Fundación Universidad de Oviedo

Universidad de Oviedo

“THE GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION OF THE “LA COVADONGA” QUARRY LIMESTONE AT SAN FELICES DE BUELNA (CANTABRIA): INDUSTRIAL APPLICATIONS.”

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MARCH 2016

CONTENT:

1. INTRODUCTION 3

2. THE WORK METHODOLOGY 4

3. TECHNICAL GROUP AND EQUIPMENT 5

4. GEOLOGICAL SETTING 6

5. THE LIMESTONE LITHOFACIES 7

6. GEOCHEMICAL CHARACTERIZATION 10

6.1. Sampling in 2009 10

6.2. Sampling in 2016 12

7. POTENTIAL INDUSTRIAL APLICATIONS 14

8. CONCLUSIONS 15

1. INTRODUCTION

In this report are presented the results of the geochemical and mineralogical characterization of the limestone quarry of Mount Dobra (Cantabria, Spain). The results of the initial study of 2009 are compared with the analysis of samples collected in 2016. This presentation shows the evolution of the exploitation banks of the quarry and its limestone quality.

2. THE WORK METHODOLOGY

The work done in this project of geological and mining research can be divided into the three following stages, in both 2009 and 2016:

- Preparation and analysis of samples of limestone for major elements (oxides of Si, Al, Fe, Ca, Mg, Na, K, Mn, Ti, P, Cr, S, LOI) and trace elements in the laboratories of the Scientific and Technical Services of the University of Oviedo.

- Petrographic study of samples collected by preparing transparent-polished sections of rocks.

- Interpretation of results and preparation of the final report.

3. TECHNICAL GROUP AND EQUIPMENT

This work has been done in 2009 and also in 2016 by the Research Group for Geology Applied to Engineering Geology of the Department of Geology of the Oviedo University, which is composed of fourteen researchers and support staff, under the direction of the Professor Doctor Daniel Arias Prieto.

The chemical analysis were performed using a Fluorescence Spectrometer of X-ray, "Philips" PW 2404, equipped with a tube Rodio 4 kw, three detectors and five analyzers crystals for determining the content of major elements (oxides of Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P) and trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br , Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Gd, Yb, Hf, Ta, W, Hg , Tl, Pb, Bi, Th, U and S). Furthermore, the ignition loss (L.O.I.) is obtained by calcination to 975°C for two hours in a muffle furnace.

For the petrographic study of rocks under the microscopy are prepared transparent-polished sections. For this work are available the next equipment: Loghitec type LP-30, ultrasonic bath Ultrasons-513, S-Selecta heating plates 157 and Thermoline 1900 and vacuum pumps Edwards ED-50, Speedvac and Telstar S4 / 30.

4. GEOLOGICAL SETTING

The limestone quarry is located in the Cabuerniga shield, a piece of carboniferous materials, where the main lithology is represented by the Mountain Limestone Formation. These rocks are affected by the Variscan Orogeny and emerges like an island surrounded by more modern materials, Triassic to Cretaceous, on riding. All the area is included in the Vasco – Cantábrica Zone of the North of Spain.

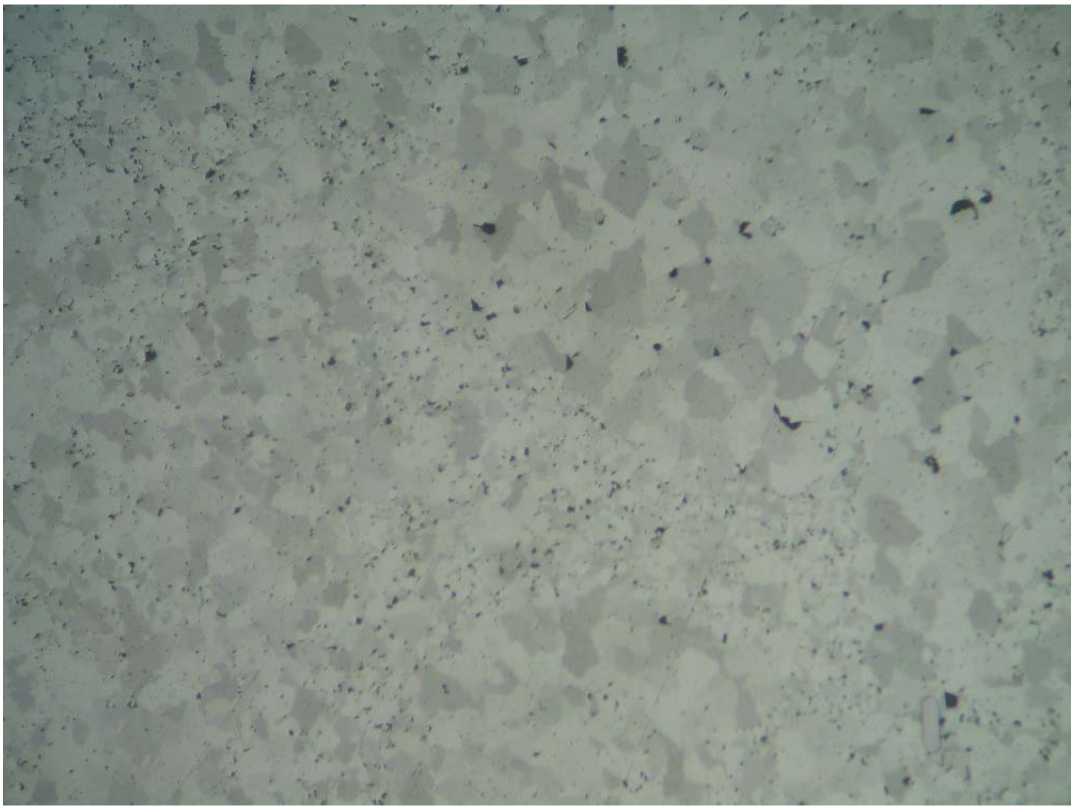
5. THE LIMESTONE LITHOFACIES

The Mountain Limestone Formation is presented in the field with a poorly defined plane-parallel stratification. Its most typical facies is that of micritic limestones, being composed essentially of calcite, with quartz and dolomite as accessories. In the area investigated the minimum thickness of this unit is about 300 m.

The dominant facies in the entire quarry corresponds to a gray limestone (figures 1 and 2). This is a massive limestone, micritic, with frequent calcite veinlets, and recrystallization (figures 3 and 4).

Under microscopic presents a granoblastic texture, with an incipient recrystallization of calcite (figures 1 and 2). It is a monomineralic rock with calcite as practically the only constituent, and without sulphides. It presents locally calcite veinlets.

Figures 1 and 2. Gray limestone in the quarry fronts.



Figures 3 and 4. Microscopic view of the gray limestone. It is showed an incipient recrystallization.

6. GEOCHEMICAL CHARACTERIZATION

Following are presented the results of the sampling carried out in 2009 and in 2016.

6.1. Sampling in 2009. Five samples have been collected in the points showed in map 1. These samples have been analyzed for major and trace elements by X-ray fluorescence, with the next results:

GREY LIMESTONE: LITHOGEOCHEMICAL ANALYSIS OF MAJOR ELEMENTS (2009)												
Sample	%SiO_2	%Al_2O_3	%Fe_2O_3	%MnO	%MgO	%CaO	%Na_2O	%K_2O	%TiO_2	%P_2O_5	%L.O.I	TOTAL	CO_3Ca
SOL-2	0.00	0.00	0.00	0.01	0.11	55.67	0.02	0.00	0.01	0.01	43.33	99.16	99.37
SOL-3	0.00	0.00	0.00	0.01	0.15	55.66	0.03	0.00	0.01	0.03	43.46	99.35	99.35
SOL-4	0.00	0.00	0.00	0.01	0.26	55.45	0.01	0.00	0.01	0.01	43.61	99.36	98.98
SOL-5	0.00	0.00	0.01	0.02	0.34	55.23	0.01	0.00	0.01	0.03	43.43	99.08	98.59
SOL-6	0.00	0.00	0.07	0.06	0.36	55.75	0.01	0.00	0.01	0.03	43.41	99.70	99.51
AVERAGE	**0.00**	**0.00**	**0.02**	**0.02**	**0.24**	**55.55**	**0.02**	**0.00**	**0.01**	**0.02**	**43.45**	**99.33**	**99.16**

GREY LIMESTONE: LITHOGEOCHEMICAL ANALYSIS OF TRACE ELEMENTS (2009)						
Element	Detection limit	SOL-2	SOL-3	SOL-4	SOL-5	SOL-6
Sc	(2 ppm)	37.8	38	39.8	35.3	36.6
V	(3 ppm)	<3	<3	<3	<3	<3
Cr	(2 ppm)	10.7	8.9	4.2	9	6.2
Co	(3 ppm)	4.4	<3	<3	3	3.2
Ni	(2 ppm)	<2	<2	<2	<2	2.1
Cu	(2 ppm)	6.9	5.2	5.5	6.2	10.6
Zn	(1 ppm)	3.1	1.3	1.1	3.8	10.5
Ga	(1 ppm)	<1	<1	<1	<1	<1
Ge	(1 ppm)	<1	<1	<1	<1	<1
As	(3 ppm)	3.9	<3	<3	<3	3.8
Se	(1 ppm)	<1	<1	<1	<1	<1
Br	(1 ppm)	<1	<1	<1	<1	<1
Rb	(1 ppm)	2.5	2.5	4.2	2.7	2.6
Sr	(1 ppm)	86.1	140.3	962.4	206.1	194.2
Y	(1 ppm)	3.9	5.8	2.3	1.8	3.9
Zr	(1 ppm)	<1	<1	<1	<1	<1
Nb	(1 ppm)	<1	<1	<1	<1	<1
Mo	(1 ppm)	<1	<1	1.1	<1	<1
Ag	(3 ppm)	<3	<3	3.2	<3	<3
Cd	(3 ppm)	<3	<3	<3	<3	<3
Sn	(2 ppm)	<2	<2	<2	<2	<2
Sb	(3 ppm)	<3	<3	<3	<3	<3
Te	(3 ppm)	<3	<3	<3	3.5	<3
I	(4 ppm)	<4	<4	<4	<4	<4
Cs	(5 ppm)	<5	<5	<5	<5	<5
Ba	(8 ppm)	<8	<8	<8	<8	<8
La	(8 ppm)	10.6	12.5	17.8	<8	16.1
Ce	(7 ppm)	<7	<7	<7	10	7
Pr	(11 ppm)	16.4	<11	<11	<11	<11
Nd	(4 ppm)	<4	<4	<4	7.3	<4
Sm	(5 ppm)	<5	<5	<5	<5	6.7
Gd	(5 ppm)	<5	<5	<5	<5	<5
Yb	(4 ppm)	<4	<4	<4	<4	<4
Hf	(3 ppm)	<3	<3	<3	<3	<3
Ta	(3 ppm)	3.3	<3	<3	<3	<3
W	(2 ppm)	23.7	13.3	9.4	7.1	8.1
Hg	(1 ppm)	<1	<1	<1	<1	<1
Tl	(2 ppm)	<2	<2	<2	<2	<2
Pb	(2 ppm)	2.2	2.2	<2	6	8.5
Bi	(1 ppm)	<1	<1	<1	<1	<1
Th	(2 ppm)	<2	<2	<2	<2	<2
U	(1 ppm)	1.7	1.8	7	5.7	2.2

The analysis of the gray limestone correspond to an extraordinarily pure limestone, composed exclusively of CaO (55.55%), resulting in a 99.16% $CaCO_3$. Of the other major elements only the 0.24% of MgO is remarkable. In terms of content of trace elements noteworthy that presents very low values of heavy elements, which are the main pollutants.

6.2. Sampling in 2016. Three samples have been collected in the points showed in map 2. These samples have been analyzed for major and trace elements by X-ray fluorescence, with the next results:

GREY LIMESTONE: LITHOGEOCHEMICAL ANALYSIS OF MAJOR ELEMENTS (2016)												
Sample	%SiO_2	%Al_2O_3	%Fe_2O_3	%MnO	%MgO	%CaO	%Na_2O	%K_2O	%TiO_2	%P_2O_5	%L.O.I	TOTAL	CO_3Ca
SOL-7	0.05	0.03	0.08	0.00	0.11	55.75	0.07	0.02	0.01	0.06	43.15	99.33	99.51
SOL-8	0.15	0.00	0.06	0.00	0.07	55.65	0.07	0.00	0.00	0.06	43.07	99.13	99.34
SOL-9	0.00	0.00	0.07	0.01	0.18	55.75	0.06	0.00	0.00	0.02	43.15	99.14	99.51
AVERAGE	**0.07**	**0.01**	**0.07**	**0.00**	**0.12**	**55.72**	**0.07**	**0.01**	**0.00**	**0.05**	**43.12**	**99.20**	**99.45**

GREY LIMESTONE: LITHOGEOCHEMICAL ANALYSIS OF TRACE ELEMENTS (2016)				
Element	Detection limit	SOL-7	SOL-8	SOL-9
Sc	(2 ppm)	37.8	39.7	41.4
V	(3 ppm)	<3	<3	<3
Cr	(2 ppm)	3.4	3.3	5.3
Co	(3 ppm)	<3	<3	3
Ni	(2 ppm)	<2	<2	<2
Cu	(2 ppm)	6.7	9.4	7.9
Zn	(1 ppm)	<1	15.2	3.8
Ga	(1 ppm)	<1	<1	<1
Ge	(1 ppm)	<1	<1	<1
As	(3 ppm)	5.3	5.5	3.6
Se	(1 ppm)	1.1	<1	1.5
Br	(1 ppm)	<1	1.4	<1
Rb	(1 ppm)	8.2	8.2	7.5
Sr	(1 ppm)	131.0	113.4	196.8
Y	(1 ppm)	4.3	3.4	2.5
Zr	(1 ppm)	<1	<1	<1
Nb	(1 ppm)	<1	<1	<1
Mo	(1 ppm)	1.3	1.5	1.1
Ag	(3 ppm)	<3	<3	3.6
Cd	(3 ppm)	<3	<3	3
Sn	(2 ppm)	<2	2.2	<2
Sb	(3 ppm)	<3	3.4	3.1
Te	(3 ppm)	4.6	5.7	5.2
I	(4 ppm)	<4	<4	<4
Cs	(5 ppm)	<5	<5	<5
Ba	(8 ppm)	<8	<8	<8
La	(8 ppm)	11.2	11.1	11.7
Ce	(7 ppm)	15.7	<7	<7
Pr	(11 ppm)	15.6	<11	<11
Nd	(4 ppm)	<4	<4	5.7
Sm	(5 ppm)	<5	<5	<5
Gd	(5 ppm)	<5	<5	<5

Yb	(4 ppm)	<4	<4	<4
Hf	(3 ppm)	<3	<3	<3
Ta	(3 ppm)	<3	<3	<3
W	(2 ppm)	<2	<2	<2
Hg	(1 ppm)	<1	<1	<1
Tl	(2 ppm)	3.1	3	<2
Pb	(2 ppm)	16.5	37.3	16.7
Bi	(1 ppm)	<1	<1	<1
Th	(2 ppm)	<2	<2	<2
U	(1 ppm)	3.9	3.8	4.1

The analysis of the gray limestone correspond to an extraordinarily pure limestone, almost exclusively composed of CaO (55.72%), resulting in a 99.45% $CaCO_3$. Of the other major elements only the 0.12% of MgO is remarkable. In terms of content of trace elements noteworthy that presents very low values of heavy elements, which are the main pollutants.

7. POTENTIAL INDUSTRIAL APLICATIONS

According to its chemical and mineralogical composition, these limestones can be use for concrete mix and for ground calcium carbonate (GCC). The limits of these potential uses are fixed by the legal normative in every country.

8. CONCLUSIONS

The limestone sampled is extraordinarily pure, with an average of 99.16% $CaCO_3$ in the samples of 2009 and 99.45% in $CaCO_3$ in the samples of 2016, with a remarkable compositional homogeneity. The content of potentially harmful trace elements is very low. By its chemical and mineralogical characteristics the field of application of these materials is very wide, from the concrete industry to the manufacture of “GCC", in both cases with the limits of the local regulations.

Oviedo, March 22, 2016

Professor Dr. Daniel Arias Prieto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SOL-2
SOL-3
GRAY LIMESTONE
SOL-5
SOL-4
SOL-6
MAP 1. LITHOGEOCHEMICAL SAMPLES IN 2009


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GRAY LIMESTONE
SOL 7
SOL 8
SOL 9
MAP 2. LITHOGEOCHEMICAL SAMPLES IN 2016