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Study of marbles from Middle Atlas (Morocco): elemental, mineralogical and structural analysis

S Khrissi[1], L Bejjit[1], M Haddad[1,*], C Falguères[2], S Ait Lyazidi[1], M El Amraoui[1]

[1] Laboratoire de Spectrométrie des matériaux et archéomatériaux (LASMAR), Unité de recherche associée au CNRST (URAC11), Université Moulay Ismail, Faculté des sciences, B. P. 11201, Zitoune, 50000, Meknès, Maroc.
[2] Département Homme et Environnement, Muséum National d'Histoire Naturelle, UMR7194, 75 013 Paris, France.

[*]E-mail: mhaddad22@yahoo.fr

Abstract. A series of marbles sampled from the region of Middle Atlas (Morocco), are characterized by different complementary spectroscopic techniques. X-Ray fluorescence is used to determine elemental composition of rock while X-Ray diffraction and the Raman spectroscopy are used to determine major crystalline phases (calcite and dolomite) and minor ones (quartz).The samples display typical EPR spectra of Mn^{2+} in calcite and reveal the presence of Fe^{3+} ions.

Keywords: Marbles; Middle Atlas (Morocco); characterization; XRF; XRD; Raman; EPR; Provenance.

1. Introduction

Marble is a naturally occurring stone mainly used in the construction industry or as a raw material for artwork. Since antiquity, it is one of the most frequently used materials for architecture and sculpture and therefore has been given an exceptional importance, particularly under the Romans [1,2]. Marble consists of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) grains interbedded with other minerals like quartz, mica, graphite, iron oxides, etc., which represent impurities [1,2].

The use of limestone and marble in the Moroccan structures and buildings goes back to Roman antiquity [3,4]. The ornamental rocks are abundant in central Morocco, this is the principal reason why marbles industry is more developed in this country [3,4].The goal of this work is to provide a multi-technical characterization of marbles and limestones, sampled from Middle Atlas quarries (Morocco). The characterization combines elemental, mineralogical and structural analyses.

2. Materials and characterization techniques

2.1. Samples

Several samples of marbles (fig.1 and table 1) were collected from quarries located in the region of Middle Atlas: Tiskram (KB and KN), Sidi Lamine (K1, K2, K3, K4 and K6) and Sidi Amer (K5 and K7); some of these areas contain fossils. The samples are listed in Table 1 with the corresponding colors and sites.

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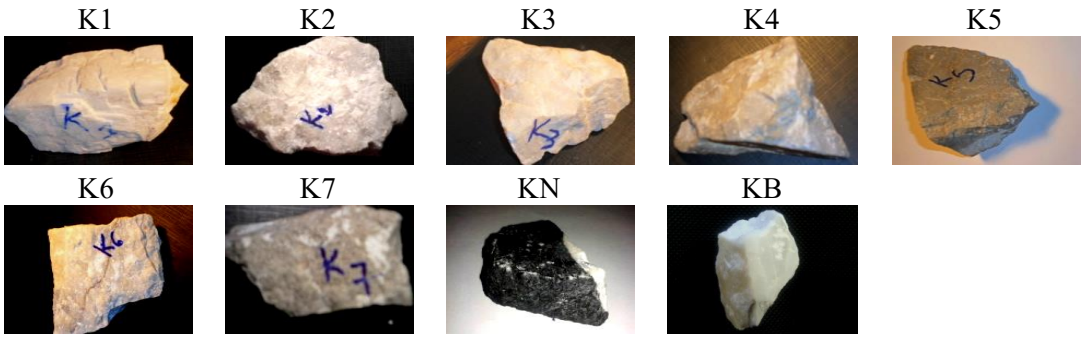

Figure 1. The samples of studied marbles.

Table 1. Samples codes and quarries of their provenance.

Sample code	Color	Provenance
K1	White	Sidi Lamine
K2	White	Sidi Lamine
K3	White/Yellow	Sidi Lamine
K4	White	Sidi Lamine
K5	Grey	Sidi Amer
K6	White	Sidi Lamine
K7	Grey	Sidi Amer
KN	Black	Tiskram
KB	White	Tiskram

2.2. Experimental techniques

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

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°.

Micro Raman spectra were recorded in the range of 100 - 2000 cm^{-1} using a Renishaw RM 1000 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 greater than 2 cm^{-1}. The samples were used directly, without any preparation or pre-size fraction.

X-band EPR spectra of the samples were recorded by a Bruker spectrometer at room temperature, the microwave frequency was 9.5 GHz with a 100 KHz modulation. EPR spectroscopy involves the resonant absorption of microwave power by a few milligrams of samples (≈ 200 mg) in powder form placed in a cavity inside a quartz tube, across which a magnetic field (5- 8000 Gauss) is scanned. It detects paramagnetic atoms and ions, unpaired electrons and free radicals.

3. Results and discussion

3.1. Elemental analyses: XRF

X-ray fluorescence spectrometry has been applied on powders of marbles to determine their chemical composition. The obtained results are summarized in Table 2, they show that the studied marbles contain CaO principally and small amounts of Fe_2O_3, SiO_2, MgO, Al_2O_3, Na_2O, SrO, MnO_2, Cl, SO_3, I, P_2O_5, Y_2O_3 and K_2O. All the samples contain CaO (50.1 - 55.1%) as major element and MgO (0.45 - 1.13%), SiO_2 (0.41 - 8.48%), Fe_2O_3 (0.06 – 1.35 %) and Al_2O_3 (0.2 – 1.13%) as minor elements. The analysis revealed also the presence of trace of other elements such as Na, Sr, Cl, Mn, I, S, P, K and Y in certain marbles.

Table 2. XRF analysis of marble samples.

	CaO	Fe_2O_3	SiO_2	MgO	Al_2O_3	Na_2O	SrO	MnO_2	Cl	SO_3	I	P_2O_5	K_2O	Y_2O_3	LOI*
K1	51.5	1.35	0.76	0.5	0.43	0.14	0.11	0.08	0.07	0.06	0.03	0.02	-	-	45
K2	54.8	0.13	1.54	0.62	0.34	0.12	0.03	-	-	0,03	0,03	0,02	-	-	42.3
K3	55.1	0.09	0.97	0.45	0.28	0.08	0.03	-	-	0.03	0.03	0.03	-	-	42.9
K4	53.2	0.21	2.45	0.68	0.78	0.07	0.03	-	0.04	0.03	0.02	0.15	0.08	-	42.2
K5	55.1	0.07	0.52	0.61	0.27	0.10	0.03	-	0.06	0.06	0.02	0.13	-	-	43
K6	52.6	0.28	2.48	0.85	0.99	0.09	0.03	-	-	0.04	0.02	0.06	0.12	-	42.4
K7	54.9	0.06	0.41	0.63	0.20	0.11	0.05	-	0.05	0.07	0.03	0.22	-	-	43.3
KN	50.1	0.37	5.07	1.43	1.13	0.19	0.12	0.06	-	0.3	0.02	0.08	0.12	0.004	41
KB	52	1.07	8.48	0.58	0.37	0.09	0.24	0.07	0.05	0.03	0.02	0.01	-	0.004	37

**LOI: Loss on ignition*

3.2. Crystallines phases: XRD

The various Bragg reflections are indexed using (JCPDS) files [5]. The marbles K1 and K6 are calcitic relatively pure; K2, K3, K4, K5, K7 and KB are calcitic also but with low contents of quartz. The sample KN is calcitic with low contents of both quartz and dolomite.

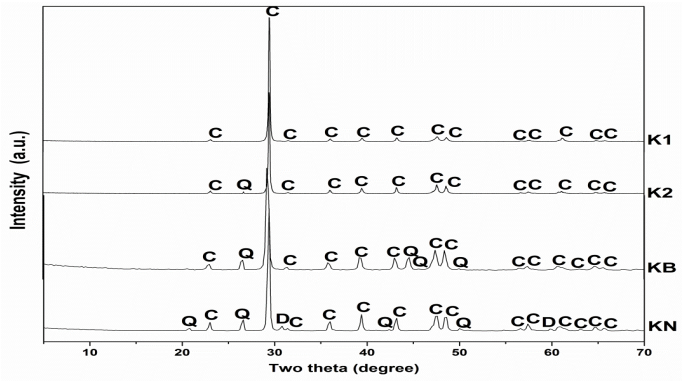

Figure 2. Powder XRD patterns of samples KN, KB, K2 and K1.
C: Calcite, D: Dolomite and Q: Quartz.

3.3. Crystallines phases: Micro Raman

The results obtained with XRD are confirmed by the Raman analyses. Indeed, the Raman spectra of marbles are similar; they show bands at 1085, 1435, 710 and 280 cm^{-1} characteristics of CO_3 groups in calcite [6-8]; the weak line at 1747 cm^{-1} may be attributed to the combination of the vibrational modes υ1 and υ4 of the CO_3.

Besides these bands, an additional wide signal at 460 cm^{-1}, signature of α-quartz SiO_2 [6,8,9], is observed in the case of the samples K5 and KN. The spectra of these two marbles also show two supplementary bands at 1325 and 1609 cm^{-1}, which are related to carbonaceous matter (graphite) in the samples [8-11]. Marbles often contain carbonaceous matter resulting in a more or less grey color [10,11].

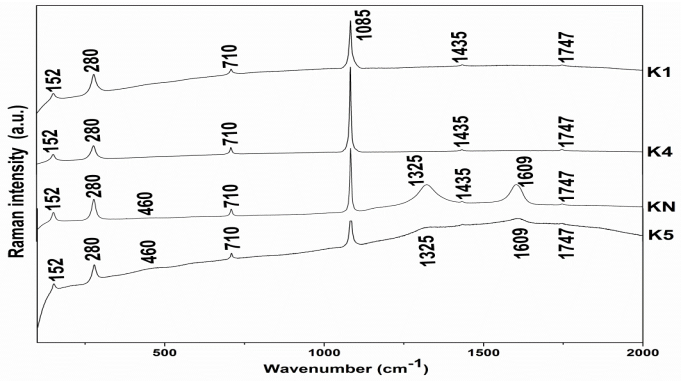

Figure 3. Raman spectra of samples K5, KN, K4 and K1.

The strongest band observed on all spectra obtained from the studied marbles corresponds to the symmetric stretching υ1 mode located around 1085 cm^{-1} and the weak lines located near 1435 and 710 cm^{-1} can be attributed respectively to the υ3 (asymmetric stretching) and υ4 (in-plane-bending) vibrational modes [12,13]. The observed frequency shifts about 152 and 280 cm^{-1} originate from the external vibrations of the CO_3 groups involving translatory and rotatory oscillations [12-14].We observe also a weak band at 1747 cm^{-1} which may be regarded as the combination band of υ1 and υ4 [12,14].

3.4. EPR spectrometry

Because of its high sensitivity, the EPR technique has been used to detect crystal imperfections that may be related to the nature of the quarry from which the marble comes; it is one of the best methods to determine the provenance of marbles. The recorded EPR spectra (fig. 4) were attributed to Mn^{2+} ions; traces of these ions are omnipresent impurities in calcium carbonates. As it possesses a $3d^5$ electronic configuration, it has six oxygen atoms as its nearest neighbours, each atom belongs to a different CO_3^{2-} group, in an octahedral structure [15-17].The Mn^{2+} presents a spectrum with six principal lines, due to the hyperfine interaction (allowed transitions), with supplementary intermediate weak lines (forbidden transitions).

The shape of the EPR features, showing dependence on the sampling quarry (fig. 4), constitutes a powerful comparison element in the provenance study of marbles. It's linked to the details of the chemical environment of the Mn^{2+} [18-20]. Indeed, in calcite ($CaCO_3$) manganese ions substitute for calcium atoms in the calcium carbonate lattice generating thus only one kind of paramagnetic site [15,18].

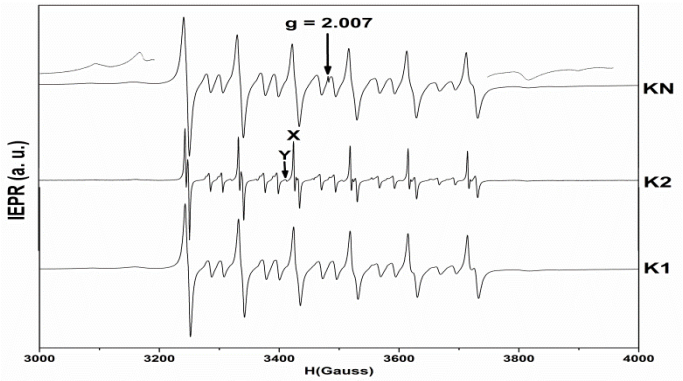

Figure 4. EPR spectra of samples K1, K2 and KN.

All EPR lines from studied marbles correspond to Mn^{2+} in Ca^{2+} sites (calcite), the other lines associated to Mn^{2+} in Mg^{2+} sites (dolomite) depend strongly on the original quarry; the dolomite/calcite ratio calculated from the EPR spectra, Y and X (fig.4) can be used as an indicator of provenance [9,21,22], it varies from one quarry to another. The other transitions are also observed in these spectra but they are very weak (fig. 4). These lines, outside the six lines of Mn^{2+}, indicate that the symmetry is slightly distorted octahedron. This is due to the presence of Mn^{2+} in a low symmetry environment caused by the random orientations in the polycrystalline powder [9,15,23].

The marble from Tiskram (KN), exhibits a weak EPR signal between the third and fourth Mn^{2+} lines at $g \approx 2.007$; (fig. 4). This signal has been attributed to a paramagnetic defect centers induced in minerals by a low level of ionizing radiation that originates from natural radioactivity. The signal intensity is an indicator of provenance and may also be useful for marble dating [9,21,24].

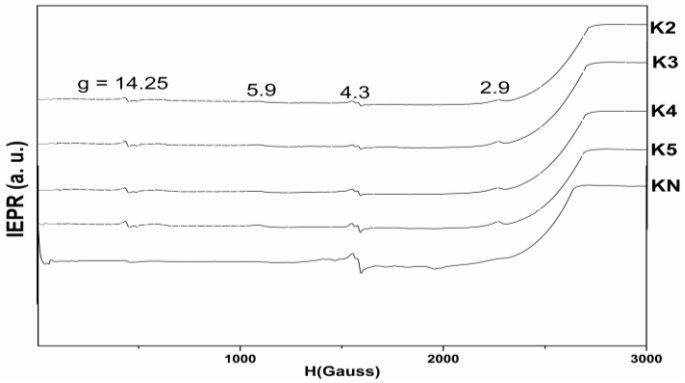

Figure 5. EPR spectra of Fe^{3+} ions in KN, K5, K4, K3 and K2 marbles.

In the low magnetic field region (fig. 5), the peaks at g≈14.25, g≈5.9 and g≈2.9 are attributed to Fe^{3+} in the calcium carbonate lattice. The peak at g≈4.3 is related to Fe^{3+} in silicates and oxides [20,21,25].

4. Conclusion

Marbles sampled at different quarries in the region of Middle Atlas (Morocco) were characterized by taking a multi-technical approach. XRD showed that the calcite is the major phase in all the marbles. These results were confirmed by Raman spectrometry which shows also the graphitic nature of marbles from certain sites. Quartz and dolomite with low content have been detected in some marbles.

The EPR study shows that all the marbles exhibit principally the same spectrum due to Mn^{2+}, but for each sample the spectrum present a shape and supplementary EPR lines which depend on the quarry origin of the marble. That means that EPR technique may be a useful method to determine the provenance of the marbles.

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