NATURAL DIOPSIDE FOR CERAMICS IN BRAZIL AND A GEOLOGICAL APPROACH TO THE STATE OF BAHIA OCCURRENCES

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1. ABSTRACT

Diopside is a monoclinic pyroxene mineral with composition $MgCaSi_2O_6$. In Brazil, diopside is used for ceramics, in glazed tile manufacture, and its overall production is around 50.000 tpa (tons per year). This raw material is exploited in three different geographic areas, as follows: states of Bahia, Alagoas and Paraná. This paper deals with Bahia occurrences, in northeastern Brazil, which are located near the city of Castro Alves, about 200 kilometers from the city of Salvador.

2. INTRODUCTION

Diopside is a monoclinic pyroxene mineral and it has a mineralogical formula $MgCaSi_2O_6$, and chemical composition of 55,49% of SiO_2, 25,9% of CaO and 18,61% of MgO.

Investigations on the behavior of diopside when used in ceramics point out favorable facts, such as providing high whiteness [1], higher strength and abrasion resistance values to the ceramic body [1, 2, 3, 4] and contributing to enhance the amount of crystalline phases in vitreous porcelain, such as anorthite, diopside, wollastonite and cordierite [1, 2, 3]. These characteristics make diopside suitable for engobe and ceramic body composition of porcelain stoneware tiles, sanitary ware, tableware and dinnerware among other potential ceramic uses.

In spite of its use and potential for a wide range of ceramic application, diopside's utilization in Brazil remains restricted to engobe formulations, in which the raw material accounts for more than 20% of the composition. According to suppliers and consumers, diopside acts as a sintering agent, provides better waterproofing to the engobe layer, avoiding water marks in the tiles, and contributes high whiteness to the engobe, replacing, at least partially, the use of zircon and zirconium silicate as opacifier.

In the Brazilian scenario, diopside is produced in three geographic areas: states of Bahia, Alagoas and Paraná, with a total production of about 50.000 tpa (tons per year). The present study focuses on the diopside occurrences in the region of Castro Alves, Bahia state, approximately 200 kilometers from the city of Salvador.

3. PURPOSE AND SCOPE OF THIS WORK

The purpose of this paper is to present the geological context, besides the mineralogical and chemical characterization of new deposits of diopside that occur in Castro Alves and the northern region, in Bahia state, northeastern Brazil. Additionally, some ceramic studies are presented for this raw material that has been successfully used in Brazilian ceramic industry as a substitute, at least partially, of zircon and zirconium silicate in engobe formulation.

4. NEW DEPOSITS OF DIOPSIDE IN BAHIA STATE, BRAZIL: FROM THEIR DISCOVERY TO CHARACTERIZATION AND USES

Until the year 2010 only two areas were producing diopside in Brazil. However, after geological researches, carried out from 2009 in the region of Castro Alves, a new province of diopside was discovered and a commercial production started in 2011 by one company. Nowadays there are two or three other companies that are preparing new deposits for production, besides the interest of several companies due the deposits characteristics and favorable geology in the region. Probably the value of the current Brazilian production (50.000 tons per year) will grow significantly with increasing demand for diopside in the domestic market.

Geologically, the study region is part of the Archean-Paleoproterozoic orogenic belt Itabuna-Salvador-Curaçá, 800 km long and up to 150 km wide, located in the eastern part of São Francisco Craton. The orogenic belt is formed by high grade metamorphic rocks, showing a flat planaltic province, composed of orthogneisses and migmatites, containing hills of metasedimentary sequence with quartzite, paragneisses, calc-silicate rocks and carbonatic sequences (marble and metadolomite) belonging to Tanque Novo-Ipirá complex. These strips of metasedimentary rock occur as discontinuous layers or lenses, oriented along the regional strike (N10E to N70W) and high dip angle, with extension of dozens to hundreds of meters, even kilometers, in length, and tens to hundred meters thick. Studies by the authors and partners [5, 6, and 7] show that the core of the sequence of calc-silicate rocks are composed of the follows associations: I) Monomineralic diopsidites with small quantities of carbonate, tremolite and/or flogopite; II) quartz diopsidites that may contain scapolite, garnet, sphene, plagioclase and/or rare wollastonite; III) microcline/orthoclase diopsidites; VI) calc-silicate gneisses interlayered with quartz-feldspathic bands and diopside bands. Surrounding the core of calc-silicate rocks, associated metacarbonatic sequences and lenses of metamafic rocks may occur. Figure 1 shows a geological map.

After mapping several strips of calc-silicate rocks, some diopsidite bodies from associations I to IV were selected to conduct further detailed studies aimed at mining. Currently, the mainly exploited diopsidite, used for engobe, is a mixture of monomineralic diopsidite and quartz diopsitite, characterized by a white color, fine to coarse-grained, with an isotropic to anisotropic structure and decussate, granoblastic or nematoblastic texture. Mineralogically, the main minerals present are diopside (70-95%), quartz (5-30%), K-feldspar (5-15%). The chemical characteristics of this industrial mineral at open pit mining and other outcrops are shown in Table 1. The average composition of the standard commercial type present is: SiO_2 - 55%; Al_2O_3 - 3%; Fe_2O_3 – 0.6%; MgO – 17.5%; CaO – 20.5%; Na_2O – 0.5%; K_2O - 1%; and L.O.I – 0.5%. The rock types associated with diopside also contain minerals of commercial interest, but they are still in the research and development phases for other purpose.

Laboratory studies of diopsides determined density between 2.90 and 3.20 g/cm^3, water absorption ranging from 0.15 to 1.36% and apparent porosity between 1.33 and 4.11%. In ceramic characterization, the standard material when fired at 1200°C, under atmospheric conditions exhibits a white to slightly yellow color, water absorption around 2% and linear shrinkage of 12%. In the fusibility tests, samples showed melting and flowing points at 1255°C and 1275°C, respectively. Details for ceramic body formulation can be seen in reference [2].

Samples	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O	LOI	Sum
Ideal Diopside	55,49	-	25,9	18,61	-	-	-	-	-	100
Mine Ed Br	55,62	3,1	20,69	17,53	0,65	0,04	0,54	1,02	0,36	99,61
RJE 39	52,1	0,74	25,47	18,65	0,67	0,04	0,04	0,01	2,21	100,01
RJE 6	54,19	1	22,98	19,64	1,08	0,08	0,06	0,01	0,8	100,02
RJS 623	53,65	1,27	25,7	18,33	0,55	0,05	0,05	0,12	0,19	100
CAU 731	54,8	2,98	22,6	15,1	1,61	<0,10	0,39	0,61	1,6	99,69
CAU 731 A	51,7	3,09	23,9	16,6	0,88	<0,10	0,23	0,33	1,6	98,33
Diop Ed	51,4	3,4	24,4	16,7	1,57	0,1	0,21	0,1	1,6	99,82
CAE-9	53,9	3,43	22,57	17,07	1,61	0,12	0,49	0,62	0,6	100,55
RJCCE 9	65,27	4,56	13,45	11,46	0,58	0,06	0,97	3,31	0,18	99,99
CAE-8	51	5,02	23,62	15,85	3,26	0,2	0,28	0,07	0,55	100,02
RJCCE 5	68,48	5,43	11,59	8,44	0,66	0,07	0,69	4,45	0,08	100,01
RJCCE 1	69,55	6,62	9,57	6,9	0,46	0,11	0,24	6,33	0,12	100,01
REG-7 (RJ)	50,9	7,34	21,9	15,56	1,25	0,08	0,24	0,29	2,03	99,66
RJE 49A	73,71	7,65	5,18	4,63	0,97	0,36	0,87	6,04	0,45	100,02
RJE 84	73,39	7,67	5,34	4,8	0,91	0,35	0,89	6,05	0,45	100,01
RJE 43	65,89	10,13	9,33	6,29	0,55	0,09	1,97	5,29	0,35	100
246	51,06	11,02	18,76	10,72	2,22	0,3	1,91	1,47	2,19	100
RJE 24	64,92	11,22	6,5	5,84	0,72	0,09	0,25	9,86	0,39	100,03

(wt%)

Table 1. *Major elements of diopsidites from different points in the northern region of Castro Alves, Bahia.*

5. CONCLUSION

The geological studies that have been done in Castro Alves and its northern vicinities, in the state of Bahia - Brazil, aiming to explore, develop and exploit diopside for ceramics, showed successfully results. Several new deposits of diopsidite were discovered and an important new raw material is now available to supply ceramic and other industries. it is possible to conclude that in this region there are several deposits with very good quality and quantity to support intensive consumption of diopside. Despite the good quality and availability of the material, additional studies, focusing on the geology, characterization and new uses for diopside, are necessary. Furthermore, the development of diopside mining would bring producers and the development needed to this region

To improve production, the mining producers should make joint efforts to enhance the consumption of diopside in ceramics as well as in other industry sectors.

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