

Petrography and geochemistry of Triassic-Early Jurassic successions of El Haouz “Dorsale Calcaire” (northern Rif, Morocco): A preliminary assessment for cement production suitability

Pétrographie et Géochimie des successions du Trias- Jurassique inférieur de la Dorsale Calcaire d'El Haouz (Rif septentrional, Maroc) : Une évaluation préliminaire de la pertinence pour la production du ciment

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Abstract. The “Dorsale Calcaire” of the El Haouz chain constitutes the frontal part of the Internal Rif Domain. It is mainly made of carbonate lithofacies. At El Mashar cement quarry, the limestone is well exposed and being worked for Tetouan cement manufactory (LAFARGE Cements II). In this study, petrographic and geochemical analysis of fifteen limestone samples were carried out. The aims of this study is to examine the major oxides in the limestone exposed in the quarry, using the X-Ray Fluorescence Spectrophotometer (XRF), and to do a preliminary assessment of these carbonates for a possible cement production. A petrographic study was also carried out, in order to characterize their mineralogical composition and the nature of the associated biogenic fraction. Results of the geochemical analysis allow to determinate three main petrofacies, mainly composed of calcite, dolomite and seldom quartz. The identified petrofacies in El Mashar quarry are: **i**) micritic and sparitic limestones, **ii**) dolomitic limestones, and **iii**) cherty limestones with cryptocrystalline irregular chert nodules. These analysis show also a wide range of variations in LOI (29.94% to 40.64%), SiO₂ (6.14% to 27.18%), CaO (37.93% to 50.78%), Al₂O₃ (0.49% to 2.27%), Fe₂O₃ (0.28% to 2.4%) and MgO (0.24% to 25.19%); K₂O and Na₂O are present in traces. The high CaO (47.17%) indicates that calcite is the principal carbonate mineral. Fe₂O₃ with average of 0.50% indicates low oxidizing conditions and that the pH of the water was not favorable for formation of Iron III oxides. Low alumina (Al₂O₃: 1.07%) probably reflects a low energy environment. CaO with LOI shows a positive correlation, whereas CaO with SiO₂ shows a negative correlation because of mineralogical factors. The low MgO contents in massive and siliceous limestones suggest a lack of dolomitization process, while it's show a high concentration in dolomitic limestone. These results suggest that these carbonaceous rocks are suitable for the cement industry.

Keywords : EL Mashar quarry, geochemistry, limestone, petrography, major oxides, northern Rif, Morocco.

Résumé. La Dorsale calcaire d'El Haouz constitue la partie frontale du Domaine Interne de la Chaîne Rifaine et se compose principalement de carbonates. Les faciès carbonatés dans la carrière d'El Mashar, sont les mieux exposés et exploités par la cimenterie LAFARGE de Tétouan (LAFARGE II). Cette étude porte sur les analyses pétrographiques et géochimiques réalisées sur 15 échantillons récoltés sur terrain. L'objectif de ce travail est d'examiner les oxydes majeurs des carbonates de la carrière d'El Mashar, déterminés par spectrométrie à fluorescence X (SFX), et de faire une évaluation préliminaire de ces carbonates pour une éventuelle utilisation en industrie de fabrication de ciment. L'étude pétrographique a également été menée afin de définir la composition minéralogique et la nature de la fraction biogénique associée. Le résultat des analyses géochimiques ont permis de déterminer trois principaux pétrofaciès, composés essentiellement de calcite, de dolomite et rarement de quartz. Les pétrofaciès identifiés dans la carrière d'El Mashar sont : **i**) calcaire micritique et sparitique, **ii**) calcaire dolomitique **iii**) calcaire à quartz microcristallin et à nodules irréguliers de silex. Les analyses géochimiques montrent une large variation de LOI (loss on ignition) (29,94% à 40,64%), SiO₂ (6,14% à 27,18%), CaO (37,93% à 50,78%), Al₂O₃ (0,49% à 2,27%), Fe₂O₃ (0,28% à 2,4%) et MgO (0,24% à 25,19%) ; K₂O et Na₂O sont sous forme de traces. La forte teneur en CaO confirme la nature carbonatée du faciès. La teneur en Fe₂O₃, en moyenne de 0,50%, indique une faible oxydation du milieu et que le pH des liquides interstitielles n'était pas favorable à la formation d'oxydes de fer III (Fe³⁺). La faible teneur en Al₂O₃ traduit une faible énergie du milieu. Par ailleurs, on note une corrélation positive entre CaO et LOI, alors que CaO et SiO₂ montrent une corrélation négative, ce qui serait en relation directe avec la composition minéralogique. La faible teneur en MgO dans les calcaires massifs et siliceux indique probablement une absence de processus de dolomitisation, alors que cette teneur s'avère assez élevée dans les calcaires dolomitiques. Ces résultats suggèrent que les carbonates de la carrière d'El Mashar sont très favorables pour l'industrie du ciment.

Mots-clés : Carrière d'El Mashar; géochimie, calcaire, pétrographie, oxydes majeurs, Rif septentrional, Maroc.

ملخص. دراسة بلورية و جيوكيميائية للتتابعات الترياسية و الجوراسية السفلى لسلسلة جبال الحوز (الريف، المغرب) : تقييم أولي لجودة إنتاج الإسمنت. تشكل سلسلة الصخور الكلسية لجبال الحوز في الريف أو ما يصطلح عليه ب «مجمع الظهر الكلسي» المقدمة الأمامية لمجال الريف الداخلي. ويتكون أساساً من صخور كلسية. في محجر المسحر للإسمنت، حيث تتواجد الصخور الكلسية المستغلة من طرف مصنع تطوان للإسمنت (لأفارج للإسمنت II) أخذت العينات، كما انجزت تحاليل جيوكيميائية لخمسة عشر عينة من الصخور الكلسية. وتهدف هذه الدراسة إلى تحديد الأكاسيد الرئيسية في الصخور الكلسية المستغلة بالمحجر وذلك باستخدام الأشعة السينية ومضان مقياس الطيف الضوئي (XRF) وذلك في افق تقييم أولي لمدى ملائمة هذه الصخور لإنتاج الإسمنت. وقد انجزت أيضاً دراسة مجهرية للعينات الكلسية لتحديد أنواع البلورات والمحتويات الأحيائية بها. هذا ولقد أسفرت نتائج التحاليل الجيوكيميائية للعينات المدروسة بتحديد ثلاث سحنات بلورية أساسية تتكون من: الكالسيت والدولوميت ونادراً من الكوارتز. إن السحنات الصخرية المتواجدة بمحجر المسحر تضم ثلاثة أنواع رئيسية: (1) صخور الكلس ذات الحبيبات الكلسية المجهرية الدقيقة والمتوسطة (2) صخور الكلس الدولوميتي و (3) صخور الكلس الصواني ذو بلورات صوان مجهرية دقيقة، إضافة إلى صخور الكلس ذات العقيقات الصوانية. وبالنسبة للتحاليل الجيوكيميائية للعينات يلاحظ تباين

واضح في نسب مؤشر الضياع بالاحتراق (LOI) (29.94% إلى 40.64%) والأوكسيد حسب العينات فنجد أن، نسب ثاني أكسيد السيليسيوم يتراوح بين 6.14% و 27.18%، أكسيد الكالسيوم بين 37.93% و 50.78%، أكسيد الألمينيوم بين 0.49% و 2.27%، أكسيد الحديد بين 0.28% و 2.4%، و أكسيد المنغنيزيوم بين 0.24% و 25.19%، و نادرا ما يتواجد أكسيدي البوتاسيوم والصوديوم على شكل آثار فقط. إن النسب العالية لأكسيد الكالسيوم (47.17%) تدل على أن بلورات الكالسييت هي المكونات الرئيسية لهذه الصخور. كما تعزى النسب الضئيلة لمعدل أكسيد الحديد، (0.50%) في هذه الصخور إلى شروط التأكسد المنخفضة وأن مؤشر القياس الحامضي/القلوي (pH) يدل على أن السوائل الداخلية للصخور لم تكن مواتية لتشكيل أكسيد الحديد الثلاثي (Fe^{3+}). كما أن معدل أكسيد الألمينيوم المنخفض (1.07%) ربما يعكس بيئة رسوبية منخفضة الطاقة الهيدرودينامية. وتظهر نسبة أكسيد الكالسيوم على مؤشر الضياع بالاحتراق (CaO/LOI) وجود علاقة إيجابية، في حين نلاحظ أن نسبة أكسيد الكالسيوم على ثاني أكسيد السيليسيوم (CaO/SiO_2) يظهر وجود علاقة سلبية بسبب المكونات البلورية للعينات. كما أن انخفاض محتويات أكسيد المنغنيزيوم في الصخور الكلسية التي لا تحتوي على طبقات وصخور الكلس الصواني قد يُفسَّر بعدم وجود صيرورة جيوكيميائية لتحويل الصخور الكلسية إلى الدولومايت الغنية بأكسيد المنغنيزيوم. و بناءا على ما سبق ذكره، فإن نتائج البحث هذه تشير إلى أن الصخور الكلسية التي تمت دراستها يمكن اعتبارها، بناء على هذا التقييم الأولي، مناسبة لصناعة الأسمنت.

كلمات مفتاحية: مسحر، جيوكيمياء، صخور كلسية، سحنات صخرية، الأوكسيد الرئيسية، شمال الريف، المغرب.

INTRODUCTION

Limestone is a sedimentary calcareous rock, mostly composed of calcite with gangue of some minerals such as quartz, feldspar and mica. Cement production is the major industries, which use limestone. Morocco is endowed with large deposits of limestone. However, the limestone deposits are not uniformly distributed in the Country. There is a concentration of the total reserves in the “Dorsale Calcaire” complex (Fallot 1937). However, the suitable limestone deposits for cement making are not uniformly distributed in the entire “Dorsale Calcaire” complex. According to cement manufacturers specifications (Johansen *et al.* 2002), limestone for cement making, should contain more than 40% CaO; Fe_2O_3 as well as Al_2O_3 1.5 % to 3%; free silica less than 13%; combined Na_2O+K_2O less than 0.6% and P_2O_5 less than 0.6%. Magnesia content of the limestone should ideally be under 3%, although more than 5% of MgO can be used in cement industry. Portland cement is produced by the high temperature reaction of a lime-bearing material (limestone) with one containing silica, alumina, and ferrous materials. The product, which is known as clinker, has four main compounds: tricalcium silicate (Ca_3S otherwise known as alite), dicalcium silicate (Ca_2S otherwise known as belite), calcium aluminate (Ca_3A) and tetracalcium aluminoferrite (Ca_4AF). It is afterwards ground with gypsum to give cement (Hawkins *et al.* 2003).

The quality of cement is determined by the composition ratio of these four components. Of these compounds, Ca_3S and Ca_3A are mainly responsible for the strength of the cement. Ca_3A causes undesirable heat and rapid reacting properties, which can be prevented by adding $CaSO_4$ to the final product. Ca_4AF makes the cement more resistant to sea water and results in somewhat a slower reaction which evolves less heat. Relatively low grade limestone containing poor CaO cannot produce sufficient Ca_2S and Ca_3S . Hence, the quality or grade of limestone not only plays an important role in the cost-effectiveness of an integrated cement plant, but also is essential for the steady operation of the plant as well as to achieve optimum plant output. Therefore, the constituents, such as calcium oxide (CaO), alumina (Al_2O_3), iron oxide (Fe_2O_3) and silica (SiO_2) of the limestone supplied to the plant be within permissible limits of the specifications meant for cement manufacture (Ingram & Daugherty 1991). It is an established fact that high SiO_2 content in the limestone has an adverse effect on kiln properties and the kiln is one of the most important units for the performance of the cement plant. It is monitored in the form of the silica ratio (SR), which is the ratio between silica and weighted sum of Al_2O_3 and Fe_2O_3 . As the silica

ratio increases, more heat is required to run the kiln.

The lime saturation factor (LSF) plays a vital role in the cement production, because it contains CaO, the primary constituent of cement. It has been found (Ingram & Daugherty 1991) that kiln operation and cement quality are improved where the CaO in limestone is more than 44%. Thus, both high LSF and a low silica ratio contribute significantly to the cost-effectiveness of a cement plant. To maintain a consistent supply of suitable limestone grades to a cement plant, mineralogical as well as geochemical characterization of the limestone is essential. However, the geochemical assessment for cement production suitability is identified as an important component of cement manufacturing process, which offers a vast potential for efficient quarry management. LAFARGE Cement manufacturers are constantly making efforts on quarry optimization for a number of limestone quarries whereby various components of mining activity are identified as key influencers. The present contribution focused on the compositional appraisal of the limestone deposits of the El Mashar quarry, and the intension is to reveal the industrial quality of the material, based on available compositional data. The impact of each improvement potential of each activity is then quantified into savings tons of raw material in order to conserve mineral resources as well as sustaining environment.

GEOLOGICAL SETTING

The Internal Domain of the Rif Chain is organized into three superimposed structural complexes, from the bottom to top: Sebides (Milliard 1959, Durand Delga & Kornprobst 1963), Ghomaride (Durand Delga *et al.* 1960-62, Durand Delga & Kornprobst 1963, Michard & Chalouan 1991) and “Dorsale Calcaire” (Fallot 1937). The “Dorsale Calcaire” complex includes several stacked tectonic slices forming the highest units of the Rif Internal Domain, defining the boundary between Internal and Flysch Basin Domains in the Rif-Betic orocline (Durand Delga & Fontboté 1980). The “Dorsale Calcaire” is geographically subdivided into three different sectors through the Rif Chain, aligned from the Gibraltar Strait to the Al Hoceima (Fig. 1a): the Haouz “Dorsale Calcaire” (Kornprobst 1966, Raoult 1966, Leikine 1969, Lallam *et al.* 1997) between Sebta and Tétouan, the “Dorsale Calcaire” (s.s.) (Fallot 1937, Griffon 1966, Gutnic 1969, Nold *et al.* 1981) between Tétouan and Jebha and finally the Bokoya “Dorsale Calcaire” (Mégard 1969, Andrieux 1971) cropping out westward of Al Hoceima. Classically, the Haouz “Dorsale Calcaire” complex is subdivided, according to the original position, into: (i) Internal ii) Intermediate and (ii) External “Dorsale Calcaire”, all are formed by Triassic-Jurassic and

Paleogene-Neogene successions (Kornprobst 1966, Raoult 1966, Leikine 1969, El Hatimi 1991, El Kadiri 1991, Ben Yaich 1981). The External “Dorsale Calcaire” usually overthrusts a transitional-sub-domain located in the inner part of the Flysch Basin Domain, known in the literature as

Pre-Dorsalian Flysch (e.g. Olivier 1984) and locally are both overturned by latter backthrusts (Hlila 1994) (Fig. 1a). The study area is a limestone deposit of LAFARGE Cement quarry (LAFARGE Cements II) located in the Saddina village, and belongs to El Mashar Unit of the External

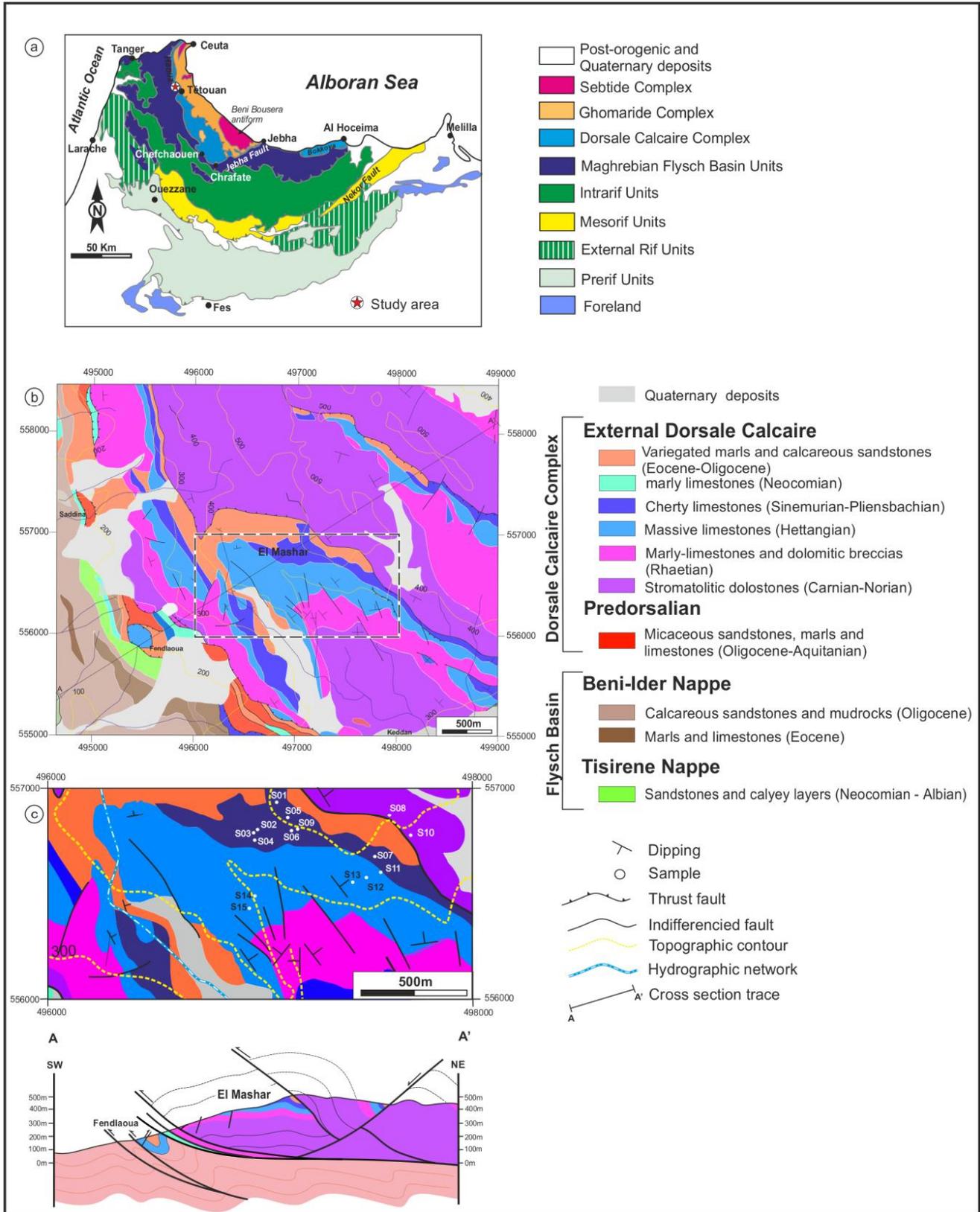


Figure 1. (a) Schematic geological map of northern Rif and study area (after Suter (1980), modified), (b) Geological map of El Mashar quarry showing location of studied limestone samples (after Leikine 1969, modified), (c) Simplified cross sections of El Mashar quarry.

Haouz “Dorsale Calcaire” (The Internal Domain) at about 10 km Northwest of the Tetouan city (Fig. 1b).

The studied limestones are mostly composed of calcite with some gangue minerals such as quartz, feldspar and mica. Northern Morocco is endowed with large deposits of limestone along the “Dorsale Calcaire” complex. Triassic-early Jurassic Limestone Formation is a carbonate unit in the Haouz Chain. Earlier studies have provided a first geological background on these rocks, established the first geological maps and defined all units of the “Dorsale Calcaire” (Kornprobst 1966, Raoul 1966, Leikine 1969). Other studies were later focused mainly on sedimentology, biostratigraphy, depositional environments of the dolomitic and calcareous successions and structural geology (El Hatimi 1991, Ben Yaïch 1981, El Kadiri 1991, Hlila 1994).

The Haouz Chain unit is organized in the rear zone by reversed slices of calcareous-dolostone alternations, truncated by high angle reverse faults dipping southwestward. Whereas the frontal area of this unit is organized into pluri-hectometric regional ramp and flat structures of Carnian-Norian stromatolitic dolostones, Hettangian massive limestones and Sinemurian-Pleinsbachian cherty limestones, all thrusting the Eocene-Oligocene marls and sandstones of the Flysch Units by mean of high angle reverse faults dipping northeastward (Fig. 1c).

El Mashar Unit displays a stratigraphic succession, mainly made of Triassic and Early Jurassic carbonates succession, topped by Aquitanian-Burdigalian siliciclastic marls, calcareous sandstones, carbonatoclastic conglomerates and Eocene-Oligocene calcareous breccias (Fig. 2).

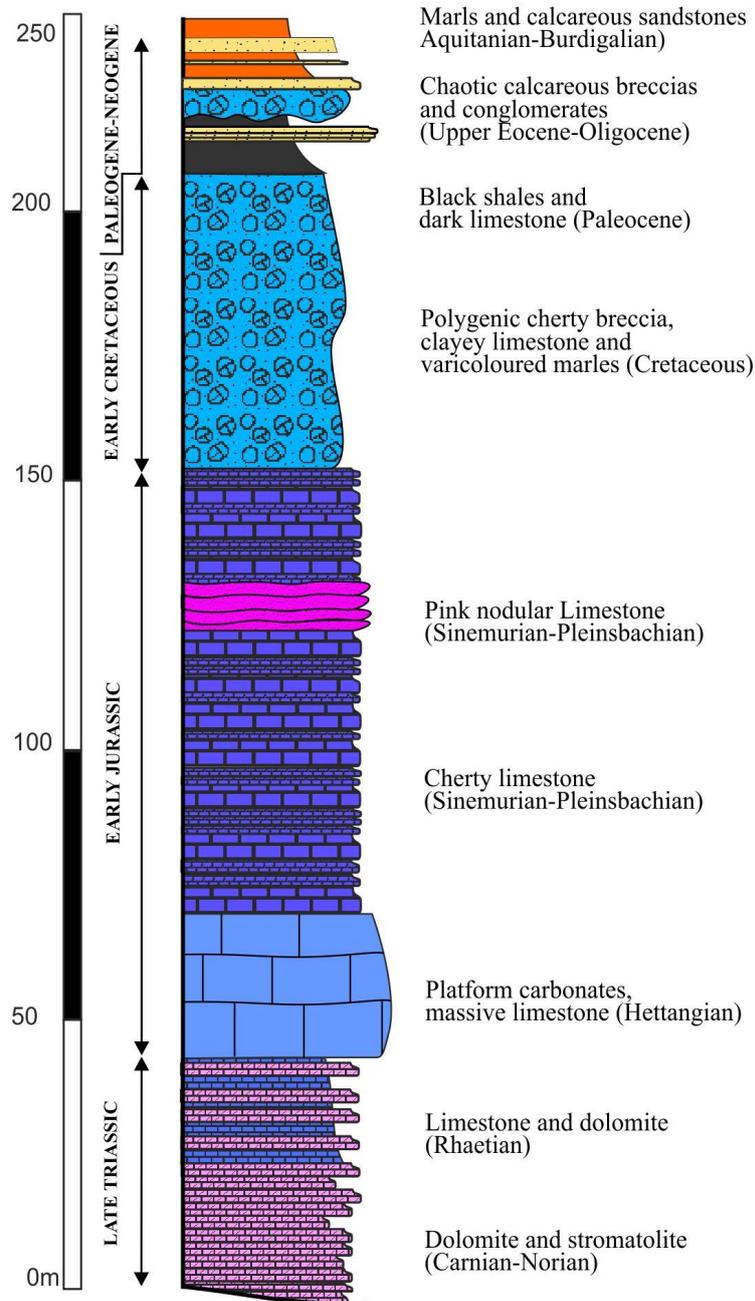


Figure 2. Synthetic stratigraphic logs of the external “Dorsale Calcaire” succession, exposed at El Mashar quarry (after El Hatimi 1991, modified).

El Mashar succession starts with about 350 m of Carnian-Norian stromatolitic dolostones, followed by Rheatian marl-limestone alternations and dolomitic breccias levels (Fig. 3a). The overlying Hettangian massive limestones or dolostones (Fig. 3b) show a lateral variation in thickness and can reach about 160 m nearby Jebel Dersa.

The Early Jurassic (Sinemurian-Pleinsbachian) external platform succession is made of about 65 m of thin-bedded cherty limestone with slumped strata (Fig. 3d). This lithofacies shows intercalation of about 15 m thick of

nodular and lenticular “Ammonitico-rosso” like Limestones (Auboin 1964, Elmi 1981) without ammonites. Upward, occurred some thick polymictic clast-supported breccias with centimeter-sized clasts, supplied from both internal and external “Dorsale Calcaire” Units. This lithofacies changes laterally and upward to cherty limestone successions. Topward, Paleogene deposits (Eocene-Oligocene) are characterized by alternation of variegated marls, calcareous sandstones, arenites, and calcareous breccias and conglomerates (Hlila 2005).

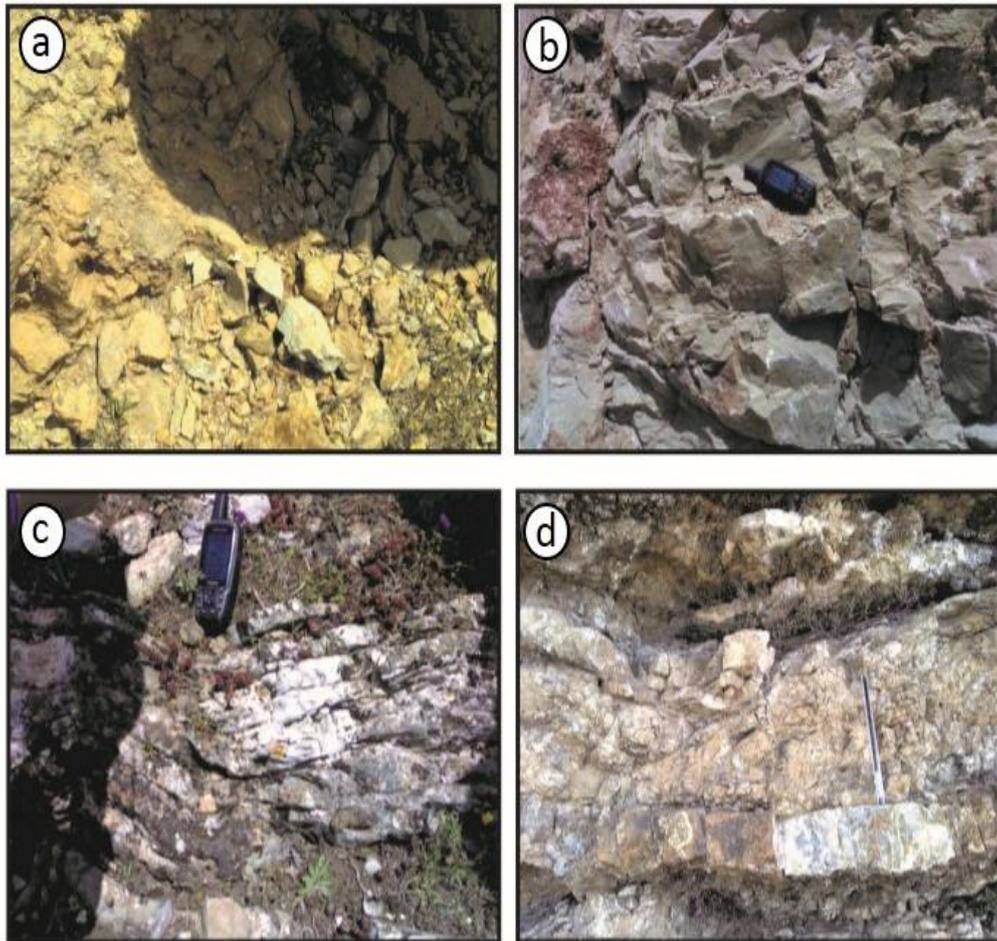


Figure 3. EL Mashar quarry lithofacies. (a) Marl-limestone alternations and dolomitic breccias, (b) Hettangian massive limestones or dolostones, (c) Cherty limestone, (d) Cherty limestone with slurred and slumped strata.

Their thicknesses do not exceed 50 m (Fig. 2). The external Dorsale cherty limestones and breccias of Sinemurian-Pleinsbachian age, that crop out near Tetouan, correspond to various facies, deposited by low, middle and high density turbidity currents and gravity flows along carbonate slopes. They are closely related to early Tethyan rifting movements, which began in the Hettangian and continued until the Toarcian-Aalenian (Lallam *et al.* 1997).

SAMPLING AND ANALYTICAL PROCEDURES

A reconnaissance survey, where detailed a thorough lithological description of the outcrop at each location, taking into account the color, texture, bedding characteristics, prominent sedimentary structures, composition and stratigraphic sequence, was conducted. The average thickness of each bed on the profile was measured and recorded. A total of fifteen limestone samples were

collected at different stratigraphic levels along the stratigraphic succession as shown in Figure 1b.

The gathered samples were taken to laboratory for treatment and standard laboratory preparation prior to analysis and thin section preparation. Polished and standard thin section preparations were carried out, using Logitech equipment at the laboratory of stratigraphy and quantitative sedimentology, FST-Tangier. Chemical analyses of selected samples were performed, using X-Ray Fluorescence Spectrophotometer technique (XRF) on fused and pressed beads at the Portland Cement LAFARGE Company Laboratory (LAFARGE cimentos Tétouan II). Accuracy was controlled by repetitive measurements of standards and each sample was measured twice. Total iron was expressed as Fe_2O_3 . Total loss on ignition (L.O.I.) was determined after heating the samples for 3h at 900°C . The geochemical results are provided in Table 1.

Table 1. Geochemical characteristics of EL Mashar limestone

Sample No	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	LOI	SO ₃	K ₂ O	Na ₂ O	SiO ₂ / Al ₂ O ₃
Siliceous limestone										
S01	9,12	1,2	0,17	51,6	0,04	37,36	0,19	0,03	0,04	7,6
S02	9,27	1,35	0,42	50,19	1,01	38,4	0,01	0,03	0,04	6,87
S03	9,38	1,26	0,52	50,21	1,01	37,2	0,01	0,03	0,04	7,44
S04	11,47	2,68	1,01	42,22	3,48	38,52	0,1	0,04	0,04	4,28
S05	26,27	1,54	1,07	37,66	0,57	33,3	0,03	0,04	0,03	17,06
S06	14,69	1,79	1,08	30,43	17,34	34,2	0,08	0,03	0,04	8,21
S07	8,14	2,59	1,27	37,56	8,96	40,25	0,35	0,04	0,04	3,14
S09	13,69	1,29	1,09	31,43	18,14	33,27	0,09	0,04	0,03	10,61
Average	12,75	1,71	0,82	41,41	6,31	36,56	0,1	0,035	0,037	8,15
Dolomitic limestone										
S08	7,05	0,74	0,49	32,78	20,68	37,45	0,36	0,03	0,03	9,53
S10	2,4	0,19	0,19	34,84	25,14	39,2	0,26	0,03	0,04	12,63
Average	4,72	0,46	0,34	33,81	22,91	38,32	0,31	0,03	0,035	11,08
Massive limestone										
S11	4,15	1,07	0,465	53,545	0,565	39,96	0	0,03	0,03	3,88
S12	1,57	0,7	0,2	51,21	3	42,79	0,18	0,03	0,02	2,24
S13	1,49	0,45	0,17	54,95	0,34	42,43	0,01	0,03	0,03	3,31
S14	2,14	0,65	0,26	49,66	4,96	41,9	0,21	0,03	0,03	3,29
S15	1,42	0,92	0,15	55,18	0,32	41,91	0	0,03	0,03	1,54
Average	2,15	0,75	0,24	52,9	1,83	41,79	0,08	0,03	0,028	2,85

RESULTS AND DISCUSSION

Petrographic characterization

Petrological study of the limestone samples characterizes three main petrofacies: dolomitic limestone, massive limestone and cherty limestone (highly siliceous limestone with cherty nodules) (Fig. 4).

Dolomitic limestone

It is characterized by a crypto- to microcrystalline crystal texture, the crystals; ranging from 2 to about 4 μm in diameter. This type of dolomitic limestone is not widespread and occurs within the micritic grains (Fig. 4a–b). The dolomite phases commonly display planar-e dolomite texture, characterized by well-developed crystal faces with sharp boundaries, with the area between crystals being either porous or filled by another mineral and locally planar-p dolomite texture with planar grains but less distinct than planar-e grains and show compromised boundaries between crystals (such as scattered euhedral rhombs occurring either individually or in clusters). Individual crystals are commonly clear and display extinction under crossed polar light. This dolomite phase is an early diagenetic product. Petrographic evidences suggest that it was precipitated prior to and during mechanical and early chemical compaction.

Massive limestone

It has fine to medium-grained granular mosaics without fossils, characterized by a fine-grained calcite matrix (Fig. 4c), consisting of crystals ranging from 5 to about 30 μm in diameter, most commonly about 5 to 7 μm and often

exhibiting a rather uniform size distribution (Fig. 4d). Thus, calcite is generally fine-grained but patches of medium to coarse-grained, anhedral calcite are also common, it is generally interlocked and contain inclusions of silicates minerals. The calcite of this limestone deposit seems to be authigenic in origin and has been precipitated in-situ. Micro-fractures filled with fine grained calcite micro-veins, which are considered to be diagenetic (Fig. 4e). Clay and iron pyrite in trace amounts are present as fine-grained disseminated material in many samples.

Cherty limestone

Samples are dominantly composed of calcite with few amounts of quartz, dolomite and rarely some opaque minerals (mostly pyrite). The chert is largely cryptocrystalline and present in inclusion (Fig. 4f). Clay and iron pyrite in trace amounts are present as fine-grained disseminated material in many samples.

Geochemistry

The major and minor basic chemistry of the limestone samples from the EL Mashar area are presented in Table 1. The chemistry of the cement largely depends upon the geochemistry of its raw materials, i.e., limestone. Approximately 75% of the cement raw material consists of lime (CaO)-bearing material (Lea 1976). The geochemical assay of limestone shows Calcium Oxide (CaO) contents ranging from 30.43% to 55.6%, which is due to the fact that the limestone is primarily calcite (Pettijohn 1975). Magnesium Oxide (MgO) values range from 0.25% to 1.01% (averaging 0.80%) in siliceous limestone and massive limestone samples. These lower values also indicate a purely calcite process, while they show a very

high concentration in dolomitic limestone samples. Fe_2O_3 values range generally from 0.80% to 3.52% with an average of 2.01%, which means a low oxidizing effect in the depositional environment. However, the reported low values indicates that the depositional environment is a reducing type and suggest the water's pH as well as the redox potential of the environment doesn't favor the formation of Iron (II) from the precipitation of Iron (III), and the oxides was leached away (Ingram & Daugherty 1991). CaO, especially in siliceous limestone, shows a positive correlation with LOI (Fig. 5a), which means that LOI presence was mainly controlled by the carbonate content of calcite.

This negative correlation between CaO and SiO_2 can be explained by different provenances of each one of them. CaO (from calcite) and SiO_2 (from quartz) are from two different mineral phases and they are not related (Fig. 5b). Alumina (Al_2O_3) in these samples ranges from 0.2% to

2.68% and shows negative correlation with CaO and strong positive correlation with iron, magnesium, soda, potash, titanium and manganese oxide which could be due to clay material, present in the limestone samples. Furthermore, the ratio of the SiO_2 to Al_2O_3 , used to determine the grains constituent is generally high with an average of 6.73%. This shows that the limestone is composed of silt size grains. Also, the appreciable mean values of SiO_2 , Al_2O_3 and K_2O from the samples suggest the presence of detrital materials, including silt size (grains) as impurities and indicate serious contamination by quartz and shaly materials (Greensmith 1978).

From the result of major oxides, CaO from calcite is dominant. Petrographic studies also indicate that the limestone is essentially biomicritic and calcite, in form of grain matrix and cement, constitutes the carbonate component suggested to be precipitated from solution by organisms and skeletal remains of these organisms.

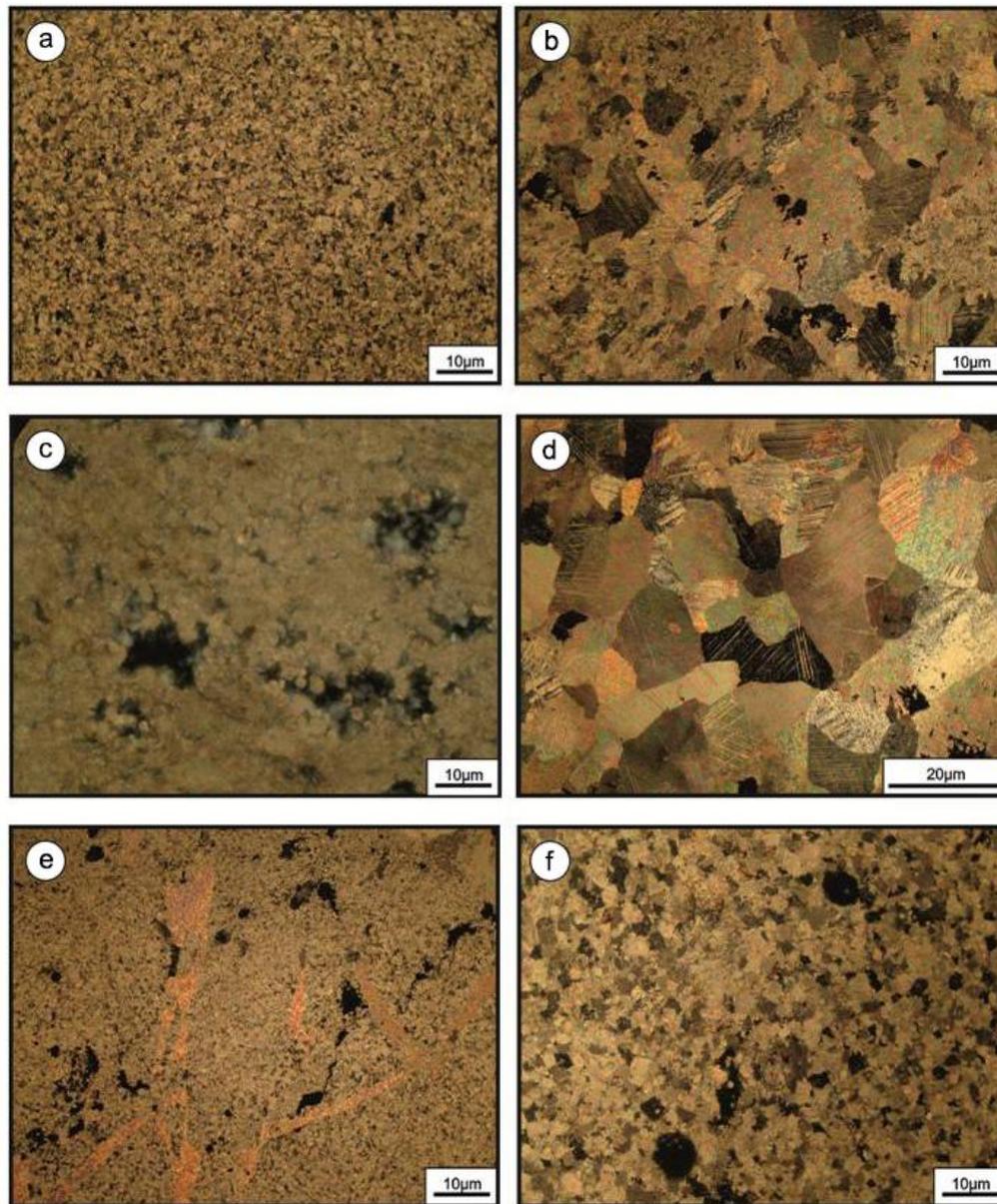


Figure 4. EL Mashar quarry petrofacies. (a) Micritic limestones, (b) Limestone breccias, (c) Siliceous limestones with cryptocrystalline irregular chert nodules, (d) Anhydrous calcite crystals in sparitic limestone, (e) Cherty limestone showing authigenic calcite precipitated in micro-veins, (f) Massive limestone with clay and iron pyrite (opaque minerals).

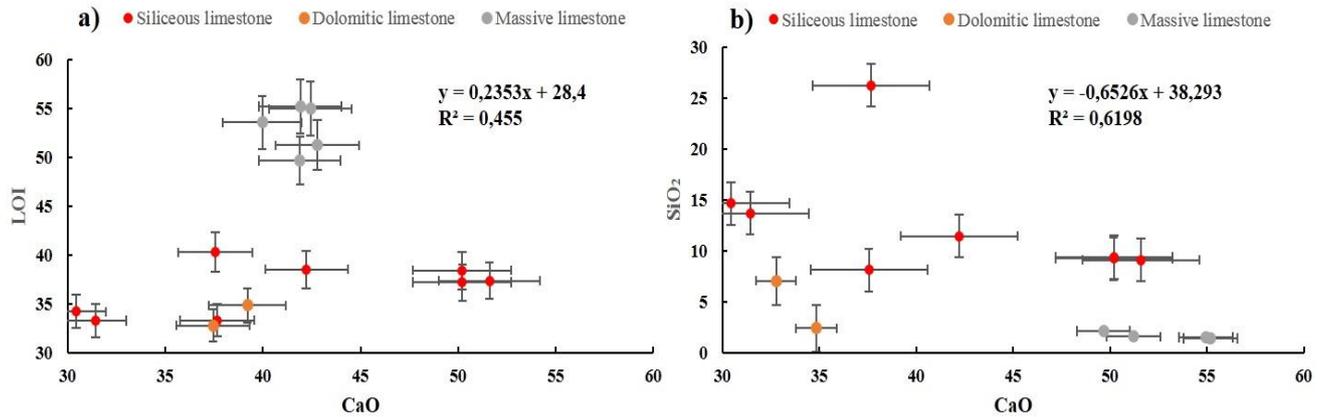


Figure 5. (a) CaO vs. LOI plotting showing positive correlation, (b) CaO vs. SiO₂ plotting showing negative correlations.

The relatively high level of CaO and low values of silica and MgO show a high degree of purity of the limestone, hence its suitability as raw material for cement. Silica concentrations in massive and dolomitic limestone is low (1.42%–4.15%), compared to other limestone deposit in EL Mashar; such as siliceous limestone (8.14%–26.27%). Magnesium could be added by dolomitization process. Moreover, magnesium concentration is also a function of temperature of formation, and often low in shells living in shallow waters (Pettijohn 1975). Thus shallow marine environment is proposed for El Mashar limestone. The aragonitic shells are usually magnesium deficient and fossil shells, like bivalves, are common in the deposit as shallow marine dwellers. The low concentration of alumina is also indicative of low energy environment (Lea, 1976). Al₂O₃ values greater than 1% occurs within units overlain by marl or shale.

Iron oxides concentration suggests a low oxidizing effect in the depositional environment. However, this low value indicates that the depositional environment is a reducing type and suggests that the pH of the water, as well as the redox potential of the environment, do not favor the precipitation of Iron (III) and that the oxides are thus leached away (Ingram & Daugherty 1991).

Industrial quality and cement production

Limestone is an invaluable raw material in the chemical industries. For a long time cement was manufactured on the basis of practical experience collected from the process of production (Rao *et al.* 2009). When comparing chemical analyses of Portland cement (Feed raw materials and/or clinker), Bensted 1995 and Moore 1982 recognize the existence of a relation between the percentage of lime and the combination of silica, alumina and iron oxide. These modulus, considering the three major chemical ratios are: Limestone Saturation Factor ($LSF = CaO / (2.8 SiO_2 + 1.2 Al_2O_3 + 0.65 Fe_2O_3)$), Silica Ratio ($SR = SiO_2 / (Al_2O_3 + Fe_2O_3)$), Alumina Ratio ($AR = (Al_2O_3) / (Fe_2O_3)$). LSF is the most important factor, because it determines the quantity of CaO that can be combined in the mix. In the cement-making industries, limestone and shale are mixed in a proportion of 4:1 and fired in a rotary kiln to produce clinker, which is responsible for cement's strength (Scott 1984, Ogbazue 1992).

Lime saturation factor (LSF)

The lime saturation factor is used for kiln feed control. A higher LSF makes it difficult to burn raw mix. Reactivity of the raw mixture for cement making is influenced greatly in pyrolysis. Reactivity of the raw mixture for cement making is influenced greatly in pyrolysis (Lea 1976, Hewlett 1998). The pyrolysis characteristics of limestone is greatly influenced by the particle size of calcite crystal, crystal shape that is characteristic of limestone itself and outside impurities such as SiO₂, Al₂O₃ and Fe₂O₃, as well as, the existence of state of accompanying minerals (Park *et al.* 2004). Limestone saturation factor is referred to as a percentage and therefore multiplied by 100 and this is mostly applied to clinkers.

In this study, the LSF ranges from 0.49 to 1.91 for siliceous limestone, 3.72 for dolomitic limestone and 8.55 for massive limestone (Tab. 2). The LSF controls the ratio of alite (Tricalcium silicate) to belite (Dicalcium silicate) in the clinker. Therefore, a clinker with a higher LSF will have a higher proportion of alite to belite than a clinker with a low LSF (Johansen *et al.* 2002). Typical LSF values in modern clinkers range from 0.92 to 0.98. Values above 1.0 indicate that free lime is likely to be present in the clinker (Ingram & Daugherty 1991).

This is because, in principle, at LSF=1.0 all the free lime should have combined with belite to form alite. If the LSF is higher than 1.0, the surplus free lime will remain free. In practice, the mixing of raw materials is never perfect and there are always regions within the clinker, where the LSF is locally either slightly above or below the target for the clinker as a whole (Rao *et al.* 2010). For the present samples, only the siliceous limestone LSF value fall in the normal range of chemical ratio, used in the industry for production of Portland cement. Although, it ranges from 0.49 to 2.52 (Tab. 2), results indicates that the CaO value it highly erratic and needs to be in uniform range for cement making.

Silica Ratio (SR)

The silica modulus has especially great influence on burning process and on some cement features. The amount of melt phase in the burning zone is a function of SR. When SR is high, the amount of melt is low and vice versa.

Table 2. Lime saturation factor, alumina and silica ratios of the EL Mashar limestone.

Sample No	LSF	SR	AR
Siliceous limestone			
S01	1,91	6,66	7,06
S02	1,8	5,24	3,21
S03	1,79	5,27	2,42
S04	1,17	3,11	2,65
S05	0,49	10,07	1,44
S06	0,69	5,12	1,66
S07	1,41	2,11	2,04
S09	0,77	5,75	1,18
Average	1,25	5,41	2,70
Dolomitic limestone			
S08	2,52	5,73	1,51
S10	4,93	6,32	1
Average	3,72	6,02	1,25
Massive limestone			
S11	4,05	2,7	2,3
S12	9,54	1,74	3,5
S13	11,39	2,4	2,65
S14	7,15	2,35	2,5
S15	10,66	1,33	6,13
Average	8,55	2,10	3,41

Therefore, when the SR is too high the formation of nodules and the chemical reactions may be slow, making it difficult to operate. The higher the SM the harder it is to burn (Johansen *et al.* 2002). When SR is too low, there may be much melt phase and the sulphur coating can become thick (Rao *et al.* 2010). Thus, low silica modulus often leads to ring formations in cement. A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0 for Portland cement clinker (Moore 1982). The SM governs the proportion of silicate phases in the clinker. The SR for the present samples ranges from 1.33 to 10.07 (Tab. 2), which indicate that the samples are higher in SiO₂ content and need to be brought below the specified limits for cement making (Frigionea *et al.* 1983).

Alumina Ratio (AR)

The temperature of melting depends on the alumina modulus. The Alumina ratio for the present samples ranges from 1.18 to 7.06 (Tab. 2). The lowest temperature is obtained when the AR is approximately 1.6 which is the optimum regarding formation of clinker minerals and nodulisation (Johansen *et al.* 2002). The AR also affects the colour of clinker and cement. The higher the AR the colour of the cement is lighter (Frigionea *et al.* 1983). Moreover, an

increase in clinker AR (also sometimes written as A/F) means there will be proportionally more aluminate and less ferrite in the clinker. In Ordinary Portland cement clinker, the AM is usually between 1 and 4. AR approximately equal to 1.4 will be easier to burn, if the AM is higher or lower. This is because at an AR of about 1.4, there is more clinker liquid at a lower temperature (Minor constituents such as MgO can alter this optimum AR).

Silica modulus and lime saturation factor from geochemistry data indicate that the siliceous limestone from El Mashar Cement quarry of Tetouan cement manufactory can be used for cement making process. They are processed for beneficiation for silica removal (to less than 8%) to required level, where the CaO can be enriched automatically (Johansen *et al.* 2002). Hence, in the EL Mashar limestone samples, if CaO content exceeds 45% and SiO₂ content is less than 7%, then the low grade siliceous limestone (massive and dolomitic limestones) sample can be utilized for cement making. While, the existing low grade siliceous limestone samples (massive and dolomitic limestone), which were considered before as waste rock in various limestone mines, can be effectively used not only for cement production but also for the industry, conservation of mineral resources and for sustaining environment (Rao *et al.* 2009). In fact, the chemical composition of a carbonate rock is an important determinant of its use in the industry. High purity limestone is used in metal and foundry industry, for oxygen steel making and as flux for reduction of iron ore. In the glass industry, a specification of CaCO₃ > 45.5%, Fe < 0.035% and very low organic matter content < 0.1 % is required to produce a colorless glass, while in the chemical industry, limestone with high percentage of CaO, 1% SiO₂ and MgO < 1.5% are required to produce a good quality's lime for steel industry (Anderrson & Vernon 1971).

CONCLUDING REMARKS

The chemical composition of a carbonate rock is an important determinant of its use in the cement industry. Generally, limestone with 35%–65% carbonate is suitable for the manufacture of Portland cement. However, Petrographic as well as X-ray diffraction pattern studies indicate that the limestone samples were crystalline and dominantly composed of calcite and quartz. They have a simple mineralogy, and yet they have variable silica and lime contents. Thus, three main petrofacies (massive limestone, dolomitic limestone and highly siliceous limestone with chert nodules) have been characterized. From geochemical study, we concluded that the calcium oxide (CaO) is the dominant constituent of the limestone from El Mashar quarry, which is due to the fact that the limestone is primarily calcite and this supports the suitability of limestone of this deposit for cement production. Geochemical studies of the EL Mashar limestone have been carried out and the results of major oxides concentrations, supported by petrographic analysis, have given some insights to the deposit and discriminate between shelf and deep sea carbonate. However, the cement lime saturations factor (LSF), silica ratio (SR) and Alumina ratio (AR) indicates that the cherty limestone of Mashar quarry is more suitable than massive and dolomitic

limestone for the manufacture of Portland cement. Massive and dolomitic limestone is considered as waste rock for cement production, and they can be used as major raw materials in the chemical industries.

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