Raman and XRD characterization of Moroccan Marbles

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Abstract. Various marbles collected from Moroccan careers, and two white reference marbles originating from Carrare-Italy and Drama-Greece, have been studied by different analytical techniques. Chemical composition of rocks has been determined by X-Ray fluorescence. X-Ray diffraction and Raman spectroscopy allowed the identification of both major (calcite and dolomite) and minor (quartz) mineralogical components. Moreover, Raman spectroscopy has been used to identify the calcium carbonate phases and to examine the graphitic ones in the marbles.

Keywords. Moroccan marbles, Characterization, XRF, XRD, Raman Spectroscopy, Calcite, Dolomite.

1. Introduction
Since antiquity, marbles are the most ornamental rocks used as building materials for architecture and sculpture owing to their aesthetical, mechanical and thermal properties [1]. The two major phases constituting the marble are calcite (CaCO3) and dolomite (CaMg(CO3)2) [2]; the variety of their colors is due to the presence of impurities such as quartz, graphite, mica, clay and iron oxides. The use of marble and ornamental rocks in Morocco date back to the Roman period (Volubilis, Sala, Lixus, Banasa, Thamusida) [3-6]. Currently, limestones and marbles industry is increasingly developed in Morocco [7]. In this sens, we have undertaken their characterization by combining different analytical techniques. Marble samples were collected at different careers in Morocco, and were characterized by mean of X-Ray fluorescence (XRF), X-Ray diffraction (XRD) and Raman spectroscopy. As reference materials, two white marbles, originating from Carrare in Italy and from Drama in Greece, were also characterized.

In this paper we report and discuss the obtained results, and we give a comparison between the studied marbles from Morocco and the two reference white marbles.
2. Materials and methods

2.1. Samples
Several samples of marbles and ornamental stones collected from different regions of Morocco are in course of study by different physicochemical techniques. This article will be limited to the results obtained on five marble samples collected at the careers of Tiskram in the region of Khénifra (KB), the careers of Sahara in the region of Tiflet (TS), the careers of Oued Amlil in the region of Taza (OA). These results will be compared to those corresponding to the reference white marbles from Carrare -Italy (BC) and Drama - Greece (G). In the case of the marbles of Khénifra, the rock is of white color, gray to black and sometimes of morello cherries or nodulated aspect; some areas locally contain fossils. The Marbles collected in Oued Amlil, show a gray to greenish beige color with, locally, heterogeneous levels of gray shades and corrugated aspect. The marble of Tiflet is light gray with a purplish shade.

![Figure 1. The samples of studied marbles.](image)

| Sample code | Color | Provenance          |
|-------------|-------|---------------------|
| KB          | White | Tiskram-Khénifra    |
| TS          | Grey  | Sahara-Tiflet       |
| OA          | Grey  | Oued Amlil-Taza     |
| BC          | White | Carrare- Italy      |
| G           | White | Drama- Greece       |

2.2. Experimental techniques
X-Ray powder diffraction analysis was carried out on powdered samples at room temperature using the Shimadzu XDR-6100 with Cu Kα radiation at the wavelength 1.5405 Å. Samples were analyzed from 5° to 70°.

Raman spectra were recorded in the range 100 - 2000 cm\(^{-1}\) using a Renishaw RM 1000 microraman spectrometer, equipped with a CCD detector and an external Leica DMLM confocal microscope with 10x, 20x, 50x, and 100x objectives. The excitation source is a He-Ne laser operating at 632.8 nm with a resolution better than 2 cm\(^{-1}\). The samples were used directly, without any preparation or prior size fraction.

Elemental analyses were determined using an AXIOS XRF spectrometer with dispersion wavelength. The samples were ground in an agate mortar in pellet form.

3. Results and discussion

3.1. Elemental analyses: XRF
The major and minor element concentrations obtained for the present marbles are summarized in the table 2. In all samples, the most important element content corresponds to CaO with a concentration range of 35.8 - 55.8%. The samples G and OA present the highest MgO concentrations as 28.8% and 7.79% respectively, while the samples BC, KB and TS show contents varying in the range 0.5 - 1.18 %.
Besides SiO₂ (0.2 - 8.48%), Fe₂O₃ (0.11 – 1.92 %) and Al₂O₃ (0.1 – 2.18%), the analyses revealed also trace elements: Na, Sr, Cl, Mn, I, S, P, K and Y.

Table 2. XRF analysis of marble samples

|     | CaO  | Fe₂O₃ | SiO₂ | MgO  | Al₂O₃ | Na₂O | SrO  | MnO₂ | Cl   | SO₃  | P₂O₅ | K₂O  | Y₂O₃ | LOI* |
|-----|------|-------|------|------|-------|------|------|------|------|------|------|------|------|------|
| BC  | 55.8 | 0.20  | 1.18 | 0.1  | 0.07  | 0.03 | -    | -    | 0.05 | 0.02 | -    | -    | -    | 42.6 |
| KB  | 52.00| 1.07  | 8.48 | 0.58 | 0.37  | 0.09 | 0.24 | 0.07 | 0.05 | 0.03 | 0.02 | 0.01 | -    | 0.004|
| TS  | 52.80| 0.11  | 1.47 | 0.84 | 0.78  | 0.12 | 0.04 | -    | 0.05 | 0.15 | 0.02 | 0.07 | 0.07 | -    | 43.5 |
| OA  | 38.50| 1.92  | 5.37 | 7.79 | 2.18  | 0.20 | 0.01 | -    | 0.06 | 0.10 | 0.02 | 0.10 | 0.19 | -    | 43.6 |
| G   | 35.80| -     | 0.35 | 28.80| 0.28  | -    | -    | -    | 0.30 | -    | -    | -    | -    | -    | 34.47|

*LOI: Loss on ignition

3.2. Crystalline phases: XRD

The various Bragg reflections are indexed using (JCPDS) files [8]. The predominate lines (2θ = 29.4° and 2θ = 30.93°) are attributed respectively to calcite and dolomite; the marble (BC) is calcitic, the marbles (KB, TS) are calcitic with low contents of quartz, the marble (OA) is calcitic-dolomitic, while the sample (G) from Drama (Greece) is dolomitic. Attributions of calcite and dolomite peaks are in good agreement with those reported by Gunasekaran and al. [9,13].

![Figure 2. Powder XRD patterns of samples BC, KB, TS, OA and G. C-Calcite, D-Dolomite and Q-Quartz.](image-url)
3.3. Crystalline phases: Micro Raman

Raman spectra of samples BC, KB, TS and OA (figure 3) exhibit bands located around 153, 280, 710, 1085, 1435 and 1747 cm\(^{-1}\) characteristic of calcite [9,10,12,14]. Therefore, these samples can be classified as calcitic limestones. Besides these bands, an additional wide signal at 460 cm\(^{-1}\), signature of quartz [8,15], is observed in the case of the sample OA. The marble TS shows also two supplementary bands at 1335 and 1608 cm\(^{-1}\) which can be attributed to carbonaceous matter [16, 17], they are often associated to marbles containing carbonaceous resulting in a more or less grey color [17]. In the case of the sample OA, these bands are probably overlapped by the fluorescence due to the presence of carbonaceous matter.

The sample from Drama - Greece (G) behaves differently with respect to all the local samples. The corresponding Raman spectrum is dominated by dolomitic bands at 180, 305, 728, 1101, 1447 and 1759 cm\(^{-1}\) [9,10,12].

![Figure 3. Raman spectra of BC, KB, TS, OA and G marbles.](image)
The strongest band observed on all spectra recorded on the studied Moroccan marbles and the Carrare -Italy reference white marble corresponds to the symmetric stretching $\nu_1$ mode located around 1084 cm$^{-1}$. This band is related to CO$_3$ groups vibrating in identical phases [18]. The other weak lines located near 1435 and 710 cm$^{-1}$ can be attributed respectively to the $\nu_3$ (asymmetric stretching) and $\nu_4$ (in-plane-bending) vibrational modes. The observed frequency shifts of about 153 and 280 cm$^{-1}$ originate from the external vibrations of the CO$_3$ groups involving translatory and rotatory oscillations [18]. A weak band observed at 1748 cm$^{-1}$ may be regarded as the combination band of $\nu_1$ and $\nu_4$ [12,14,19-22].

The results obtained from both XRD and Raman structural analyses of all marbles are combined and summarized on Table 3.

| Region         | Sample code | Career     | Main Phase | Others                      |
|----------------|-------------|------------|------------|-----------------------------|
| Carrare- Italy | BC          | Carrare    | Calcite    | -                           |
| Khénifra-Morocco | KB         | Tiskram    | Calcite    | Quartz                      |
| Tiflet- Morocco | TS          | Sahara     | Calcite    | Quartz, Graphite, Dolomite  |
| Taza- Morocco   | OA          | Oued Amlil | Calcite    | Quartz, Graphite, Dolomite  |
| Drama- Greece   | G           | Drama      | Dolomite   | Calcite                     |

4. Conclusion
This work is part of an extensive study in progress on the marbles and stones of ornamentation from different careers of Morocco (several tens of samples). The main objective is to characterize these materials and to identify indicators likely to link the sample of marble with his career of provenance. Several techniques in the laboratory have been used (XRF, XRD, Optical absorption, Colorimetry, Raman and EPR). The white marbles references originating from careers well known (Drama and Carrare) have been also analyzed by the same techniques.

This preliminary study shows firstly that there is a clear difference between Moroccan and the reference marbles, and secondly some differences between the marbles of Morocco from different careers. XRD showed that the calcite is the major phase in the all Moroccan marbles and in the marble of Carrare - Italy, while the marble from Drama - Greece is dolomitic. These results were confirmed by micro Raman spectrometry, which also shows the graphitic nature of marbles from certain sites. Quartz with low content has been detected in Moroccan marbles.

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