com).

complexes, ortho- and paragneisses, as well as amphibolites (Bestmann et al. 2000). These marble complexes are known as the Falakron Marbles. They are composed almost purely of calcite, with rare quartz and dolomite crystals (De Wall et al. 2000). They are up to 500 m thick and are separated from the underlying gneisses by a transition zone of about 300 m thick consisting of alternating dolomitic and calcitic marbles, intercalated by schists and gneisses.

3. Analytical Methods

3.1. Raman Spectroscopy

Raman spectroscopy is a technique used to observe vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering (the Raman scattering) of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. It offers several advantages for microscopic analysis. For example, it does not require sample preparation, therefore specimens do not need to be fixed or sectioned, although flattened surfaces give better-resolved Raman spectra. It is also a non-destructive technique that produces characteristically distinct spectra, easing the identification of mineral phases, even mineral polytypes.

We used the RM1000 Ramascope microRaman system from Renishaw. This is based on optical microscope from Leica attached to a spectrometer with a grating of 1800lines/mm and an entrance slit of 50μm. The laser system used is a HeAr laser at 632.8 nm with the energy at the focus point on the sample not exceeding 7 mW, when the ×50 objective lens is used. With this lens, the spot size is about 4μm. Spectra acquisition is performed on a peltier-cooled CCD camera. During the analyses, the spot size was deliberately varied by changing the focus on the sample in order to sample more area, therefore more mineral phases. A combination of the WiRE software from Renishaw and the Grams spectroscopy software from Thermo Scientific was used to store and manipulate the spectra.

3.2. X-Ray Diffraction

X-Ray Diffraction is a destructive technique, which is used to characterize and identify the crystallographic structure of natural and manufactured materials. It is one of the most powerful and well-established techniques for qualitative and quantitative analysis of crystalline compounds (Zussman, 1967).

The preparation of the specimen requires powdering in sizes between 0.1 μm and 40 μm. The XRD system used is the D8 from Brucker. X-rays are produced from a copper lamp operated at 40kV and 40mA, and the slit sizes used are of 1 mm. Both the Raman system and the XRD instrument are property of the National Technical University of Athens, School of Mining and Metallurgical Engineering.

4. Sampling Areas - Petrography of Samples

For the purposes of the current study, we used two different marbles (Laskaridis et al. 2000): a dolomite-rich (L1), and a calcite-rich (L2), both from the area of Thassos island. Sample L1 was taken from Tsipoptsi Limenas location. Its commercial name is Thassos Lienas White- Prinos. The second sample (L2) was taken from Stavrolagkada Theologou location. Its commercial name is Crystallina Theologou Thassou. Both marbles are coarse-grained with granoblastic texture. Sample L1 has a grain size ranging from 0.1-2.0 mm whereas sample L2 has a grain size varying from 0.1-3.0 mm. The predominant mineral phase in L1 is dolomite (94 %) and in L2 calcite (95 %).

5. Experimental Work - Methodology

Isometric 2 cm cubic-shaped samples from each marble were calcined in a furnace at three different temperatures, 900, 1050 and 1200^{o}C for 2 hours in order to produce quick lime on a laboratory scale. Similar procedure has been followed by Kantiranis et al., (1999) and Kantiranis (2001). After calcination, the quicklime cubes were stored in a dryer for 24h in order to cool evenly down to atmospheric conditions**.**

We applied Raman spectroscopy, analysing the exterior (at the surface) and interior (near core) part of the cubic samples. X-ray diffraction was applied on the bulk rock specimens in order to verify the mineral transformation process during heating of the initial material.

For reactivity measurement we used the suitably modulated arrangement that is shown in Figure 2. The quick-lime sieved for 5 min in a mechanical mortar down to a size of ~90 μm.

This arrangement is based on the European standard examination method of structural lime EN – 459:2 (2010), which is typically a calorimeter setup. It requires a Dewar vessel that is enclosed in a container with adiabatic walls so that heat loss is minimum. A high-accuracy thermometer is firmly immersed into the Dewar vessel. The device also includes a mechanical stirring system. Temperature readings are acquired from the digital thermometer connected to a computer through acquisition hardware and software.

Quality control of the applied methodology is provided by the reactivity tests. A lime/water = ¼ ratio was used at ambient temperature (~20 ^{0}C) to produce hydrated lime through the highly exothermic reaction #2. The chemical “reactivity” of the produced slaked lime and, ultimately, the quality of the calcination process, is inferred by the rise in temperature of hydration reaction. Acquired data where used to produce slaking curves for the three temperatures of the experiment

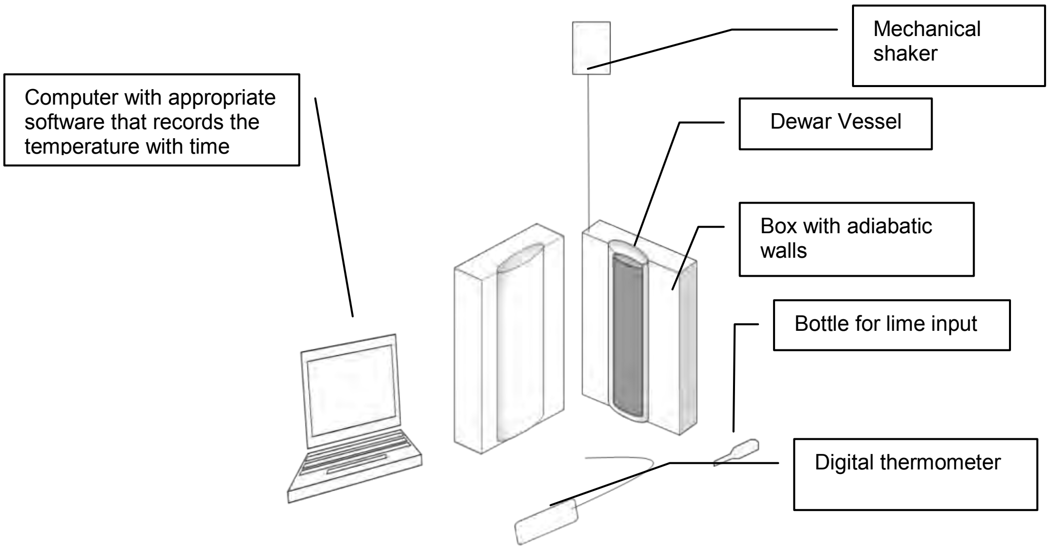

Figure 2 - Experimental arrangement for reactivity lime measurement (before CaO setting).

for each calcined sample. Three methodologies were used for the quantitative definition of the reactivity. These are:

Methodology 1: According to the EN459-2:2001 standard, the reactivity requires the definition of the maximum temperature of the reaction reached by the water-lime system. Then, the reactivity is equal to the temperature given by the formula $80\%*T_{max}+20\%*T_{in}$, where T_{max} is the maximum measured temperature and T_{in} is the initial temperature of the water (before the reaction starts).

Methodology 2: The simplest methodology of the quantitative definition of the reactivity is described in Baziotis et al. (2011). More specifically, the reactivity is computed as the difference between the maximum temperature that has been measured inside the water from the initial temperature of the water before the reaction.

Methodology 3: In this model, the reactivity parameter R_{DIN} is considered which results from the division of 2400 ($40^oC \times 60$ sec/min) by the time (in sec) required so that the temperature reaches 60^oC (Potgieter et al. 2002). The reactivity of lime, based on the R_{DIN} parameter, is divided into three categories: highly reactive lime $R_{DIN}>30$, reactive lime $10<R_{DIN}<30$, and unreactive lime $R_{DIN}<10$. Actually, this model reflects the kinetics of the reaction, and how fast the material will react with the water so that it modulates the respective value of reactivity (R_{DIN}).

6. Results and Discussion

6.1. Raman Analysis

Raman spectroscopy applied in order to study possible variations of the degree of calcination in the external and the internal volume of the samples. Thus, RS evaluates the quality of the calcination process using the modal of calcite, dolomite, lime and periclase in the sample. Figures 3 and 4 show spectra from the outer and inner volume of the cubic samples. Representative spectra are selected from a large number of analyses in order to better demonstrate the full range of transition/final products.

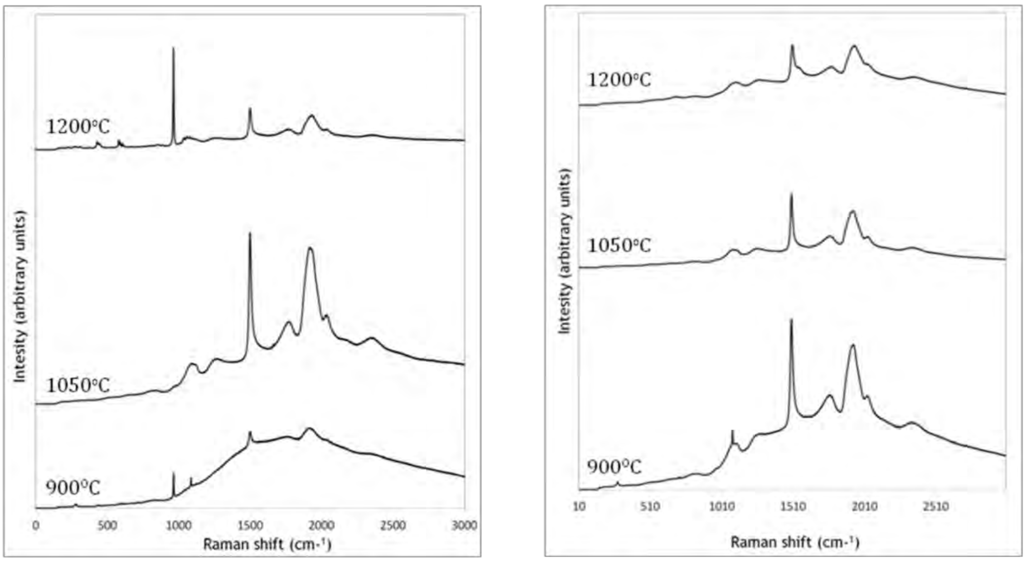

Figure 3 - Raman analyses for sample Q1 (dolomite-rich), showing acquired spectra from its interior (left) and its surface (right).

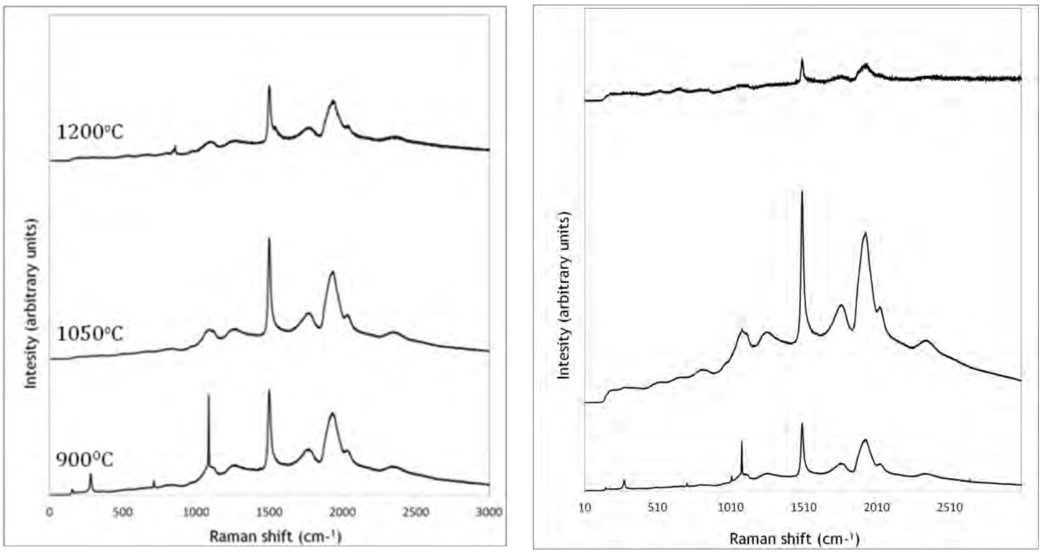

Figure 4 - Raman analyses for sample Q2 (calcite-rich), showing acquired spectra from its interior (left) and its surface (right).

Periclase (MgO) and Lime (CaO) crystallize both in the cubic system, with a the crystal lattice similar to the cubic arrangement of Sodium Chloride's (NaCl) structure (Boynton 1980); the latter forbids first-order Raman spectrum as it possesses inversion symmetry (Schlecht and Böckelmann 1973). It is therefore, not possible to detect MgO (or CaO) from the Raman spectrum (Sharma et al. 1991). Thus remain controversial in the literature the assignment of the observed Raman bands. Following Walzak et al. (2001), indeed Raman spectrum is due to second-order scattering but the defects in the micro-crystals could make them occasionally available as first-order bands. Further, the authors identify slight shifting of the peaks using different exciting sources (green to red laser excitation source) due to fluorescence; the latter has vibrational structure with a characteristic spectrum for both defects in the microcrystals and crystalline lattice itself.

The broad peak at ~1085 cm^{-1} is assigned to the presence of un-burned material. This is indicated by the presence of calcite and dolomite that remained in large quantities from the initial carbonate precursors. The non-conversion process is strongly influenced from the location of the Raman spot and the calcined temperature. It is reasonable as soon as, the mineral dissociation is evolved from the outer to the inner through certain heat paths.

At 900 ^{0}C the conversion from carbonate to lime is incomplete. However, at temperatures of 1050 and 1200 ^{0}C, Raman spectroscopy shows similar to each other mineralogical features, signifying the complete conversion of carbonate minerals to their oxide equivalents. In particular, the principal bands at ~1500 (narrow peak) and 1930-1940 cm^1, assigned to alkaline-earth oxides (CaO and MgO), but due to aforementioned reasons (fluorescence vibrational structure, similar Raman spectra from both Ca- and Mg-rich quicklime) we are unable to assign the peaks either to CaO or MgO.

6.2. XRD Analysis

Results similar to the Raman analysis, are obtained from the bulk analysis of the XRD analysis (Figure 5). In particular, at 900 ^{0}C the un-burned carbonate minerals (calcite and dolomite) varies from 35 to 65 %, for the dolomitic and calcitic marble, respectively. At 1050 and 1200 ^{0}C after 2 hours of firing, the oxide calcium and magnesium minerals (CaO and MgO for the dolomitic, and CaO for the calcitic marble respectively) dominate in the calcined samples, approaching values of 100 %.

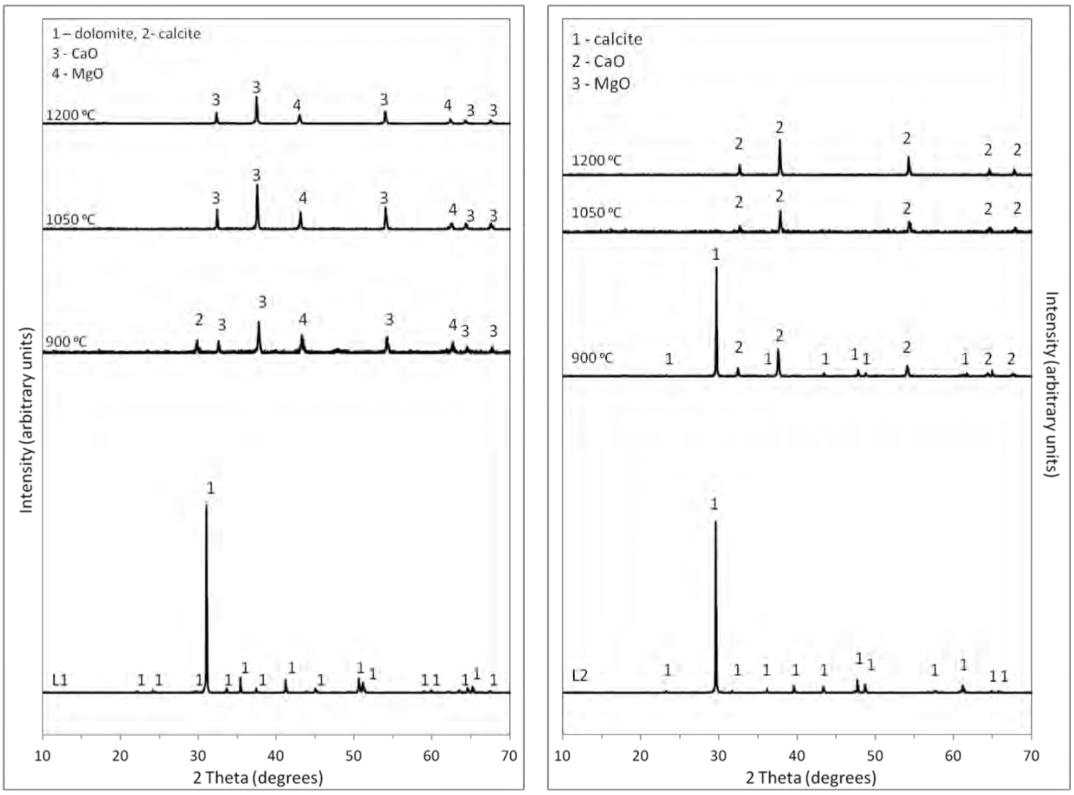

Figure 5 - XRD analyses of Q1 (left figure) and Q2 (right figure) samples for different calcination temperatures (900, 1050 and 1200^0 C).

6.3. Reactivity Test Analysis

From the above results we applied the reactivity test method. The hydration reaction shows that the optimum reactivity value is observed at the temperature of 1050^{o}C (Table 1).

Table 1 - Reactivity values of Q1 and Q2 samples at temperatures 900, 1050 and 1200 0C

Sample	900^{o}C	1050^{o}C	1200^{o}C	Qualitative definition
Q1	22.78* 39.66 ** -***	58.67 67.4 3.37	51,90 61,33 2.41	$^{+}$Inactive lime
Q2	24.15 41.07 -	58.49 66.47 48	44,96 55,86 1.78	$^{+}$Highly reactive lime

*: Reactivity computed according to Baziotis et al. (2011)
**: Reactivity computed according to EN459-2 standard
***: Reactivity computed according to 12485 standard of 1996 (European Norm En 12485)
+: Characterization of lime for 1050^{o}C temperature that is based on following breadths: >30 very effective lime, 10-30 effective lime, <10 inactive lime according to 12485 standard of 1996 (European Norm En 12485)

Also, Figures 6 and 7 provide identification of the various regimes (e.g., Commandrè et al., 2007) of the hydration process over time. Furthermore it is clearly shown that the optimum temperature for both dolomitic (Q1) and calcitic (Q2) marbles is that of 1050 ^{0}C. Furthermore, the presence of magnesium plays an important role in the hard-burnt development (at 1200 ^{0}C) showing a "delaying" slaking curve due to late hydration (Figure 7).

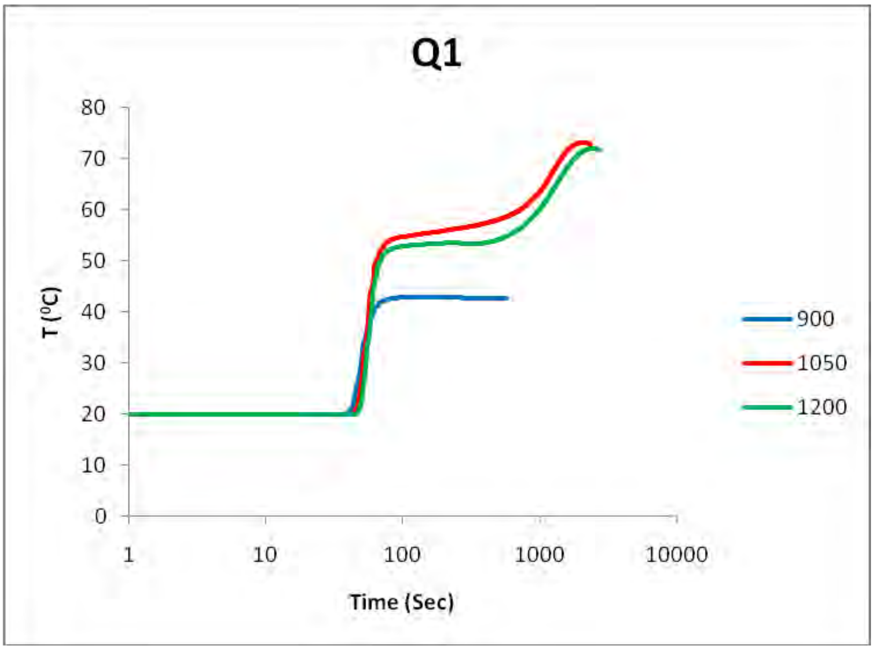

Figure 6 - Slaking curves in lognormal scale for magnesium-rich marble that came from three heating temperatures at 900, 1050 and 1200 ^{0}C.

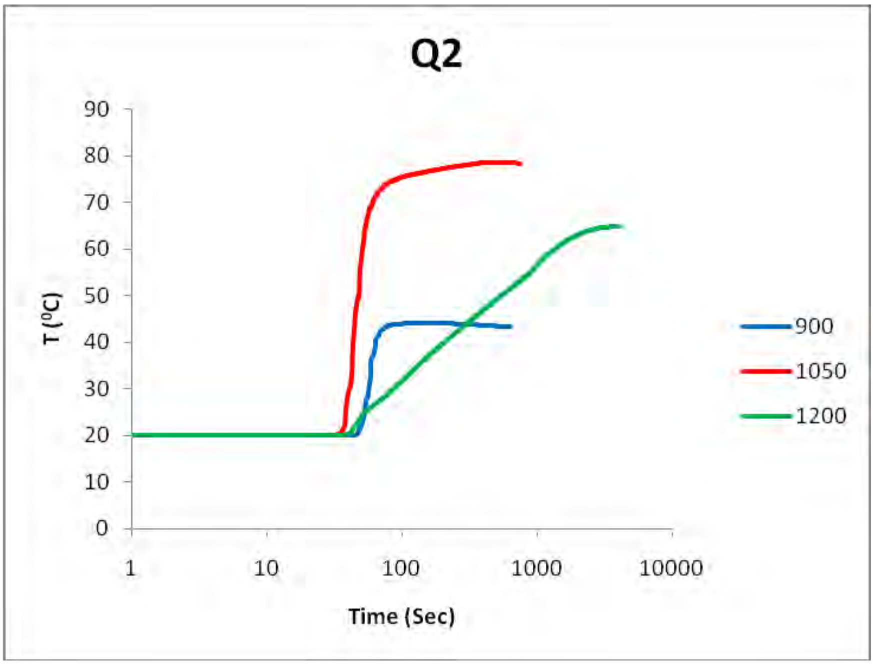

Figure 7 - Slaking curves in lognormal scale for calcium-rich marble that came from three heating temperatures at 900, 1050 and 1200 ^{0}C.

7. Conclusions

Raman and XRD results show unburned material (presence of residual calcite and dolomite) at the lowest measured temperature (900 ^{0}C). The above, combined with the low reactivity values, suggest that the conditions of 900 ^{0}C/2 h are not enough to complete the dissociation of carbonates. After that, we conclude using the current methodology the worst calcination temperature was that of 900 ^{0}C. Raman spectra from both the surface and core of the lime suggest that the carbonate minerals were almost fully converted to newly formed oxides (mainly CaO) at the temperature of 1050 ^{0}C. The above, combined with the results from the reactivity tests (highest reactivity value) suggest that 1050 ^{0}C is the optimum temperature for the studied system. The combination of the spectroscopic methods alone should be applied with caution, however, is able to provide the necessary information on the transformation of the initial material during progressive heating.

8. Acknowledgements

We gratefully acknowledge the helpful remarks by reviewers, G. Triantafyllou and an anonymous one. Also Prof. Manoutsoglou is thanked for his excellent editorial handling. Sincere thanks to Onassis Foundation for the financial support to G. Leontakianakos. G.L. is grateful to Dr K. Laskaridis who provide the samples of the current study.

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