

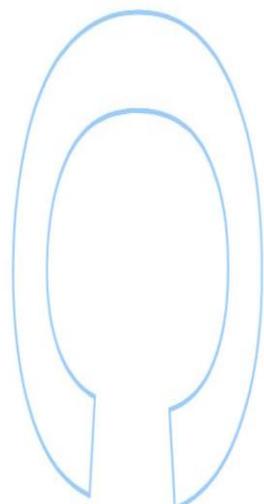
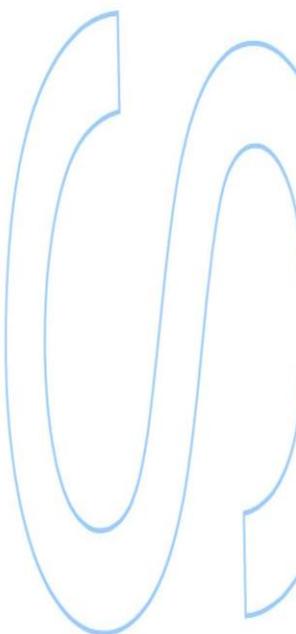
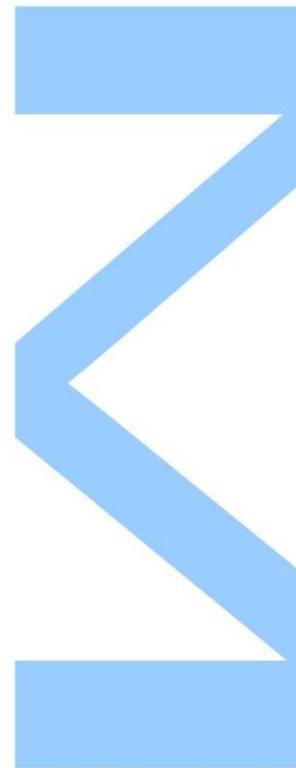


A Comparative Analysis between Portuguese and Jamaican Bauxite Rocks: Their Geo-Economic Potential for the Aluminum Industry

Michigan MADOURIE

Dissertação apresentada para obter o Título de Mestre em Geologia
Mestrado em Geomateriais e Recursos Geológicos

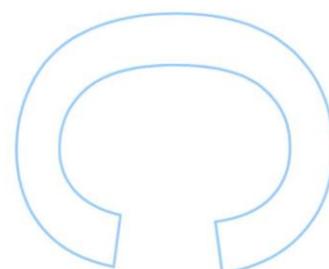
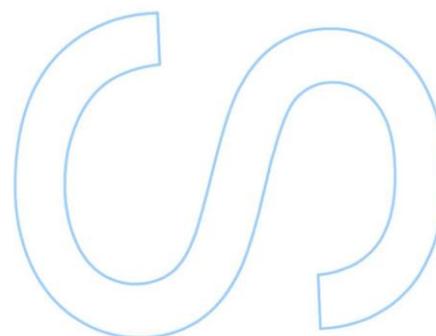
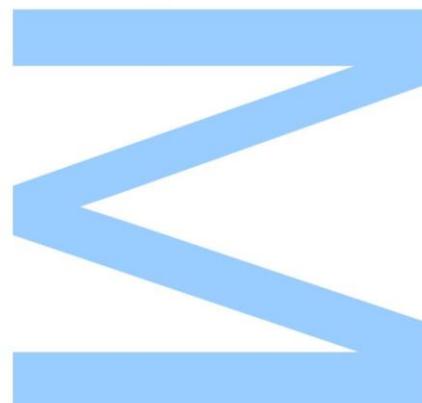
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ORIENTAÇÃO:

IULIU BOBOS

PROFESSOR ASSOCIADO /COM AGREGAÇÃO

DEPARTAMENTO DE GEOCIÊNCIAS, AMBIENTE E ORDENAMENTO DO TERRITÓRIO

FACULDADE DE CIÊNCIAS, UNIVERSIDADE DO PORTO

ABSTRACT

The hyperaluminous clays of Portugal in the Andornha-Cantanhede region make an interesting matchup against lateritic bauxite deposits of Jamaica. In several parts of the region of Andorinha, bauxitic facies occur, overlying argillaceous and arkosic (Grés Belasiano) sandstone. The bauxitic clays are weathering product from the sandstone in the region. The clays fill karst cavities that are up to 12 meters deep and increases in depth moving from east to west. In Jamaica bauxite shows a strong correlation with the White Limestone group in general and in the Central Inlier of the country the bauxitic facies show a slight evidence of igneous or volcanic origin. Jamaica's principal bauxitic rocks are located in the parishes of Manchester, St. Elizabeth and St. Ann. Other important deposits occur in St. Catehrine, Clarendon and Trelawny.

Laboratory studies have been carried out on the bauxitic rocks and clay samples taken from Andorinha-Cantanhede. The bauxitic samples of Andorinha have been subjected to X-ray diffraction, IR spectroscopy and XRF analysis. Furthermore, rock samples were optically assessed to identify the correlation between rock and bauxitic minerals in clay.

Bauxitic clays of Andorinha were found related with the kaolinite rich matrix of the sandstone of the area, they also demonstrate strong autochthonous characteristics. Low-diagenetic processes over time have altered the chemical and mineral composition, hardness, texture and appearance of the bauxitic rocks and clays across the region and in sinkholes, respectively. Jamaican bauxites have a high aluminum content, just over 75% of the deposits have more than 69% gibbsite. Also present in the bauxite are several heavy minerals and the silica content increases with altitude making the bauxite in highlands harder to beneficiate.

Portugal's bauxitic resources are not currently mined for the alumina and aluminum industries due to quantity and grade. Jamaica's bauxitic reserves are well over 1million tonnes and the country will continue to be a high ranked producer well into the next century.

Acknowledgement

Firstly, I would like to thank God for granting me the wisdom, knowledge, and strength required to complete this project; without His blessings it would not have been possible.

Additionally, I would like to say a special thanks to the European Union and the organizers of the Erasmus Mundus Action II programme for affording me this wonderful opportunity to complete my master education here at the Universidade do Porto. Also, my sincerest gratitude goes out to Barbara Costa and Ana Castro Paiva from the Reitoria at the Universidade do Porto for their unwavering support and constant motivation. More so, my sincerest gratitude goes out to Sofia Santos at the Universidade do Porto, Post Graduate section, for her kind assistance rendered to me throughout my studies.

I owe a great debt of gratitude to my supervising professor, Dr. Iuliu Bobos Radu. His ethics, eye for detail along with his immense knowledge and experience have made this dissertation a success. Sir, thank you so much.

Last but by no means the least; I want to thank my family, friends and a very special friend Terrence James for their unwavering love and support. Their undying nature to inspire and motivate me, especially in trying times, has kept me grounded, inspired and motivated.

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OBJECTIVES OF THE STUDY

The completion of this master thesis is a strong component for the awarding of the Master of Science (MSc.) in the Geological Resources and Materials degree program at the Universidade do Porto, Portugal.

This study aims to create a comparative analysis of bauxitic rocks in Portugal and Jamaica and identify their geo-economic potential for the aluminum industry.

There are several objectives of the study, and these include:

- To identify the differences and similarities if condition that led to bauxitization in the two areas;
- Establish the similarities and differences in bauxite samples from Portugal and Jamaica;
- To scientifically observe and analyze bauxitic rock samples from Portugal and Jamaica;
- Explain in great detail the scientific findings on Portuguese and Jamaican bauxite
- Provide a detail summary explaining the geo-economic potential of Jamaican and Portuguese bauxite and;
- Add to existing knowledge in the study area and be used as a guide or reference for future studies any level.

1 INTRODUCTION

Aluminum is the earth's most abundant metallic element, making up approximately 8% of the planet's crust (Hill & Sehnka, 2006) and, it is found in virtually every common rock type. The occurrence of aluminum in rocks is not in its pure form. It may occur as oxide and hydroxides, which is extracted and processed for industrial application and making it one of the most widely used metals in modern technology.

Generally, the combination of these hydroxides (minerals) and other gangue minerals as a naturally occurring, heterogeneous weathering product is collectively referred to as bauxite.

The term bauxite was introduced by Berthier (1821) to describe sediments rich in alumina from Les Baux in the vicinity of Alpilles (Bouches du Rohne), France. However, it was not until 1845 that the name was widely applied to rocks which fit the description of having a relatively soft earthy, whitish gray, to reddish-brown solid, with a pisolitic structure. Ever since, the term became popular and widely accepted in soil science and has been adopted and modified by the world. The United States Geological Society (USGS) identifies bauxite as a naturally occurring, heterogeneous material composed primarily of one or more aluminum hydroxide minerals, plus various mixtures of silica, iron oxide, titania, aluminosilicate, and other impurities in minor or trace amounts.

The derivation of bauxite is extremely variable and includes a variety of source rocks. Most commonly, it is a residual or transported constituent of clay deposits at or near the earth's surface. These are widely distributed geographically, predominantly in tropical to subtropical countries all over the world. Bauxite may be found in large buried deposits, occurring as a thick massive blanket or as lensoid bodies in small pockets running for several hundred meters. It is usually mined by the open pit method and the minerals (aluminum hydroxides) are extracted and converted into alumina by the Bayer process followed by the Hall-Hérault process; which uses electrolysis to reduce alumina to metallic aluminum.

More than 90 per cent of the world's bauxite is produced by six countries. The top five world producers of bauxite in 2010 were Australia, China, Brazil, India and Guinea in that same order (USGS). The bulk of bauxite produced in the world is currently used as a feed for manufacturing aluminum. Approximately 85% of the bauxite mined is ultimately converted into aluminum metal (Hill & Sehnka, 2006),

an additional 10% goes to non-metal uses such as various form of alumina (the oxide of aluminum), and the remaining 5% goes to non-metallic grade bauxite applications.

In Portugal, although present, bauxite is one of the least popular mineral ore deposits. The economic resource can be found in the Andorinha-Cantanhede region of central Portugal, overlying the karst limestone group. The region covers several square kilometers and is blanketed with the brick-red bauxitic clay, most of which fills karst sinks. And, although the deposit may be several thousand metric tons, there has been no serious discussion to commercially exploit it.

On the other hand, Jamaica has been consecutively ranked in the top eight of highest producing countries, ever since the country commenced the mining of bauxite, well over 50 years ago. There is no doubt that Jamaica exerts some dominance in the global alumina/aluminum industry. The mapped reserves demonstrate that the country can afford to mine for another hundred or so years. Where Portugal is concerned however, much is left to be explored regarding the volume, content and concentration of the ore and the impact it will have if any, on the aluminum industry.

The main goal of this study is to explore the bauxitic rocks from both countries, carefully examining the mineralogy, geology and other factors that have led to the formation of the ore deposits. The study will also highlight the impact or economic potential, if any the presence of bauxite in Portugal may have on the aluminum industry, whilst taking a look at the continued presence Jamaica will have on aluminum production internationally.

2 GEOLOGY OF BAUXITIC ROCKS

2.1 FRAMEWORK DEFINITION

Bauxite is a sedimentary rock enriched in aluminum hydroxide minerals (Bárdossy, 1982) being the main raw material used for the aluminum industry (Patterson, Kurtz, & Olson, 1986). Also, bauxitic rocks are weathering products formed as residual deposit at or near the earth's surface under tropical and sub tropical conditions (Kogel, 2006). The bauxite rocks are classified into three basic types with respect to mineralogical composition (Patterson et. al. 1986): i) trihydrate, consisting chiefly of gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; ii) monohydrate, consisting mainly of bohemite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and iii) mixed bauxite, consisting of both gibbsite and bohemite.

2.2 DISTRIBUTION OF BAUXITIC ROCKS AROUND THE WORLD

Occurrences of bauxite rocks are well known around the world. Although, they might be chemically and physically different due to their underlying parent material and existing environmental factors. The mineralogical characteristics and geologic ages make it easy to group bauxites into geological belts, even though they may have been shifted by plate tectonics (Patterson et al. 1986).

The largest deposits with higher concentrations and economic grade are to be found in tropical belts, between latitude 30° N and 30° S (**Fig. 1**). Bauxites occur as thick massive blanket type or lensoid bodies running for several hundred meters. These deposits are nearly all the Upper Tertiary and younger lateritic-type deposits. The Mesozoic and Lower Tertiary bauxites are distributed in a global belt between latitude 35° N and 50° N and from latitude 50° N to 68° N the bauxites from the Paleozoic era predominate. However, the distribution of bauxitic deposits may be collectively grouped in large and small provinces across the world. Gow (1993) indicates that the deposits in the Caribbean and Central America make up the large Caribbean Province whilst the Guyana and Brazilian Shields comprise the South American Province. The Guinea Shield Province and Cameroon constitute the large African Province and the distribution in Australia makes up that sub-continental Province.

The smaller provinces occur in China, India, Indonesia, Malaysia, Southern Europe, and Arkansas in the US, also small provinces are located in countries of the former Soviet Union. Furthermore, there is a close relationship between geographic distribution of bauxite deposits and their geotechnical position (Bárdossy, 1982).

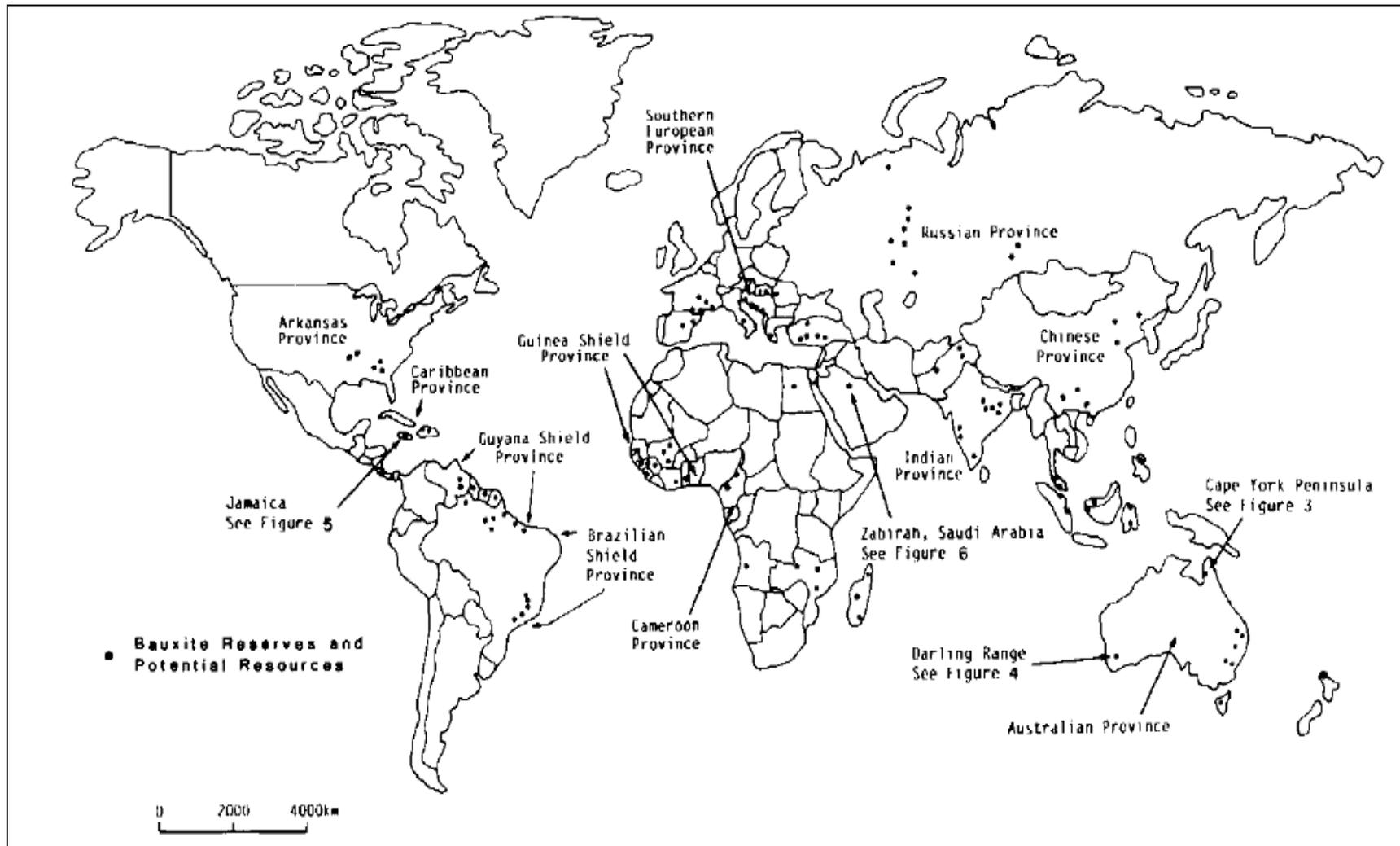


Figure 1 The distribution of bauxite deposits across the world (Gow, 1993).

Bardossy (1982) shows a strong connection between the geographic distribution of bauxites and geotectonic settings (Table 1). Lateritic bauxites tend to be associated with rocks situated on continental platforms that are tectonically stable whilst, karst bauxites are more associated with orogenic belts.

Tectonic Unit	Lateritic Bauxite (%)	Karst Bauxite (%)	Tichwin-Type Bauxite (%)
Continental Platform	96	8	100
Orogenic Belts	3	92	-
Oceanic Basin	1	-	-

Table 1 Geographical distribution of bauxite deposits and their geotectonic position (adapted from Bárdossy, 1982).

2.3 ORIGINS OF BAUXITIC ROCKS

Several theories were put forward to explain the origin and formation of bauxite throughout recent times (Patterson et al., 1986). These theories include: i) precipitation from hot waters rich in aluminum salts; ii) alteration of aluminous parent material in seawater; iii) Deposition of aluminum material in lakes and; iiiii) leaching of aluminous rocks by naturally evolved acid. From all the theories postulated, it is generally accepted by geologists that bauxitic rocks are formed by weathering processes under favorable conditions for the retention of alumina and leaching of other conditions of parent rock (Patterson et al., 1986).

Gow (1993), explains that bauxitization is a complex process and is practically impossible at depth below a thick overburden. He further outlined eight factors that greatly affect the formation of bauxite. These factors were amended from Harder (1952), who summarized the following factors or conditions which favor the formation of bauxite: i) the presence of rocks with easily soluble minerals yielding residues rich in alumina; ii) effective rocky porosity, enabling easy access and free circulation of water; iii) normal to abundant rainfall alternating with dry periods; iv) vegetation, including bacteria, advantageously distributed; v) available sources of appropriate solution and precipitation agencies; vi) a tropical or at least warm climate vii) low to topographic relief, allowing free movement of the water table but a minimum erosion; and viii) long quiet periods in earth history.

Bauxite is formed from almost every type of rocks (Fox, 1932) that contain alumina. A majority of the bauxite is formed more readily from rocks that are high in aluminum and have little or no resistance to weathering. Importantly, parent material is not very important in producing bauxite when compared to the intensity and duration of weathering (Patterson et al., 1986).

Geologists have mapped large bauxite deposits across the world, these deposits have shown varied parental material origins such as; the clayey sandstone deposit of Weipa, Australia which has as little as 4% Al_2O_3 (Loughan and Bayliss, 1961) and in Jamaica a very pure isolated limestone occur (Hose, 1961). There has also been bauxite on quartzite with 92 percent silica in Guinea (Patterson et al., 1986). The nepheline syenites in Arkansas, United States have produced the bauxite deposits (Gordon et al., 1958).

Also, bauxite has been developed on several sedimentary and metamorphic rocks. Examples of these include bauxite deposits in Madagascar, formed from weathered gneiss (Balet, 1966), and the feldspathic and hyperstene gneiss rocks in Sierra Leone (Patterson et al., 1986; Bramwell, 1962). Additionally, deposits occur on phyllites in Ghana in addition to those occurring on tuffs of Precambrian age and shale of Carboniferous age (Patterson et al., 1986; Cooper, 1936). Grubb (1970) points to the Game district in Australia where bauxite has been originated on shales, siltstone and sandstone of Cretaceous age.

2.4 MINERALOGICAL CHARACTERISTICS OF BAUXITE

The mineralogy of bauxite is dependent, to a good extent, on the geology of the parent rock and other factors such as climatic and biological factors. The major (ore) minerals in bauxite comprise several forms of hydrated aluminum oxide. These include gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), bohemite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). In addition, there are over another 170 minerals that have been identified in bauxites, but only ten have been known to occur in rock-forming quantities (including the ones listed above), namely: corundum, goethite, hematite, kaolinite, halloysite, anatase and rutile (Kogel et al., 2006). Other gangue and contaminant minerals found in trace amounts in bauxite include calcite, dolomite, and quartz, along with the manganese and phosphate minerals.

Gibbsite, is a trihydroxide of aluminum $(\text{Al}(\text{OH})_3)$, in some European literature it is also called "hydrargillite". The mineral is the major constituent of bauxite in many large lateritic-type deposits in tropical countries. It has three basic polymorphs; bayerite,

nordstandite and doyleite. Gibbsite may be metamorphosed into bohemite and diasporite at higher grades they may be converted to corundum.

Bohemite, is a monohydrate of alumina and is commonly referred to as aluminum oxide hydroxide [AlO (OH)]. It is the most commonly occurring minerals in many bauxite desposits especially the karstic ones of China and Europe. The mineral is responsible for about 20 percent of bauxite deposits in the Caribbean and it is also in minor amounts in many laterite-type deposits.

Diasporite, [AlO (OH)] has the same chemical composition as Bohemite but differs physically due to its atomic structure, being more compact, the mineral is much harder. The mineral is a product of the metamorphosis of regional aluminous rocks recycled from earlier bauxite. It is more common, however, in China, Vietnam, central Greece, Romania and Turkey (Bárdossy, 1982).

Mineral	Common chemical formula	Alternative formula and name	Crystal system	Al Content weight (%)	Combined water and weight (%)	Specific Gravity	Hardness
Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Al trihydrate	$(\text{AlOH})_3$ aluminum trihydroxide	Monoclinic	63.35	34.65	2.3-2.4	2.2-3.5
Bohemite	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ alumina monohydrate	$\text{AlO}(\text{OH})$ aluminum oxyhydroxide	Orthorhombic	84.97	15.03	3.01-3.06	4-5
Diaspore	Al_2O_3	Al_2O_3	Trigonal	84.98	15.02	3.3-3.5	6.5-7

Table 2 Crystal chemistry and physical properties of bauxite minerals (Patterson et al., 1986)

In addition to the major bauxite minerals, aluminum also occurs in several other minerals and in some non-crystalline matter. Corundum (Al_2O_3) is a common, simple aluminum mineral, and it is recognized to be one of the most common emery deposits that occur in bauxite. The mineral is concentrated in pisolites of bauxites and dominates the deposits of the former Soviet Union. Other aluminous minerals found in bauxite are often the non-crystalline, poorly ordered hydrated aluminous solids of allophone and imogolite. Allophone, being a non crystalline mineral has a similar general composition to that of kaolinite. Imogolite is similar to allophone in composition and is more widely distributed in the lateritic-type bauxites especially those of a young age.

The most dominant clay mineral found in bauxite tends to be kaolinite $[(\text{OH})_8 \text{Si}_4 \text{Al}_4\text{O}_{10}]$. However, other lesser known forms of kaolinite, halloysite $[(\text{OH})_8 \text{Si}_4 \text{Al}_4\text{O}_{10}]$ and endellite $(\text{OH})_8 \text{Si}_4 \text{Al}_4\text{O}_{10}$ are often times present. In high aluminous clayey bauxite, the hydrated form of halloysite tends to be extremely common. They occur as pure pockets, veins, concretions, and intergrowths with aluminum and iron bearing minerals (Patterson, et al., 1986). Kaolinite occurs as a well ordered mineral in most bauxite and is most common in bauxites from the Eocene. However, the mineral is also found to be present in a disordered or disarrayed structure, in some deposits. Another clay-like mineral of the chlorite group chamosite $(\text{Fe}^{2+}, \text{Mg})_5 \text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$ is present in some karst bauxites of the Paleozoic and Mesozoic age according to Bárdossy (1982). In some cases, the mineral makes up approximately 60 percent of diasporic bauxite (Patterson et al., 1986).

The distinctly bright colors of bauxite are owed to the presence of iron minerals. The minerals hematite Fe_2O_3 and goethite $\text{FeO}(\text{OH})$ are by far the most abundant impurities (gangue) minerals found in bauxite deposits. They occur as nodules, concretions, and as finely disseminated forms of intergrowth with aluminous minerals (Patterson et al., 1986). The bright reddish brown color which is a characteristic feature of many types of bauxite is a result of hematite, whilst the brownish yellow deposits tend to have goethite as the most abundant iron mineral present. Stahl (1971) explains that there is as much as 5 percent of goethite in bauxite; this is due to the level of aluminum-iron substitution that takes place. However, in some deposits the number tends to be higher depending on environmental factors.

In Jamaica for example, Davis (1973) described the goethite present in bauxite deposits to be 7%. Nonetheless, other iron minerals also occur in bauxites,

especially deposits which develop in the regions of mafic igneous rocks. These minerals include magnetite $\text{Fe}^{2+} \text{Fe}_2^{3+} \text{O}_4$ and ilmenite $[\text{FeTiO}_3]$.

Rutile (TiO_2) is the most common titanium mineral followed by ilmenite and titaniferous magnetite with anatase and leucoxene (secondary minerals) are the ones found in bauxite. These minerals are formed during the weathering process. Weathered ilmenite is usually coated by leucoxene which also acts a pseudomorphic replacement of other titanium-bearing minerals.

Quartz SiO_2 occurs in minor amounts in bauxitic deposits, but tend to be quite abundant in deposits that have made with contact of sandstone or regional quartzite. Calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$ are found in bauxite deposits that are associated with carbonate rocks. The nature of the occurrence can be attributed to the carbonic acid solution that dissolves into karstic regions.

There are several manganese minerals which occur in bauxite, however, these tend to be in minor quantities. This is the case in Jamaica as described by Sabiston (1975). Minerals such as lithioporite $(\text{Al,Li})\text{MnO}_2(\text{OH})_2$ and hausmannite Mn_3O_4 , manganite $\text{MnO}(\text{OH})$, and woodruffite $2(\text{Zn, Mn}) \cdot 5\text{MnO}_2 \cdot 4\text{H}_2\text{O}$ are the most common ones.

Also present in some bauxites are phosphate minerals, however, these are present in minor amounts, as the occurrence of phosphorous minerals in bauxite is quite rare. Gomes (1993) explained that the average P_2O_5 content in all the world bauxites and bauxitic clays investigated ranges from 0.4 to 0.6 %. Apatite and vivianite are two of the most common minerals reported in bauxite. Also represented are crandallite, francolite and evansite the latter minerals are known to be epigenetic.

Additionally, accessory minerals and other impurities are found in bauxite. Most of these are minerals that are highly resistant to weathering and are found in the parent rock of the deposit. These accessory or secondary minerals include zircon, garnet, tourmaline, andalusite and kyanite. They may have been formed during or after the bauxite.

2.5 PHYSICAL CHARACTERISTICS OF BAUXITE

The occurrence of bauxite is wide and varied; this is manifested in its structure, texture and other physical properties. Bauxites which develop in karstic regions are dense, massive, earthy materials with close to no recognizable structural features. Many bauxites, however, demonstrate pisolitic or oolitic structure and in which the

pisolites are enclosed by compound and larger pisolites range in size from 1-2mm to over 2cm. It is also common to find bauxite showing layering with tabular form. More so, bauxite also shows brecciation, some occur as nodules with varying spongy textures. In the pisolites are concentric banding, these indicate the cyclic formation of the bauxite.

Some bauxites may retain structural and textural features of rocks which they originate from. Other deposits may contain water rounded particles ranging from sand sized to cobbles; a strong feature of transported bauxite. There are also bauxites with slump and other subsidence features, but, these are to be found in karstic types. Generally, fossils are not present in bauxites, but when they are found they tend to be of marine origins. Patterson et al. (1986) explained that fossils tend to have their original material replaced by bauxite minerals.

Bauxitic colours range quite widely. The most obvious and common bauxites are shades of red or brown. Description of bauxite has been accepted to be brick red, reddish brown, pinkish brown or various hues of brown. A low iron content yields colors that are gray, brownish gray, light gray or nearly white. Other colors have been described as violet, pink and yellow in some areas, bauxite has also shown shades of green. In other areas characterized by a rich organic matter the bauxite is nearly black. Notwithstanding the fact that most bauxites exist as unconsolidated earthy material, there are bauxites that also exist as huge, dense, hard rocks.

2.6 AGE OF BAUXITIC ROCKS AND BAUXITIZATION EVENTS

Bauxite has formed intermittently throughout most of the period of geologic history from the Precambrian to present (Kogel, 2006) and more intensely during certain periods than others (Patterson et al., 1986). Most geologist have stayed cleared from putting an exact time on the initial formation except for Bárdossy (1982), who believes that the oldest known bauxites are about 3100 Ma; referring to slightly metamorphosed lateritic bauxites located in Swaziland, South Africa.

On the other hand, (Patterson et al., 1986) explained that the oldest known deposits are to be found in the East Sayan Mountains of the former U.S.S.R. Major bauxite deposits have been formed during the Lower Carboniferous, but only few deposits were formed during the Permian, Triassic and Jurassic. Gow (1993) explained that structural and geomorphological evidence indicate that high laterization which resulted in bauxitization in West Africa, India and Australia started in the Upper Cretaceous and reached its peak in the Paleocene and Eocene. The Late

Proterozoic to Early Cambrian resulted in the first karstic bauxite deposit but it was not until the Devonian that this type was formed in enormous and economic quantity, in the Ural Mountains (Gow, 1993). Records show that more karst-type deposit was formed during the Carboniferous in China, however, it was in the Miocene and Pliocene that large quantities of karst bauxite were formed in Jamaica and the rest of the Caribbean.

The youngest karst-type bauxite is found on elevated coral reefs in Pacific islands (Patterson et al., 1986). Approximately three-fourths of the world's bauxite resources occur in relatively young deposits (Kogel, 2006). Additionally, a vast majority of these occurrences developed in the late Tertiary and continue throughout the Quaternary to very recent times. The conditions throughout the Tertiary were extremely favorable to bauxitization and as such widespread laterization resulted in the formation of high-grade, large deposits.

2.7. CLASSIFICATION OF BAUXITIC DEPOSITS

Generally, it is accepted that bauxite is classified according to the bedrock on which it is constituted. However, Bárdossy (1982) explained that classifying bauxite depends less on host rock but more on its depositional features. As a result, there are three basic types of bauxitic deposits: i) lateritic bauxite deposit, produced by *in situ* tropical weathering and underlain by aluminosilicate or other rocks; ii) karstic deposit, covers uneven, karstified surface of limestone and dolomites, and iii) tichwin-type deposit, overlies unconformably the surface of different aluminosilicate rocks but shows no direct genetic relation with them; it is said their material was transported from elsewhere. This study will focus on the two major types that developed on the host rocks.

Both lateritic and karst bauxites are formed by the desilication of ferrallitic soils; the product of pedogenic processes under weathering conditions which result in alumina concentration. Shellmann (1975) modified the classification of bauxite deposits into a two-fold model replacing the term "laterite" with "silicate" and "karst" with "carbonate", this classification he themed "laterite-karst or silicate-carbonate" classification. The basis for his idea was, that all silicate bauxites formed by lateritic weathering of siliceous rocks and all carbonate bauxite deposits are associated with limestone or dolomite (Patterson et al., 1986). This classification is not without skepticism, Lyew Ayee (1986), looking at bauxites in Jamaica explained that karstic bauxite demonstrates a volcanic source for the most part. Over 92% of karst bauxite deposits

are formed in tectonically active settings which are active island arc settings within tropical areas (see table 1). Therefore, it is likely that the bauxite is a combination of volcanic parent material and carbonate rocks. On the other hand, lateritic bauxites derived from a variety of parent materials and formed in a variety of paleogeographic settings (continental platforms).

2.8 GENESIS OF BAUXITE

Bauxite and laterite are products of weathering from one or many types of rocks or their weathered derivatives. Rocks that are generally or moderately high in alumina content and have a relatively large percentage of soluble constituents are predisposed to laterization and bauxitization.

Limestone is known to be an important source rock for bauxitization coupled with other geological and environmental conditions. These factors play a significant role in the genesis of bauxite; the composition, level and pH of ground water, topographic relief, and climatic conditions such as rainfall and temperature are heavy influences on bauxitization.

Bauxitization and laterization are neither limited to areas that are predominantly limestone nor predisposed to it. Bauxitization tends to take place in igneous and metamorphic environments, also. Bauxites have been developed on syenites, diorite and granites and also on metamorphic volcanic sediments, as those in Malaya, Guiana, and the Netherland Antilles (Harder, 1952). Laterization and bauxitization have been evidenced on nepheline syenites and phonolites, arkose, slate and phyllite. Therefore, bauxitization is a process that does not discriminate against source rocks but rather depends heavily on surrounding geological conditions. An environment that is conducive to bauxitization is one which has all the factors outlined above.

2.8.1 LATERITIC BAUXITE

Lateritic bauxites make up 85% of the world's total deposit (Bárdossy, 1982). Laterites which result in bauxitization are formed from the leaching of minerals rich in alumina from igneous, metamorphic and sedimentary rocks. The laterites usually occur or located near residual soils. Initial products of weathering are essentially kaolinized rocks called saprolites. There is a wetting and drying process which is commonly confined to old peneplains in warm, humid climatic regions.

Lateritic deposits occur mostly as blanket deposits, this due to the fact that they occur near or at the surface and consists of a flat-lying layer of variable thickness extent. This type of deposit is residual and very high in iron, yielding a rusty-red appearance. Lateritic deposits also occur as discontinuous beds and lenses interstratified in sedimentary or igneous rocks or along contacts between igneous or metamorphic or younger rocks. The interlayer deposits of laterites are chiefly remnants of old residual blanket deposits (Patterson et al., 1986) covered by younger rocks.

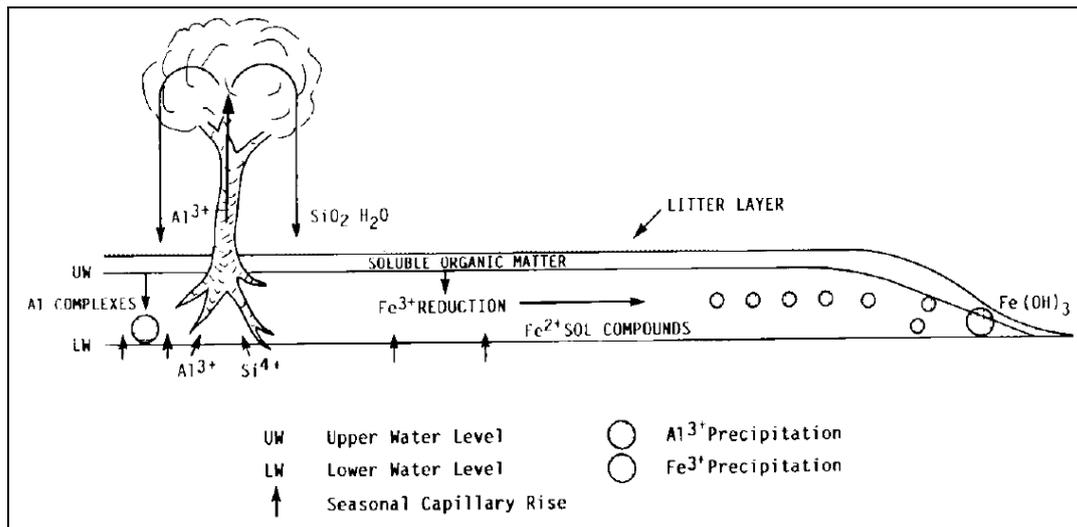


Figure 2 Geochemical evolution of laterite bauxitic soils (Gow, 1993).

Laterites consist mainly of immobilized minerals of quartz and oxides of titanium, zircon, iron, tin, aluminum and manganese which remain during weathering. Quartz is the most abundant relic mineral from parent rock; the iron oxides are derived from mafic igneous rocks and other iron-rich rocks. The order of mineral stability is the reverse order of mineral crystallization, the felsic rocks composed mainly of tectosilicates which have a greater resistance to weathering than mafic rocks which are rich in layered silicates.

2.8.2 KARST BAUXITE

Karst generated bauxite are hosted in carbonate rocks and is the result of weathering processes which lead to ferrallitization of aluminosilicate residue derived from the dissolution of limestone, volcanic tuffs, or alluvial material from adjacent formations. There is usually an unconformity or at least a disconformity between the deposit and the bedrock. Approximately 14 percent of the world's bauxite supply is karst bauxite (Bárdossy, 1982). There are about five different subtypes of karst bauxite, figure 3 below illustrates.

Karst bauxite formation tends to involve one or several reworkings of the primary weathering products which makes it very difficult to ascertain the parent rock. Therefore, there has been much speculation about its genesis. However, chemical and physical conditions play a very important role in the formation and preservation of karstic bauxite. Acidic conditions promote carbonate dissolution which alters limestone and dolomites and allow drainage which is critical to the removal of residual silicates.

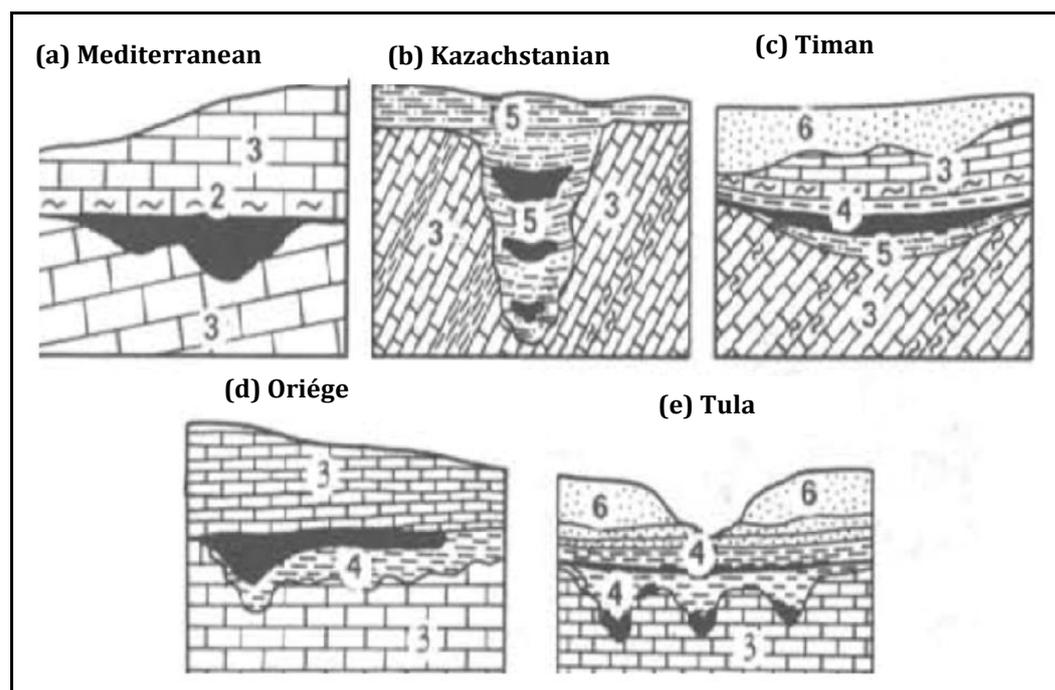


Figure 3 Showing the five types of karstic bauxite; [1] (Black) bauxite and bauxitic clay; [2] Marl; [3] Limestone or dolostone; [4] Clay or claystone; [5] Sandy clay; and [6] Sand. (Bárdossy, 1982).

The increased carbon dioxide (CO_2) in solution helps to liberate Ca^{2+} ions which encourage the hydrolysis of silicates. This desilication process results when the layered lattices are broken and organo-metallic complexes of iron and aluminum are precipitated. Residual ferraltic metals are transported during periods of rainfall and accumulated as fillings, pockets or lensoid bodies in sinkholes, cavities and grooves of karst topography (figure 3). Nearly all deposits are partly red or are separated from the underlying strata by zones of red clay or other fine-grained rock, referred to as terra rossa.

3 GEOLOGICAL CHARACTERIZATION OF PORTUGUESE AND JAMAICAN BAUXITIC ROCKS

3.1 GEOLOGY OF PORTUGUESE BAUXITE ROCKS

Portugal hosts one of the smallest bauxite deposits in the entire Europe where conditions have been favorable for bauxitic formation. This deposit is geologically similar to the karst bauxite across the European continent, which belongs to the Mediterranean bauxite belt that follows the Alpine orogen belt.

This belt links bauxite regions of similar geologic setting and history. It begins in Spain and ends in Turkey, and the bauxite represents a common paleographic and paleoclimatic framework (Gomes, 1996). The highlands of Cantanhede in the region of the Beira Litoral zone, is home to Portugal's small bauxite deposit (**Fig. 4**). The Andorinha area favors the formation of the Dogger carbonate which results in karstification thereby developing the karst type lateritic-rich bauxitic clay of the region. The karst limestone and oolitic micrites give rise to a terrigenous hyperaluminous clay deposit. It is theorized that karst formation in the Cantanhede region started in the Late Cretaceous and Tertiary however, it was the climate and vegetation which had great effect in clay formation. Marco et al. (1994) explain that at the end of the Pliocene a marine transgression covered the plateau, then, during the Quaternary eustatic changes in the sea level led to erosion and reactivated the karst.

The karst landscape of the Cantanhede plateau is made up by soils and detrital deposits. The karst of the region has shown geological evolution over time. This is so as the complex phase of karst development took place in the Jurassic; however, during the Lower Cretaceous, the entire area was buried. The tropical and sub-tropical climates during the Upper Cretaceous led to weathering and exhumation of paleolandforms and new karst development accompanied with the heaping of red sands in the karst landforms (Marco et al., 1994). The Pliocene resulted in a transgressive phase exposing detrital deposits and also more burial of the karst landscape.

The geological map with the distribution of the Cretaceous sedimentary deposits (limestones) from the Cantanhede to Leiria and Nazaré region is shown in Figure 4. The bauxitic rocks in Portugal are described by several authors (Gomes, 1991) it is located close to Andorinha village and is marked by an arrow (**Fig 4**).

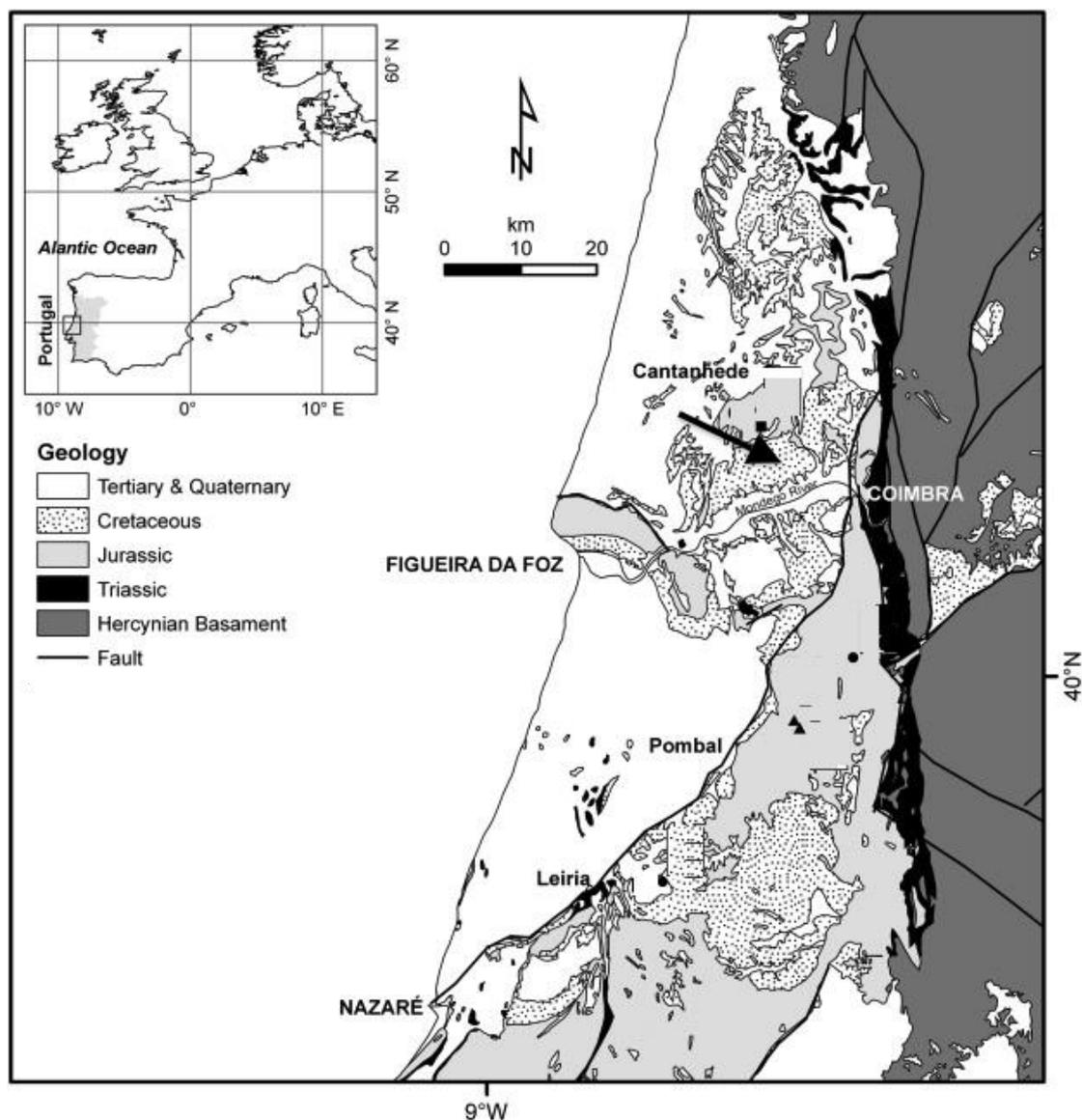


Figure 4 Geological map of the Cretaceous limestones deposits from Cantanhede to Leiria region. Bauxite deposit from Andorinha is marked by an arrow (De Almeida, 1990).

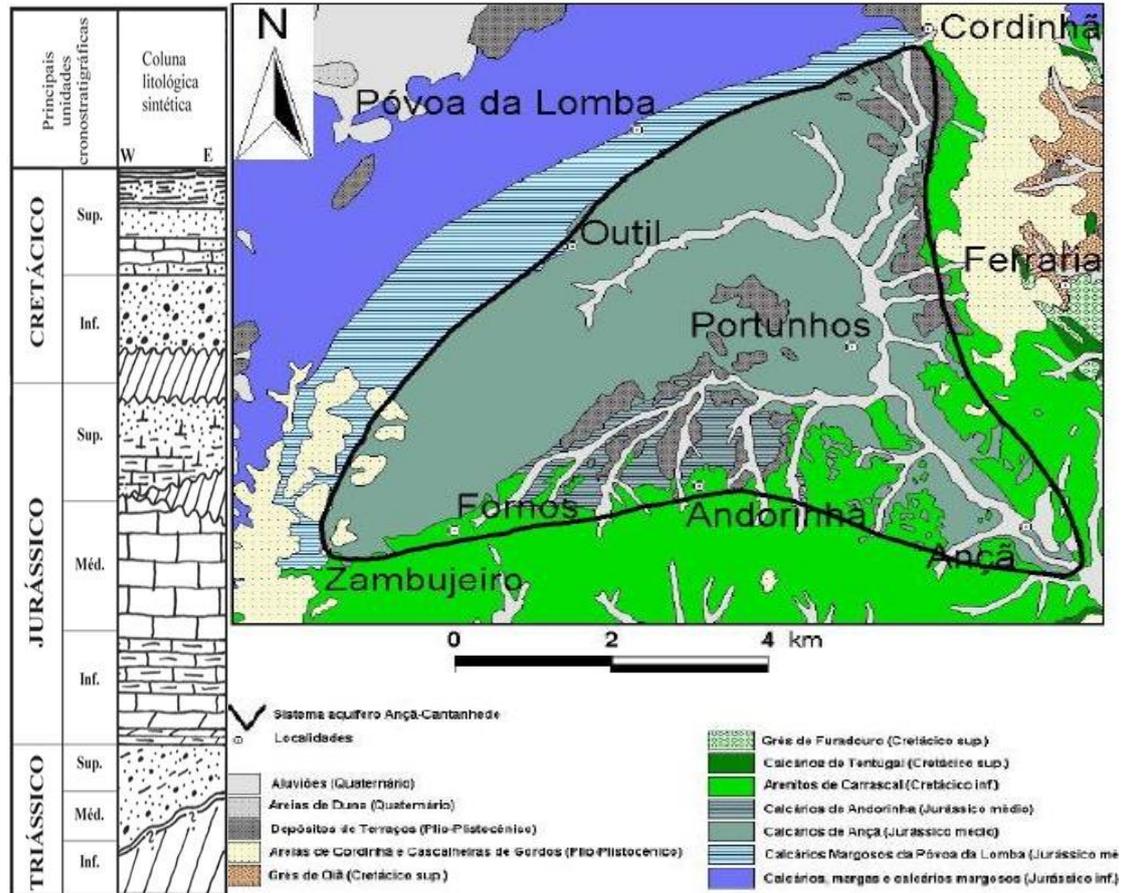


Figure 5 Lithological column and geological map; illustrating the location of the occurrence of the hyperaluminous clay of Andorinha, Portugal (Gomes 1991; Geological map, 1:50.000, Cantanhede sheet; Almeida et al. 2000)

As mentioned previously, the bauxitic facies of the Andorinha area occurs as a hyperaluminous clay with pisolitic, nodular, argillaceous, clayey and breccia-like facies running along a tectonic structural line in a E-W direction and is approximately 2.9 kilometers in length (see map). This structural line, according to Gomes (1991), is an area where dissolution and karstification on the oolitic-pisolitic limestone was favored. Soares (1966) considered this direction as the attitude of the axial plane of a Cretaceous broad anticline. He further went on to describe the folding as being superimposed by the Jurassic syncline with an axial plane approximately NNW-SSE.

The sinkholes of Andorinha are of shallow depth measuring up to 10 meters in some areas and a little over 10 meters approaching westward. The shallowness of the sinkholes is indicative of the position of the water table. The water table tends to appear at deeper depths in the west than areas in the east, giving rise to greater bauxitization.

On top of the hyperaluminous clay deposits of Andorinha occurs as a coarse and angular to sub-angular quartz sand with varying colors indicating a strong hematite presence, and bearing little clay matrix. The clay matrix is rich in kaolinite. Above this sand is a layer of sandstone, identified locally as the “grés Belasiano”, which constitutes three distinct members (lower C_a^2 , middle C_b^2 and upper C_c^2) and records a thickness of approximately 100 meters, overall (Gomes et al., 1991; Soares, 1966).

The lower C_a^2 member is poorly sorted, angular to sub-angular and has a very coarse texture, according to Gomes (1996) this is due to the quartz grains and is accompanied by a strong presence of kaolinized feldspar grains with idiomorphic forms. The lower deposit is approximately 5-10 meters thick. In some areas across Andorinha, the base of the lower C_a^2 member is heavily mixed with the bauxitic clay.

The middle C_b^2 member contains a kaolinitic matrix and shows a variable degree of alteration. Also, there are several colors that are associated with the clay matrix: white, pink, purple, violet, rusty-brown or red. The sandstone is moderately to poorly sorted and the sand grains and pebbles are angular to sub-angular. The sandstone also shows evidence of fluvial transport; Gomes (1991) explained that the transport was over a very short distance and likely came from a granitic source in the east at the location of the Hesperic Massif that have been subjected to strong weathering. This took place towards the end of the Jurassic or closer to the beginning of the Cretaceous period giving rise to the laterite profiles in the Andorinha region.

The C_c^2 or upper member is characterized by a coarse to medium and sub-angular to sub-rounded quartz sand that is poor in clay matrix and feldspar (Gomes, 1991). This member has been described in literature to have evidence of marine influence towards the top, whilst the lower and middle members illustrate some characteristics of fluvial transport.

3.1.1 GENESIS OF PORTUGUESE BAUXITE

Bauxite deposits in Andorinha show a variety of facies and as such several genetic approaches can be used to describe its development. However, the best explanation for the development of the deposit has been put forward by Gomes (1991) who theorized that the argillaceous bauxite facies were derived, most probably, from ferraltic profiles developed on granitic rocks of the Hesperic Massif, in the proximal east. He further lamented that the climatic conditions (moist and warm sub-tropical to tropical) that existed in the Upper Jurassic or Early Cretaceous played a crucial role in the weathering process.

During the same period, the ferraltic profiles underwent further disintegration (kaolinite and argillaceous top layers) and the materials were taken up and transported over a short distance by nearby streams. The transported material (mud and sand) were deposited and accumulated into depressions which are located in the tectonically controlled lower-lying littoral platform, which has been formed by the Dogger limestone. The colloidal suspension was enriched with Al, Si, Fe, P, Ti, and S; the mixture was also rich in organic matter, he further explained.

In the same geological period, more weathered materials were eroded, transported and deposited in karst sinks by high velocity streams, on top of finer sediments. These materials were coarser and represent weathered particles from the mantle layer. In later periods the deposited materials underwent "*in situ*" weathering and bauxitization (Gomes, 1996), especially in the areas where the water table was at reasonable depth and drainage was good. The nodular and brecciated facies were most likely formed by the periodic wetting and desiccation processes that enable the minerals to be precipitated after remobilization. Gomes (1996) also noted that the presence of sedimentary structures and slip planes in colloidal materials indicate that the bauxitization process began at the same time as the formation of the karst.

It is also highlighted in Gomes' (1991, 1996) works that the karst bauxite of Andorinha share many similarities with the karst bauxite of Provence, France and that the genetic approaches that have been used to explain the formation in Provence, can also be used to explain the formation locally. The autochthonous theory which was proposed by de Lapparent (1930), explains that the bauxitic material is the "*in situ*" weathering of clay residues freed by the dissolution of the carbonate floor rock. The allochthonous theory (proposed by Roch, 1956 and Nicholas, 1969) is basically the same theory proposed by Gomes that, the bauxite

deposit develops from the erosion of surrounding ferraltic profiles, transported by wind and water and deposited in karst depression. The other two theories the mixed and the modified autochthonous consider the transport and deposition of little weathered materials in karst depression with subsequent 'in situ' weathering (Gomes, 1996).

3.2 GEOLOGY OF BAUXITE ROCKS FROM JAMAICA

Jamaica lies on the north-west rim of the Caribbean plate, which has moved east-north-easterly about 1400 km since the late Eocene (38 m.y) by transform motion with respect to North America (Green, 1977). It is the third largest island in the Greater Antilles with an area of 11,425 square kilometers; it is an emergent of the Nicaraguan Rise, which is a broad, dominantly submerged belt of crustal thickening extending from Honduras to Jamaica (Donovan, 1994). The island therefore lies on the junction between two plates (North American and South American); it is separated from the North American Plate by the east-west trending of the Cayman Trench.

Jamaica lies on the emergent part of the northeast-trending Nicaraguan Rise, a broad submerged belt of intermediate crustal thickness (~22 km) that extends from Central America to the west of Hispaniola (Simpson, 1989). Figure 6 illustrates the geological setting of Jamaica in the Caribbean region. Geologically, Jamaica consists mainly of a cretaceous volcano-plutonic arc sequence that is unconformably overlain by Cenozoic limestones, which form about 70% of the island.

The cretaceous sequence, which is exposed in a series of inliers, is typical of island-arc settings having blueschist metamorphism and serpentized ultramafics, particularly in the Blue Mountain Inlier in the east along with calc alkaline igneous rocks and volcanoclastics and arc-related sedimentary basins (Grippi et al., 1980). The island has a strong east-west trending anticlinal structure that is intensified by intense block-faulting. The principal geomorphological units of Jamaica are shown in Figure 7.

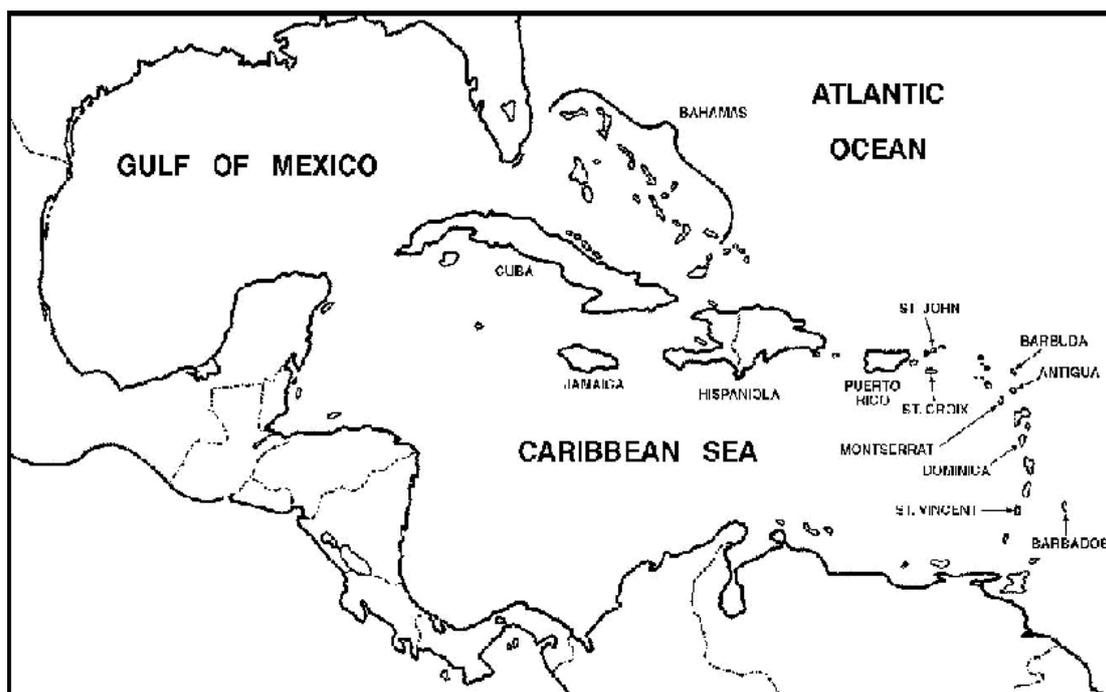


Figure 6 The regional setting of Jamaica (amended from Jackson, 1994).

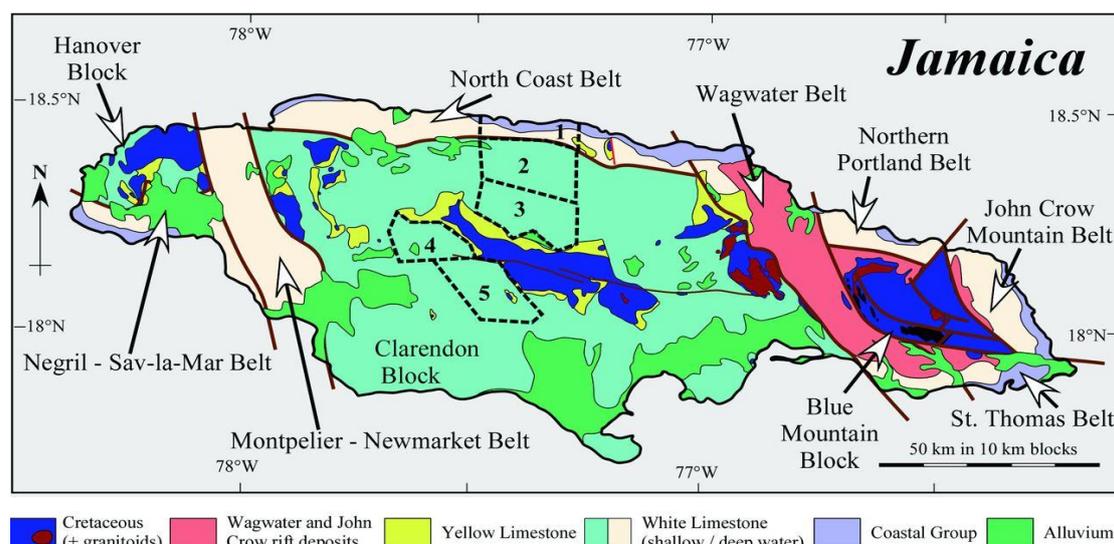


Figure 7 Geological map of Jamaica (geoscienceworld.org).

Jamaica is host to one of the world's largest source of commercial high-grade bauxite. The deposits were discovered in 1942, as a result of geochemical tests carried out on soils to determine the cause in the lack of fertility in several vast farming areas. Jamaican bauxite occurs as pockets or infill of karst sinkholes, caves, and pipes or blankets on the karst surface developed in the late Eocene-Miocene on White Limestones. Robinson (1975) indicates that the bauxite in Jamaica falls within the terra rossa, limestone, or Mediterranean group. Approximately two thirds of the land surface of Jamaica is occupied by Tertiary Limestones; the Coastal Limestone, Yellow Limestone and the White Limestone group. The White Limestone Group is the

most important stratigraphic succession and accounts for the development of bauxite and bauxitic clays.

Jamaica's bauxite occurs in a series of deposits mainly across the middle of the island, east to west. The largest deposits are located in the parishes of St. Ann, Manchester, St. Elizabeth, and Trelawny, with smaller deposits in Clarendon, St. Catherine and St. James (**fig. 8**). The bauxite is found in the highlands, from about 1,000 feet above sea level, with its best grades found between 1000ft and 3000ft, lying in the pockets of the limestone.

Most of Jamaica's bauxite is red or reddish-brown; however, localized variations in color have been observed ranging from white, yellow, light brown, brown, red, dark red to black (Anderson, 1976). The bauxite shows no overburden, contrary to deposits in many other countries, the ore is located upon the surface of tertiary limestones. The economically exploitable deposits are found on the White Limestone series whilst other clays and the Yellow Limestone group indicates marginal to substantial deposits of low to very low grades.

The general trend is roughly NW-SE and is localized by a block fault widening in the SE direction (Hall, 1956). In close geographic association with these deposits are those controlled by the step faulting of the St. Elizabeth region starting from Spur Tree and extending along the axis of these faults to Alligator Pond and Santa Cruz. The third major belt extends from Mount Brasso through the Claremont-Moneague basin in the parish of St. Ann. The deposits in this area tend to be discontinuous and in general patchy. There are minor occurrences of ore in the karst area of Trelawny, and in the limestone area at the foot of Mount Diablo. Figure 8 illustrates the geographical distribution of bauxite deposit across Jamaica.

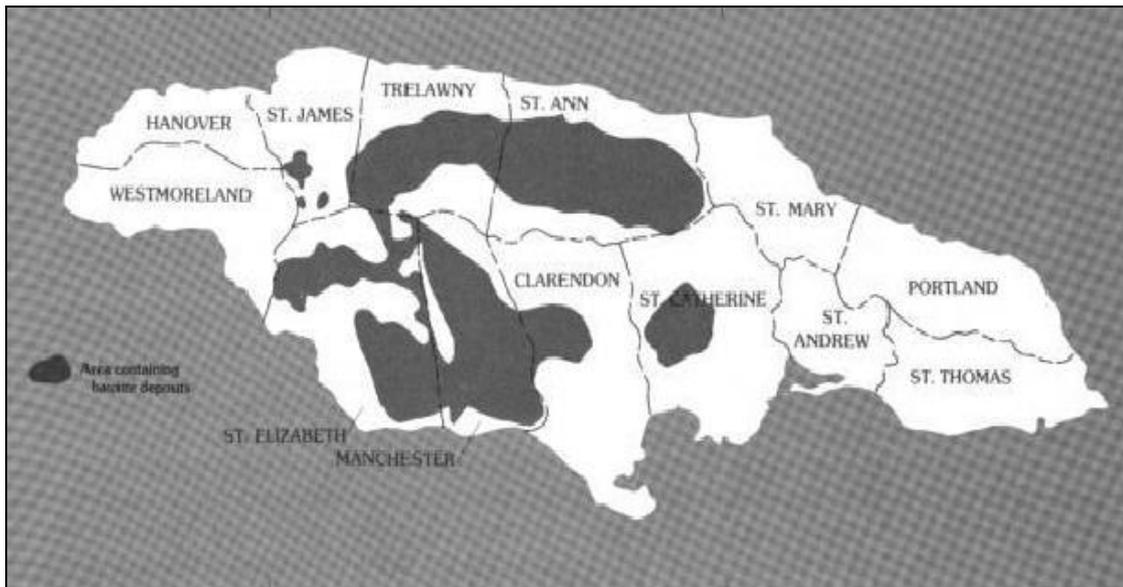


Figure 8 A map of Jamaica showing areas of large bauxite deposits (adapted from Patterson, et al., 1985).



Figure 9 Bauxite deposit in an open mine St. Ann, Jamaica (Jamaica Observer, 2013).

3.2.1 MORPHOLOGY OF JAMAICAN BAUXITE

Zans (1954, pp. 317-318) explained that bauxite is only associated with the White Limestone Formation in Jamaica. On the other hand, a few other geologists have explained the possibility of the bauxite being developed in situ from all Tertiary Limestone (Hill, 1955; Sinclair, 1967) and then there is the association made with volcanic ash (Comer, 1984; Lew Ayee, 1986). However, the most widely accepted theory is that the bauxite is directly associated with the White Limestone.

The White Limestone Formation is a dominant member of the Tertiary Limestone group that is of middle to upper Eocene age. They are of succeeding beds which are crystalline or compact and is formed by hard compact dolomites and dolomitic limestones with dichotomies. The lowest horizon is the one which is associated in most outcrops with bauxite and terra rossa deposits (Zans, 1954). The deposits, however, are small owing to the narrowness of the solution hollows excavated in extremely hard, compacted rocks. Lithologically, this series consists of extremely pure white limestone, often nodular or chalky and brecciated along fault zones (Hill, 1975 and Zans, 1954). It is this series which carries the rich bauxite deposits in Jamaica, most of them being associated in particular with beds of Upper Eocene age. Beds in the western parts of the island shows an unconformity by less compacted Upper Oligocene Limestone, which indicates a break in sedimentation during Lower and Middle Oligocene times, which may have involved the first stage of karstification (Zans, 1954). The lowest part of the succeeding Upper Oligocene contains a typical Antiguan fauna of *Lepidocyclina* and again carries terra rossa and bauxite.

The older Yellow Limestone and the younger Coastal Limestone are both members of the Tertiary Limestone Group which are overlain by bauxitic material that is not so well developed, erratic and lacks commercial quality.

The major structural feature is an anticline with axis of approximately NW-SE trend. The Pre-cretaceous basement complex was part of a stable land mass that suffered subsidence, and on which were deposited unconformably the younger sediments which lap out from the ancient core (Hill, 1958). A rather complex fault pattern has been superimposed on this during the Miocene deformation. It is this orogeny that determined the present physiographic features of the island. The major faults trend from E-W and from NW-SE. These faults determine the present coast-lines of the island. Across the central regions where the accumulation of limestone is thickest

there are a series of subsidiary N-S faults (**Fig. 7**). The intense faulting is the result of the adjustments of the limestone covering to the tectonic forces. The uplift and shattering of the rocks resulted in the development of the present karst topography, the fault and fracture zones acting as channels for the subsurface drainage pattern.

Jamaican bauxite shows a clear cut junction between the limestone and bauxite itself. Anderson (1975) explains that there is a sharp demarcation between the red bauxite and the White Limestone. However, this is not the case with the deposits in some localities, as Anderson (1975) further explains that there is an interruption where a thin phosphatic band sharply cuts the bauxite and limestone. Jamaican bauxites show no internal structural characteristics, instead, it is characterized by a deep uniform dark-red with variations from off-white to yellow. The thickness of the bauxite covering the limestone is extremely variable and ranges from 2 or 4 feet to as much as 60 and over 100 feet in some areas.



Figure 10 Yellow orange bauxite in the parish of St. Elizabeth, Jamaica (Jamaica Observer, 2010).

The bauxitic deposits on the upper surface of the limestone demonstrate little relationship to the underlying limestone surface. The general morphology of the individual deposits across the Jamaica show a variation in continuous trend from pipe-like masses through long tabular shapes to the blanket types in troughs up to twenty miles long and ten miles wide (Hill, 1958).

The deposit tends to occupy the bottom of karsts hollows that are not connected to the each other. The deposits are not exclusive to hollows and flat surfaces; they are

formed in domes, or heaped into mounds covering the peaks between hollows in the limestone. An example of this is the case can be located in the parish of Manchester, southern Jamaica.

Furthermore, the bauxitic rocks in some areas are overlain by younger sediments of weathered and reconstituted limestone, having a 'chalky marl' appearance. Other deposits have rounded limestone boulders and pebbles overlying the deep low grade deposit. Anderson (1975) explains that this alluvial deposit is found at elevations of 500 feet above sea level, and was probably formed by an intermittent stream emanating from higher ground and subjected to periodic floods. It is common to find thick-layered gravel-like sediments on top of bauxite deposits in areas that have been drained by rivers.

3.2.2 GENESIS OF JAMAICAN BAUXITE

There are three hypotheses that have been put forward regarding the origin of Jamaican bauxites; the "alluvial hypothesis" (Zans, 1959; Burns, 1961), the "residual limestone" hypothesis (Hill, 1955; Sinclair, 1967) and the "volcanic ash" hypothesis (Comer, 1984; Lyew Ayee, 1986).

Zans (1954) outlines the formation for Jamaican bauxite via the "alluvial hypothesis". He stated that eroded material from the underlying Cretaceous volcanic rocks was transported into limestone areas via cavern systems and karst streams thereby depositing suitable alumina-rich materials in and on the Tertiary Limestones. Weathering of the Limestone was exacerbated by prevailing climatic conditions within the Eocene- Miocene period and this took place high above the water table which resulted in bauxitization. Robinson (1975) supported this theory explaining that in the Miocene to Pliocene experienced a stages uplift solution of limestone which created the possible source for the superficial deposits in the limestone regions. He further suggested that the drainage characteristics were not greatly modified until the Late Pliocene, when faulting and warping caused local impeding of the subsurface karst drainage. This resulted in the ponding of sediments and also the development of poljes which were later accompanied by the deposition of Cretaceous volcanic detritus on the White Limestone.

The "residual hypothesis" was postulated by Hill (1959) and Sinclair (1967); both men explained that Jamaican bauxite is formed by in situ weathering of limestone. The hypothesis is based on the theory that the thickness of limestone correlates to the volume of bauxite being deposited in karst regions. It was estimated by Sinclair

(1967) that limestone ranging from 750 ft to at least 3000 ft in thickness was removed, thus satisfying the residual requirements. These figures were later agreed to be reasonable and could be achieved by solution of the limestone in Miocene times (Robinson, 1975). Smith (1971) explained that his calculations demonstrated that the solution rates of Jamaican limestones in that period were high enough to have removed well over 780 ft required by the residual hypothesis within the last six million years.

Comer and Lew Ayee (1984 and 1986) maintain that Jamaican bauxite developed as a result of weathering of volcanic ash. They postulated that given Jamaica's geological history and its bauxite has been a result of volcanic ash being laid down during the Cenozoic was subjected to weathering in the Miocene which resulted in bauxitization. This is after several geochemical analyses have indicated the presence of heavy metals that were unlikely to be found in the Tertiary Limes tones which support the initial two theories.

MILLIONS OF YEARS	PERIOD		REMARK	EVENTS IN CENTRAL JAMAICA	BAUXITE DEVELOPMENT
5	PLIOCENE		Younger rocks involved in major fault movements.	Period of Maximum uplift, faulting and warping	Bauxite Terra Rosa and Lateritic soils of various kinds
	PLIESTOCENE				
10	MIOCENE	UPPER	Appearance of coarse clastic in Coastal Group Sediments	General Emergence	Period of high grade bauxite formation
		MIDDLE	<ul style="list-style-type: none"> • Youngest definite Newport Limestone 		
		LOWER	<ul style="list-style-type: none"> • Upper Newport Limestone 		
20	OLIGOCENE	LOWER	Lower Newport Limestones Local discordance	Gradual southward tilting of Clarendon Block	Bauxites of St. Ann and Trewlany may date, in part, from this time.
		UPPER	Walderton and Brown Town limestones.		
25	OLIGOCENE	UPPER		Possible Emergence of Northern Central Jamaica	
30		LOWER		Clarendon Block submerged as Shallow Banks.	

Table 3 The possible sequence of events governing the formation of bauxite in Jamaica (Robinson, 1971)

4 FIELD WORK, MATERIALS AND ANALYTICAL TECHNIQUES

4.1 STRATEGY AND MANAGEMENT OF PROJECT

The data gathering process was done in three phases, which was carried out over a period of six months.

Phase I: involves the planning and organization stage. During this phase various literatures were consulted, inclusive but not excluding journals, periodicals, books, and technical reports. Also, maps (geological and topographic) were consulted.

Phase II: (i) involves field sampling exercises, which included field work, inclusive of reconnaissance geology, and site visitation collection; (ii) preparation and analyzing of samples collected in the field utilizing X-ray diffraction (XRD), Infrared Spectroscopy (IR), X-ray fluorescence (XRF), granulometry and mineral optics.

Phase III: involves the revisiting of the field and collecting additional samples (rocks and soil). Correlating the data and making final analyses and also the writing up and editing of the dissertation.

4.2 FIELDWORK AND GEOLOGICAL OUTCROPS DESCRIPTION

Representative samples were taken from a few communities within a 10-15 km radius in Andorinha where outcrops exist. These were good samples of bauxitic rocks, sediments, and limestone on which the bauxite makes contact. Soil and sediment samples were collected at surface level; bauxitic rocks were collected in an area outside Outíl, a community in Andorinha. The limestone was collected from a strip mine with layers of exposed bauxite resting in pipes or cavities.

A rock hammer was used to break large consolidated rocks into smaller fragments that were then placed into small plastic bags and labeled with a sample number and the location where it was taken from. The samples collected were also marked on the field map and were used in future reference. These points were later transferred to Google Maps and the actual areas where samples were collected were identified and pinned using the placemark tool, this is shown in the figure 11.

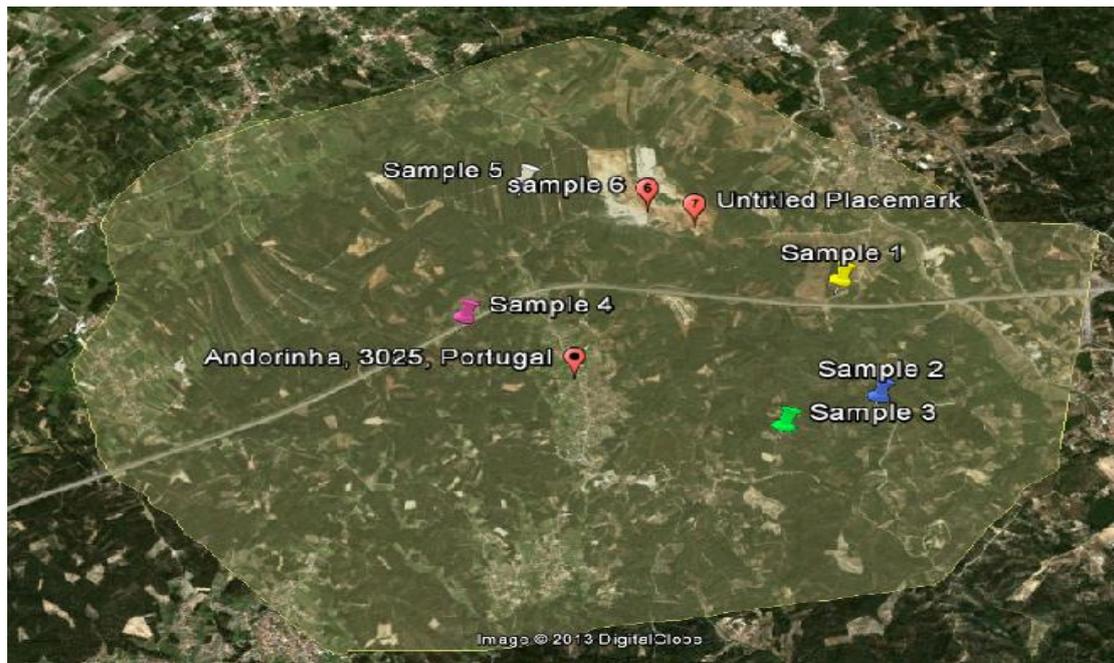


Figure 11 Location of samples collected from Outil and Andorinha village (using Google map)

The outcrop observed in the Outil open-pit mine (Fig.12a) show a karst-sinkhole morphology where the clays are accumulated.



Figure 12 Karst sinkhole with “hyperaluminous” clay deposit (a) in the Outil limestone open-pit mine (b), Portugal (Author, 2012).



Figure 13 The Belasiano sandstone (“Grés Belasiano”) afloriment (a and b) near the Andorinha village, Portugal (Author, 2012). The sandstone supported an intense bauxitization.

The area near to the Andorinha village is characterized by large forested density where few outcrops were identified. The outcrops show a red yellow color constituted mainly by kaolin (**Fig. 13**).

4.3 SAMPLING CHARACTERIZATION

Sample	Macroscopic Description
L1 S1	Hard, consolidated rock sample with banded-like layer. Deep red earthy brown with thin white layer. Red clay matrix. Particles crumble in hand when crushed.
L2 S2	Hard, consolidated rock sample. Deep purple color. Powdery white matrix layer about 2mm thick. Deep red bauxitic clay in grooves and crevices of rock.
L3 S3	Lightly weathered coarse-grained rock (carbonated sandstone) with heavy bauxitic clay inter-layers. Predominantly red but some purple color also present.
L4 S4 (Outil)	Hard reddish to yellowish-brown clay with some sandstone grains. Fine grained with limestone clasts and organic matter.
L5 S5	Fine grained unconsolidated to somewhat consolidated rock with fine texture. Yellowish-brown to off white with some organic matter.
L6 S6	Clay material; yellow brown to orange. Fine grained with organic content.

Table 4 Shows the macroscopic description of samples collected across the study area (Author, 2013).

4.4 SAMPLE PREPARATION

Representative samples collected in Andorinha were taken to the lab where they were air dried at room temperature. After 48 hours, the samples were carefully prepared for granulometric, mineralogical, and chemical analyses.

Soil samples were subjected to granulometric analysis to determine its grain-size distribution. The soils were mixed with a solution of distilled water and a weak base to release the small particles. Rock samples were cut into thin sections and polished for microscopic analysis.

The sediments from the heavily weathered bauxitic rock were separated where there was a sharp demarcation between red, white and yellow bands. The sediments were then crushed into a fine powder by a mortar and pestle. The red sediments were then analyzed by X-ray diffraction (XRD) whilst, the white and yellow powders were further treated with Br (Br) then compressed into pellets that were analyzed using infrared spectroscopy (FT-IR). The analyses were carried out to identify the mineralogy and other major chemical constituents of the bauxite to determine its source and overall composition.

4.5 SEDIMENTATION

Bulk samples of bauxite (approximately 50 grams) were added to distilled water in Atterberg cylinders for sedimentation analysis (Fig. 14). Distilled water was added for dispersion of clays.



Figure 14 Sedimentation of clays in Atterberg cylinders and extraction of clay suspension according with Stokes law (Author, 2013).

The mixture was shaken vigorously and then allowed to settle for a time period of 24 - 48 hrs. The $<2\mu\text{m}$ clay fractions were extracted according to Stokes law.

4.6 SAMPLES PREPARATION FOR X-RAY DIFFRACTION

The oriented clay specimens were prepared by pipetting and drying a clay suspension of the $<2\ \mu\text{m}$ fraction onto glass slides for XRD, whereas randomly oriented clay-aggregate specimens were prepared by the side loading method. Mounds were filled with finely grounded powder of bauxite and placed onto the holder (Fig. 15).

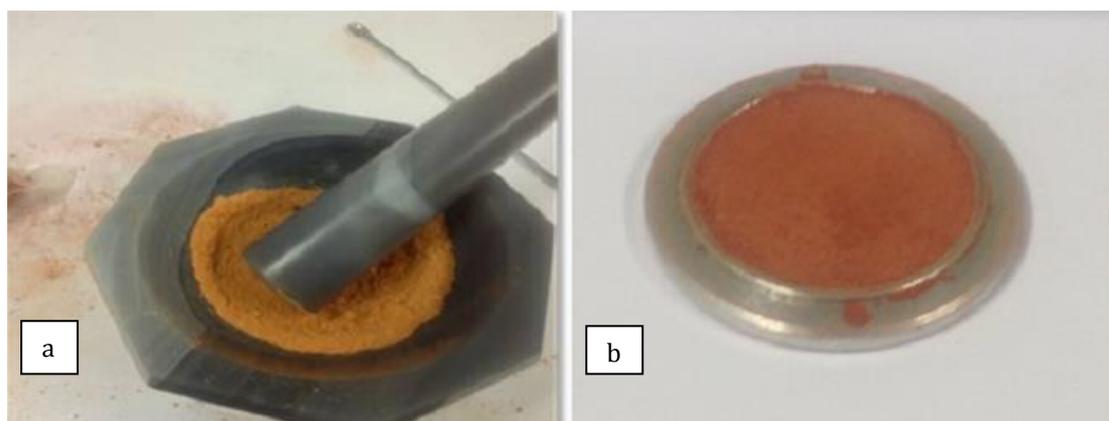


Figure 15 (a) Sample of bauxite well grounded in an agate mortar and, (b) showing red bauxite being mounted for X-ray analysis (Author, 2013).

4.7 SAMPLES PREPARATION FOR IR SPECTROSCOPY

The white veins located in rock samples were carefully and skillfully removed using a 10 cm small 'spatula'. The white crystals were grounded into a fine powder using a mortar and pestle. Approximately 20 mg of the finely grounded powder was mixed with KBr then placed in a metallic chamber where it was compressed using the over 100psi. This resulted into an extremely thin, almost completely transparent plastic-like pellet which was then placed into the FT-IR machine for approximately 1 minute to get an effective reading. The results were observed from a computer monitor that is attached to the equipment and further analyzed for the concentration of CO_3^{2-} and PO_4^{3-} .

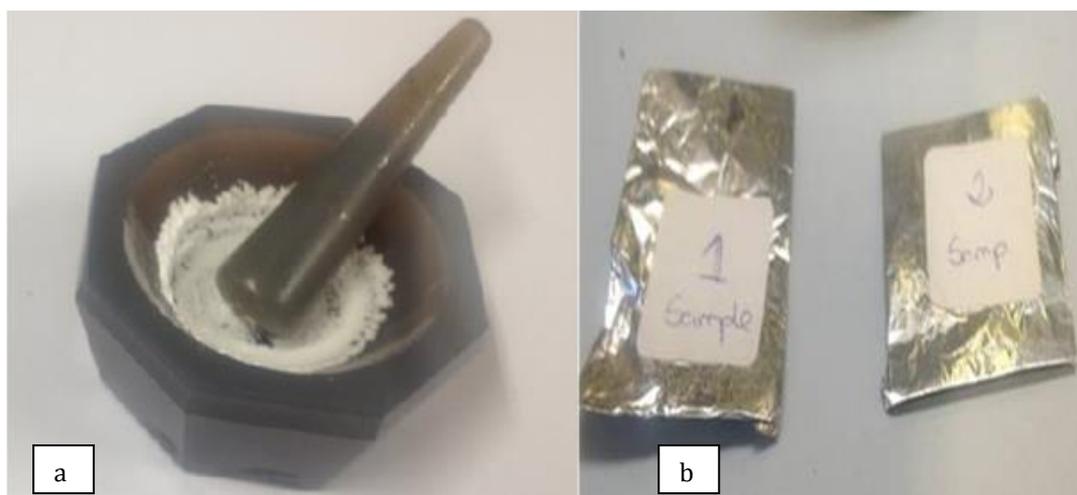


Figure 16 Shows the crystals extracted from white veins in the rocks being grounded into very fine powder and, (b) shows the samples being prepared and labeled for FT-IR analysis. (Author, 2013)

4.8. ANALYTICAL TECHNIQUES

4.8.1 X-RAY DIFFRACTION

X-rays powder diffraction is a powerful tool which allow to identify each mineral phase or for detailed determination of crystal structure and unit cell size. X-rays are electromagnetic waves with wavelengths between 0.02 Å and 100 Å (1 Å= 10⁻¹⁰ meters). The fact that X-rays have wavelengths similar to the size of atoms, they are very useful to explore within crystals. Also, the ability of X-rays to penetrate matter easily makes is suitable in mineralogical identification.

XRD patterns of oriented specimens were obtained using a Rigaku Geigerflex D/max. - C series automated diffraction system equipped with a graphite monochromator and Cu K α radiation. Samples were analyzed in the range 2 – 50 °2 θ , using a 1 σ divergence slit, a step increment of 0.05 °2 θ and a counting time of 5 s/step. XRD patterns of randomly oriented clay-aggregate fractions were obtained with a Rigaku Geigerflex diffractometer. CuK α radiation, a graphite monochromator, an automatic divergence slit and a 0.5-receiving slit were used. A step size of 0.05 °2 θ and a 5 second counting time were chosen to measure the intensities.

X-ray powder diffraction analyses were conducted in the XRD lab of DGAOT- FCUP. The scanning produces a series of peaks and troughs that were recorded by the connected computer. The X-ray intensity plotted against the 2 θ angle was further analyzed by calculating the angle (or d-spacing) using the Bragg's equation:

$$d = n\lambda / 2 \sin \theta$$

The values obtained were then used to identify the corresponding minerals observed by the peaks in the graph produced.

4.8.2. IR-SPECTROSCOPY

IR spectra in transmission mode were recorded in the range of 4000 - 400 cm^{-1} using a Bruker 510 DX FTIR spectrometer. The measurements of the absorption bands integrated intensity were made using the OMNIC software supplied by the Bruker Instrument. The pellet discs of 1.5 cm diameter were prepared by mixing 1 mg sample with 200 mg KBr and pressing at 14 kg/cm^2 . Prior to analysis, the pellets were heated overnight at 150 $^{\circ}\text{C}$ in order to remove any adsorbed water.

4.8.3. X-RAY FLUORESCENCE

Major and trace elements concentrations were analyzed by X-ray fluorescence (XRF) at the University of Aveiro. Seven samples of bauxite deposits were prepared following the fusion techniques (50:50 $\text{Li}_2\text{B}_4\text{O}_7$: LiBO_2) and ten drops of LiNO_3 and NH_3 were added to the crucible to make the sample more liquid. The crucible was placed into an oven at 1050 $^{\circ}\text{C}$ for major element analyses. Ten grams of the powdered bauxite samples were pressed into 40 mm diameter pellet for trace element analysis using a polymethacrylate binder that is dissolved in acetone. Both the glass disk and were analyzed on a Philips 2.4KW sequential spectrometer fitted with flow detectors, PX1, PE002, Ge111 crystals and LiF 2000. A previously prepared calibration curve was used to determine the concentration, which is derived from analyses of reference materials of USGS. The loss of ignition (LOI) of the bauxite samples were determined gravimetrically by roasting 0.8 g separate sample of the bauxite powders at 925 $^{\circ}\text{C}$ for 45 minutes.

5 MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF PORTUGUESE AND JAMAICAN BAUXITIC ROCKS

5.1 MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF PORTUGUESE BAUXITIC ROCKS

The bauxitic clays of (Andorinha) Portugal show similar mineralogical characteristics to the karst-type bauxites of southern Europe (Gomes, 1991; Gomes et al., 1996). The clay matrices exhibit strong color variations occurring in brick-red, pink, purple, yellow and white.

Kaolinite is the dominant clay mineral found in the bauxitic clay of Portugal and shows strong association to hematite, goethite, gibbsite, bohemite and anatase. In some of the clay samples located across the Andorinha region; in the western section, where the bauxitic clay is cut by narrow white veinlets and in some other areas, nodules of irregular dispersion shows the rare association of the strontium (Sr²⁺) and aluminum (Al) phosphate-sulphate (i.e. svanbergite). Also heavy minerals such as rutile and pyrolusite are described, as well as akagenite and hematite (Gomes et al., 1996).

5.1.1 MINERALOGY

A total of seven samples selected for mineralogical analysis were collected from several areas (described in chapter 3) across Andorinha. These samples were subjected to x-ray and infrared analysis along with microscopic analysis.

5.1.2 OPTICAL MICROSCOPY

Thin sections corresponding to limestones from Outil quarry were studied by optical microscopy in transmission mode. The limestone exhibits a micritic cement and fossilized species of Foraminefera.

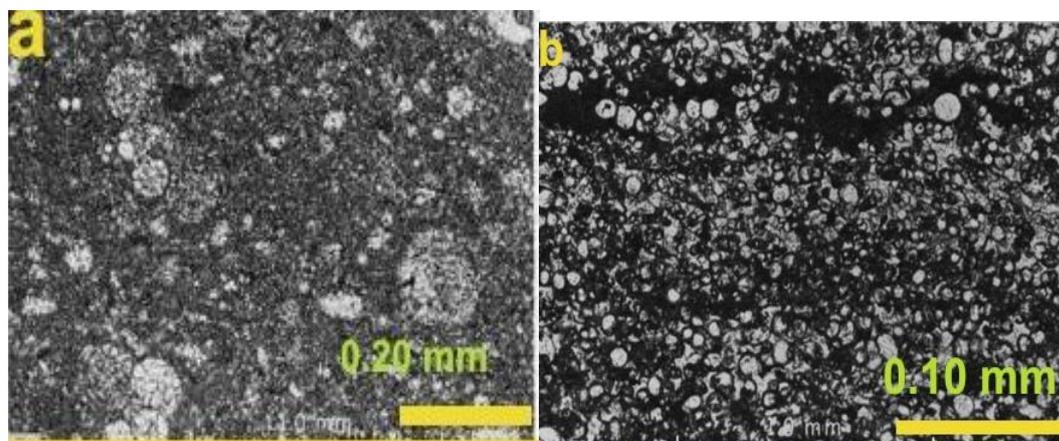
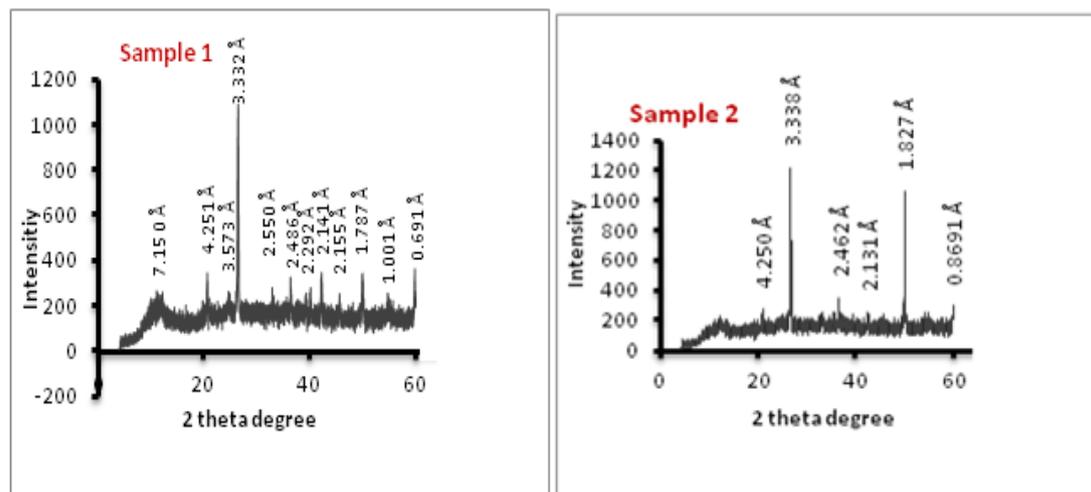


Figure 17 Microscopic image showing the texture of limestone rocks, Outeiro (Author, 2013)

5.1.3 X-RAY DIFFRACTION

Whole bauxite rocks collected from the Cantanhede region were mineralogical investigated by XRD. The XRD patterns (Fig. 18) show the $d(hkl)$



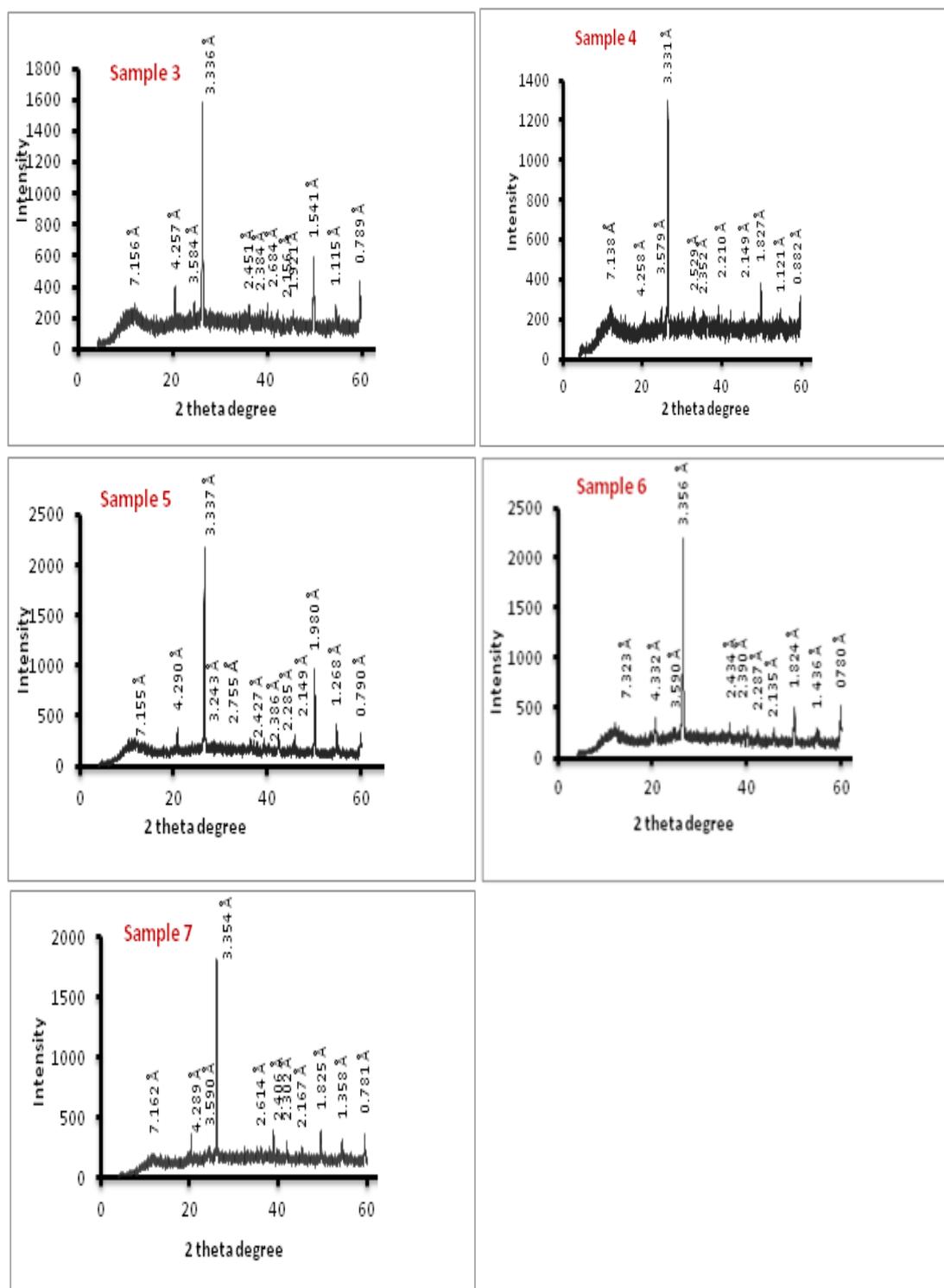


Figure 18 XRD patterns of randomly oriented 60 μm clay fractions collected from Portuguese bauxite rocks (Author, 2013).

values corresponding to kaolinite and quartz. In the samples examined, it was noted that there are high amounts of quartz and subsidiary kaolinite does occur. The d(hkl) corresponding to quartz occur at 3.33 Å (which is high in intensity and very sharp and 4.21 Å (small in intensity and sharp), whereas the 7Å peak corresponds to the kaolinite (Fig. 18).

Clay fractions collected by sedimentation from bauxite rocks were investigated by XRD (oriented specimens). XRD pattern of the $< 2 \mu\text{m}$ clay fractions oriented specimens (Fig. 19) shows the $d(00l)$ reflections corresponding to kaolinite: 7 \AA and 3.55 \AA correspond to 001 and 002 diffraction planes. The X-ray patterns show some specificities regarding to $d(hkl)$ reflections, characteristic of three dimensional order. Structurally, kaolinite from bauxite rocks is characterized by poorly-resolved reflections in both (02,11) and (13,20) bands. The basal reflections are sharp and the group of (020), (110) and (111) reflections are well resolved. Both basal and non-basal reflections are sharp and well defined.

The XRD patterns of the $<2 (10) \mu\text{m}$ clay fractions containing kaolinite and quartz are shown in Fig. 19. Randomly oriented specimens show that a poorly ordered kaolinite.

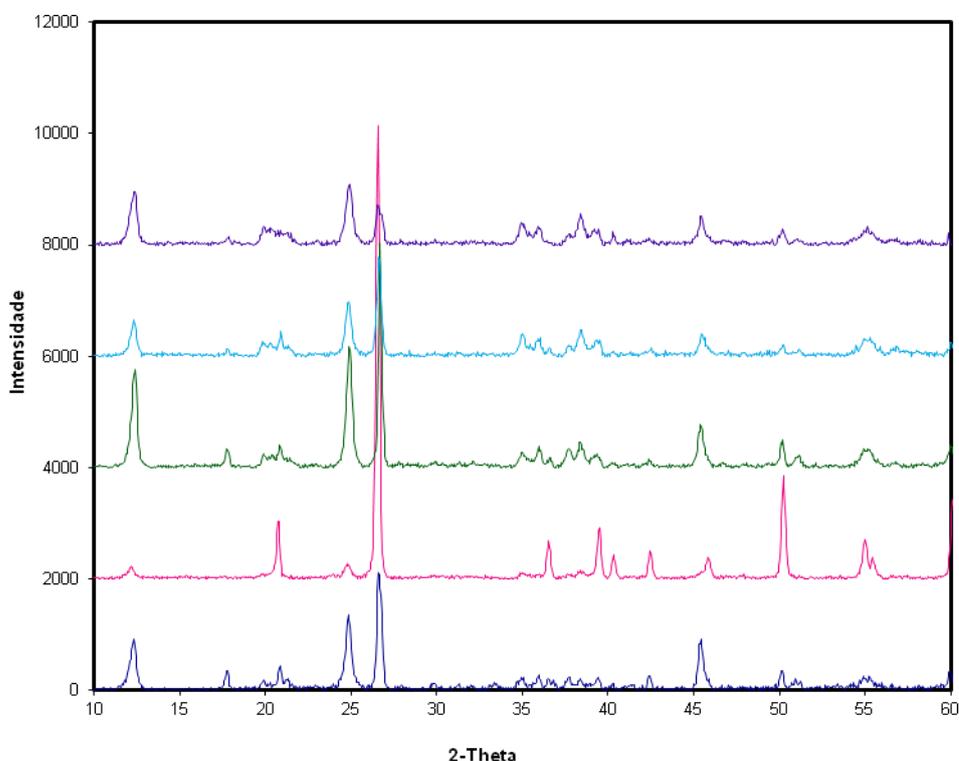


Figure 19 XRD patterns of oriented specimens (a) and randomly oriented specimens of the $< 2 \mu\text{m}$ clay fractions extracted from bauxite rocks (Author, 2013).

5.1.4 IR SPECTROSCOPY

Crystal chemistry of kaolinite was followed using IR spectroscopy techniques. Special emphasis was paid to OH stretching bands, water deformation bands and Si-O-Al stretching bands. For high and medium ordered kaolinites, the OH- stretching region is characterized by two bands essentially unchanged: 3694 cm^{-1} and 3620 cm^{-1} suggesting a poorly ordered structure of kaolinite (Fig. 20). However, as far as

the structural order decreases, some changes could be found particularly in the H-O-H deformation band at 1635 cm^{-1} . Its intensity and broadening increases are caused by variation of the interlayer water content. The Al-O bond at 939 cm^{-1} is very sensitive to structural order-disorder. This feature is more notorious in well-ordered kaolinite, where the band tends to disappear when disorder becomes more pronounced.

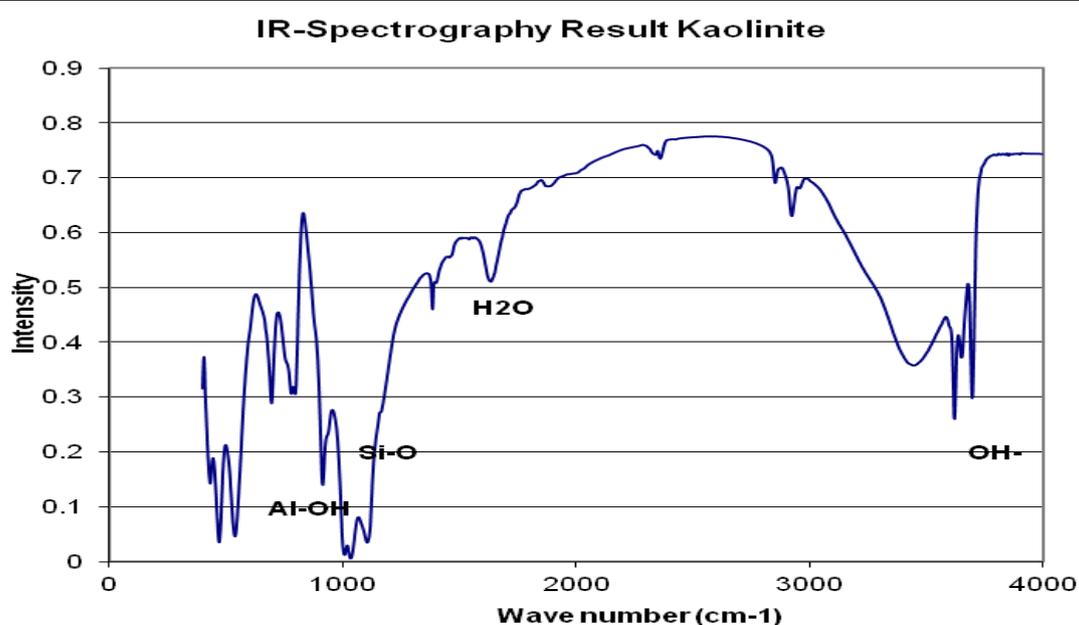


Figure 20. IR-spectrum of kaolinite from Andorinha (Author, 2013).

Another peculiarity was observed in the spectral region corresponding to the range 800 to 750 cm^{-1} , more exactly in what concerns the relative intensities of bands at 788 cm^{-1} and 754 cm^{-1} . I_{788}/I_{754} cm^{-1} ratio decreases insofar kaolinite structural order decreases. Poorly ordered kaolinite crystals are characterized by two OH stretching bands at 3700 cm^{-1} and 3620 cm^{-1} (Fig. 20); the H-O-H deformation band at 1635 cm^{-1} is more intense and broad comparatively to well and medium ordered kaolinite. Finally, intensities ratio of the stretching bands at 788 cm^{-1} and 754 cm^{-1} show the smallest values in case of halloysite-7Å. The ratio between intensities of the OH stretching bands at 3690 cm^{-1} and 3620 cm^{-1} was chosen as a crystallinity index to assess the crystallinity of kaolinite.

5.1.5 MAJOR AND TRACE ELEMENTS IN PORTUGUESE BAUXITE

Chemical data (major and trace elements) of bauxite rocks from Andorinha - Cantanhede region were published by Gomes et al. (1996). Trace elements are shown in Table 5.

Trace Element (in ppm)	Location 1	Location 2	Location 3	Location 4
Cr	25	30	10	10
Ga	20	60	20	40
V	40	20	10	15
Ni	25	40	20	3
Co	25	20	10	60
Zr	100	80	30	40
Sc	20	10	10	20
Y	30	<10	15	40
Cu	15	10	30	30
Sr	30	40	40	60

Table 5 Geochemistry of trace elements identified in bauxitic clays of Andorinha.

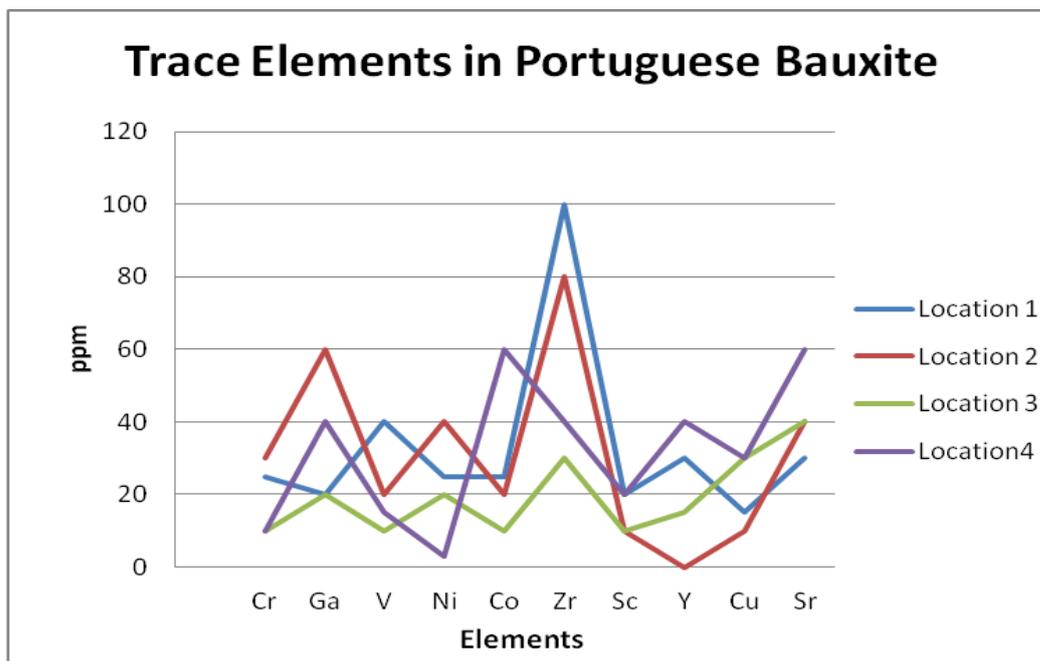


Figure 21 Trace chemical elements distribution in Portuguese Bauxite (Gomes et al., 1996).

From the graph above it is clear that Zr concentrations are higher across the locale when compared to all other major and trace elements represented. Zirconium (Zr) concentrations vary from 30 ppm to 100 ppm.

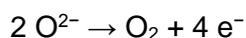
5.1.6 ALUMINUM IN BAUXITIC PORTUGUESE ROCKS

Western Europe and Portugal in particular are deficient in Al ore deposits. Pinto Coelho (1977) suggested that one alternative for Portugal is to extract Al from nephelinic syenites, namely from the Monchique area. Thus, there is an open-pit mining in the south of Portugal where a mining company explores these rocks as ornamental rocks. The nephelinic syenite rocks may be utilized for this purpose because the nepheline offers some advantages above suggested, being assayed profitable. By laboratorial processes, the author puts forward these advantages and calls the attention for the necessity of to accomplish essays about the nepheline (by the acid's method) and to carried out a petrographical detailed studied and geological reconnaissance of the Montague syenitic massif.

There are several technological processes proposed by Pinto Coelho (1977) in order to extract Al from nephelinic syenite rocks. The electrolytic process involved the reduction of anhydrous aluminum chloride with potassium. Both of the electrodes used in the electrolysis of aluminum oxide are carbon. Once the refined alumina is dissolved in the electrolyte, it disassociates and its ions are free to move around. The reaction at the cathode is:



Here the aluminum ion is being reduced. The aluminum metal then sinks to the bottom and is tapped off, usually cast into large blocks called aluminum billets for further processing. At the anode oxygen is formed:



To some extent, the carbon anode is consumed by subsequent reaction with oxygen to form carbon dioxide. The anodes in a reduction cell must therefore be replaced regularly, since they are consumed in the process. The cathodes do erode, mainly due to electrochemical processes and metal movement. After five to ten years, depending on the current used in the electrolysis, a cell has to be rebuilt because of cathode wear.

Aluminum electrolysis with the Hall-Héroult process consumes a lot of energy, but alternative processes were always found to be less viable economically and/or ecologically. The worldwide average specific energy consumption is approximately 15 ± 0.5 Kw/h per kilogram of aluminum produced (52 to 56 MJ/kg). The Hall-Héroult

process produces aluminum with a purity of above 99%. Further purification can be done by the Hope process. The process involves the electrolysis of molten aluminum with a sodium, barium and aluminum fluoride electrolyte. The resulting aluminum has a purity of 99.99%.

Nevertheless, recent studies developed in the last 10 years show that the technological processes for the Al extraction from magmatic rocks are very expensive.

The content of Al_2O_3 in nepheline syenitic rocks round at about 20 to 24%, whereas in bauxite rocks, the Al_2O_3 is around 35 – 38 % concentrated in kaolinite.

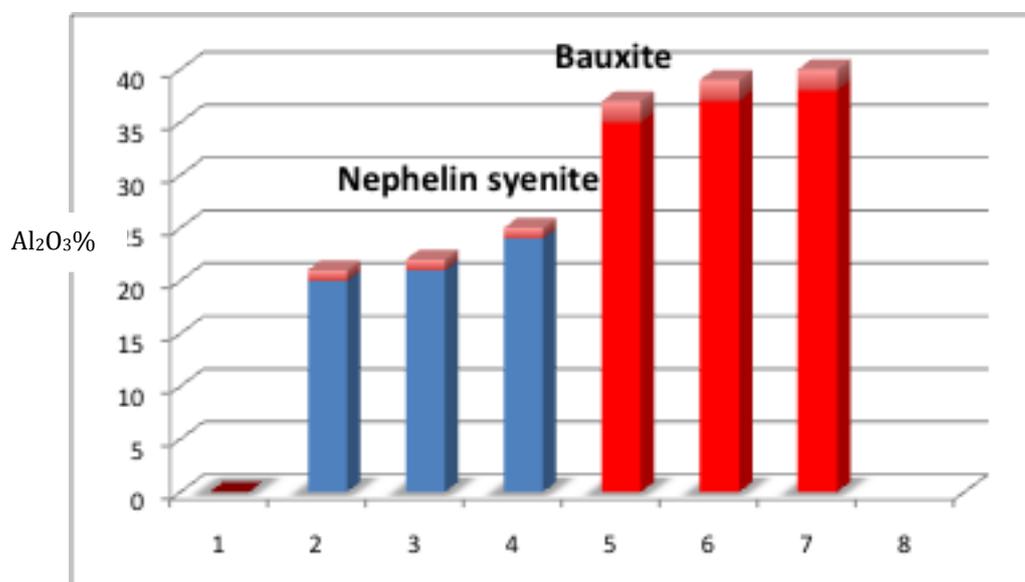


Figure 22 Distribution of Aluminum in nepheline syenite and bauxite rocks. Aluminum data obtained from (Gomes et al., 1996)

5.2 MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF JAMAICAN BAUXITIC ROCKS

In general, Jamaican bauxites have a mineral composition that is very consistent throughout the island. However, slight variations in percentage concentrations are noticed in the proportions of materials which reflect underlying parent material and the colors red and yellow. The composition of individual ore bodies is relatively constant when mature, whilst there are more systematic variations observed in the much younger deposits.

The marked differences observed in the ore can be seen in deposits from St. Elizabeth in the southern end of the island and the ore from the Williamsfield-Mile Gully trough. In St. Catherine, however, the ore is considered very young and therefore demonstrates small differences in composition from the more mature deposits.

The predominant minerals of Jamaican bauxite are: gibbsite, bohemite, hematite and goethite. Other minerals present in minor quantities include quartz, kaolin, halloysite, rutile, anatase, apatite, manganite, hausmannite and woodruffite. There are several accessory mineral suites which include a variety of resistance and authigenic minerals. Most of these, of course, depend on the location of the bauxite deposit.

5.2.1 MINERALOGY

Gibbsite, $\text{Al}(\text{OH})_3$, is found to be the most abundant mineral occurring in the Jamaican bauxite ore, and in some locations, it accounts for approximately 75% of the mineralogical composition. However, this is only the case with the red bauxites as the yellow bauxite reveals a much lower percentage on average (69 %) when compared (Table 6). The highest percentage of gibbsite in Jamaican bauxitic ores has been found in the parishes of Clarendon and St. Ann. In general, the average percentage concentration of gibbsite in Jamaican bauxite is approximately 45% (Anderson, Robinson, 1972). The gibbsite identified in Jamaican bauxite have crystals averaging size of 0.2 microns and give sharp x-ray diffraction patterns, (Hill, 1974).

Bohemite, $(\text{AlO}.\text{OH})$, accounts for the second highest aluminum hydrate minerals found in Jamaican bauxite ore. The mineral varies from approximately 5-20% and even goes up to 25 % in some areas, especially the south western parish of St. Elizabeth and in sections of Manchester and St. Ann. However, in areas of St.

Catherine the content falls to 3%, or fewer. In many cases the mineral exceeds 5% by weight of the total bauxite. Bohemite found in Jamaican bauxite has poorly developed crystal morphologies and averages size of up to 0.2 microns like gibbsite. The mineral has a much higher presence in the yellow deposit on average when compared to the red deposit.

Variably small concentrations of goethite has been found in the ore in several locations, but, predominantly in the parish of St. Elizabeth where it predominates over hematite in the lower grade yellow bauxites, found closer to the water table at the lower elevations. In this case average percentages are reported at approximately 2 per cent (Robinson, 1971). The goethite accounts for 14 to 24 percent of aluminous mineral in the yellow bauxites whilst, a low value of 5 to 8 percent is recorded for the red sample. The mineral occurs as an isomorphous substitution of aluminum for iron in the goethite crystal lattice. This makes the aluminum difficult to be extracted by the Bayer process.

The principal clay minerals occurring in Jamaican bauxite are kaolinite and halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), which accounts for approximately 3% of the composition of the high grade bauxite used for aluminum production. These minerals are extremely fine grained with a particle size ranging from 0.1 to 0.4 microns, and are poorly developed. The halloysite crystals show the characteristic tubular morphology under the electron microscope, but have poor outlines and frayed edges (Hall, 1977).

The bauxite deposit found at higher elevation, in parishes such as Manchester, Clarendon and St. Ann generally have 1-3 percent of halloysite and is determined to be good-grade bauxites due to the low SiO_2 content. The lower level deposit in St. Elizabeth and St. Catherine have about two times or more the SiO_2 content and is of lower economic grade. In other areas across the country the bauxite has been found to contain greater than 10 percent SiO_2 . These are of non-commercial grade. Notwithstanding, a high silica content is not unique to any one area of Jamaican bauxite, the variation is also reported in areas of good-grade bauxite, with frequent anomalies seen at the margins of extremely low silica deposits. The low silica bauxites found in the elevated regions of the bauxite belt in the country have been benefited by the leaching of silica during the breakdown of the clay minerals; a process favored by the low water table in these elevated regions.

Hematite, (Fe_2O_3) is present in ferruginous concretionary pellets or oolites occurring in all bauxite deposits across the country. The diameter of these oolites is

approximately 2 to 3 millimeters (Robinson and Hill, 1971), larger specimens can be found in some areas in St. Ann, Manchester and Clarendon. These pellets are found to contain up to 45 % of Fe₂O₃ which coats the bauxite. The pellets are responsible for 1 to 12 % of the mass of total bauxite in some regions (Robinson, 1971). This pellet may also be referred to as a colloidal iron oxide, and is responsible for the variation of color seen in the bauxite deposit across the country. The color varies from yellowish brown to red. However, where a minor amount of pyrolusite (MnO₂) is present, the deposit takes on a much darker tone. Also, color change observed in some deposits is due to the change in valency of the Fe³⁺ ion.

Titanium oxide (TiO₂) is a normal and constant constituent of Jamaican bauxite; it ranges from 1 to 3 percent in both the red and yellow bauxites. The mineral occurs mostly as minute crystals of anatase and rutile (Hill, 1974) notwithstanding, the mineral ilmenite and titanomagenite have been found to be in association with some deposits.

Mineral	Red Bauxite (%)	Yellow Bauxite (%)
Gibbsite	69-75	64-69
Bohemite	1-4	3-5
Kaolinite/halloysite	1-3	1-3
Hematite	10-14	1-5
Goethite	5-8	14-24
Apatite	<2	<<1
Anatase	<1-3	<1-3
Secondary phosphates (wavellite, crandallite, variscite)	<1	<4

Table 6 Mineralogy identified in Jamaican red and yellow bauxites (adapted from Grubbs et al., 1980).

Minor amounts of the aluminum phosphate mineral crandallite, CaAl₃(PO₄)₂(OH)5.H₂O and trace amounts of apatite, Ca₃(PO₄, CO₃)₃(F,OH,Cl) can be found in Jamaican bauxite. Additionally, two other secondary phosphates, wavellite and variscite have also been found in samples collected in the Mocho Mountain region of Clarendon (Grubbs, 1982). In the case of anatase, the average is approximately 0.5

percent (Robinson; Anderson, 1971), but when separated in terms of color the average ranges from 1.5 percent for red and a similar value for yellow bauxite.

A high of 3 percent has been recorded for samples taken from valley bottoms in certain parishes. This increased percentage may be attributed zoning and the chemical weathering process which takes place in the karstic environment. Phosphate is produced by decayed organic matter and stored in the limestone. When it rains the weak carbonic acid dissolves the limestone and carries the calcium phosphate in solution where it later deposited in huge joints and sinks where it accumulates over time.

The Jamaican bauxite deposits contain manganese varying minerals (Robinson, 1971). The manganese minerals in Jamaican bauxite are: lithioporite (Al, Li) $MnO_2(OH)_2$, hausmannite, Mn_3O_4 , manganite $MnO(OH)$, and woodruffite, $2(Zn, Mn).5MnO_2.4H_2O$. The average percentage of manganese in Jamaican bauxite is approximately 0.3 percent. The localized enrichment of manganese minerals tends to occur at bauxite-limestone interface and in some cases up to 30 % of MnO has been determined (Robinson; Anderson, 1971).

Accessory minerals have been detected in Jamaican bauxite at very low percentages and reflect the parent material of the locality. The resistant minerals found in the bauxite deposit include zircon, tourmaline, kyanite and garnet (Grubbs, 1982).

5.2.2 GEOCHEMISTRY OF MAJOR AND TRACE ELEMENTS

Jamaican bauxite has been found to contain the following elements: Ca, Fe, Ti, Na, K, Si, C, Al, Mn, and P. Where trace elements are concerned, the following elements have been found: Ag, Ba, Be, Dc, Co, Cr, Cu, Ga, Mg, Ni, Sr, V, Li, Yt, Zn, and Vr (Robinson and Anderson, 1971). The major element data obtained for Jamaican bauxites are shown in the table (7) and figure 23 below.

Major Elements wt. %	St. Ann	Manchester	St. Elizabeth	Range
Al ₂ O ₃	47.52	46.04	42.08	45.0 -52.0%
H ₂ O	27.62	27.40	26.04	18.0 -28.0%
Fe ₂ O ₃	20.33	20.51	26.66	15.0 -25.0%
SiO ₂	0.52	2.75	0.42	0.1 -10.0%
TiO ₂	2.58	2.17	2.53	2.0 – 2.6%
P ₂ O ₅	0.42	0.23	0.96	0.1 – 5.0%
MnO	0.79	0.37	0.46	0.1 – 3.0%
MgO	0.01	0.025	0.10	0.01 -0.1%
CaO	0.21	0.45	0.65	0.45- 1.0%

Table 7 Percentage concentration of major elemental oxide in Jamaican bauxite (Hill, 1972).

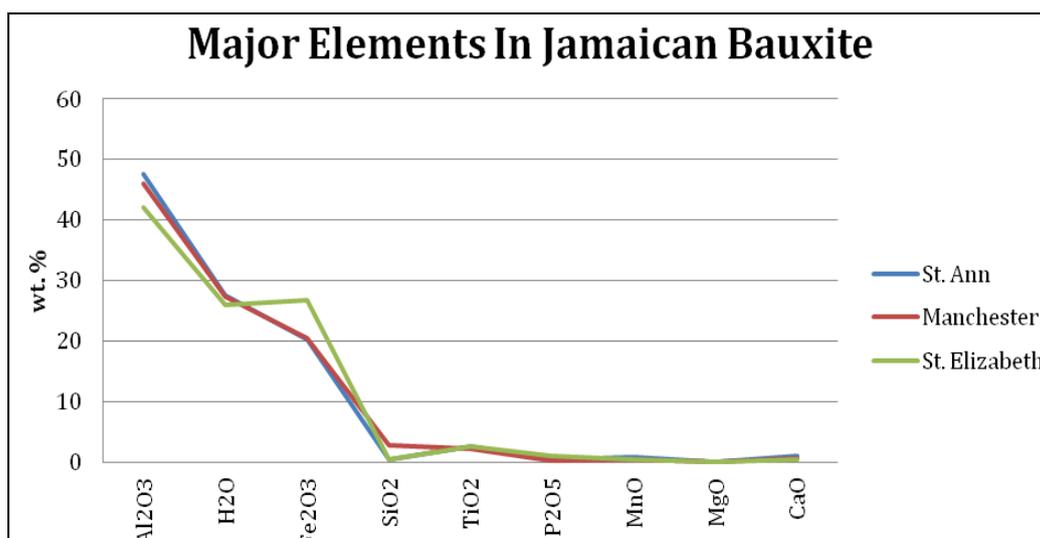


Figure 23 Distribution of the major elements from the Jamaican bauxite (modified from Hill, 1972)

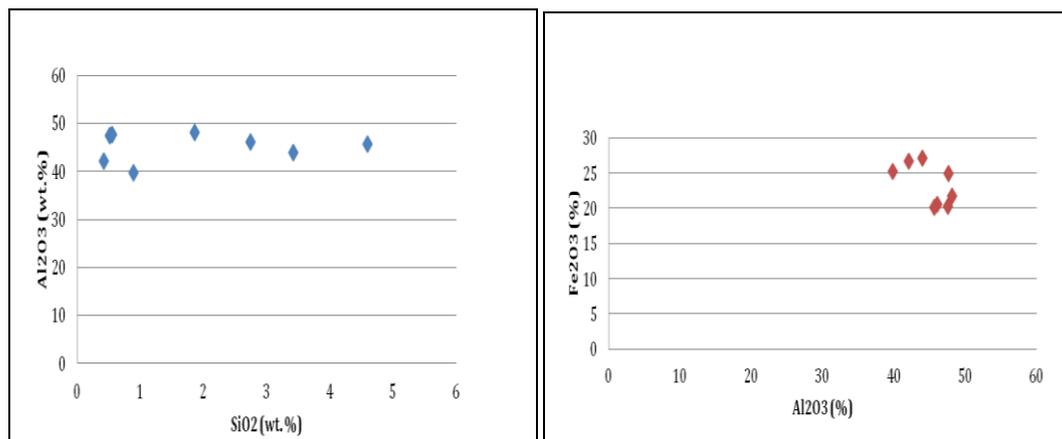


Figure 24 Correlation diagrams between Al₂O₃ vs. SiO₂ and Fe₂O₃ vs. Al₂O₃ in the Jamaican bauxite deposits.

The Al₂O₃ content in Jamaican bauxite ranges from 42.08% to 47.52% with an average range of 45.0 to 52.0%. The iron (Fe₂O₃) content ranges from a low of 20.33% weight to 26.66%, having an average of 15.0 to 25.0%. The SiO₂ content is found to contain as great as 10% in some areas, however; in general, the silica content is relatively low with a range of 0.42% to 2.75%. TiO₂ content occupies a range of 2.0-2.6% and shows very little variation in all three areas studied.

The P₂O₅ has a low of 0.23% and a high of 0.96%, generally, the range tends to be from 0.1 to 5.0%. MnO found in Jamaican bauxites is in the range of 0.1 to 3.0% reflecting mild fluctuations in weight percent across all three locations studied. Both CaO and MgO have very small presence in Jamaican bauxite. The weight of these major elements ranges from a high of 1.0% to a low of 0.10% respectively. Importantly, the H₂O content of Jamaican bauxite is relatively high and is in the range of 18.0 to 28.0% where the average weight recorded across all three locations is at 27.02%.

Trace Elements (ppm)	St. Ann	Manchester	St. Elizabeth	Clarendon
Cr	731	695	216	905
Ga	40.44	65.78	70.12	76.87
V	156	132	92	209
Ni	18	44	77	43
Hf	40	33	35	41
Nb	147	146	191	210
Sc	46	43	27	40
Zn	50.9	71.6	29.8	67.8
Cu	17	12	14	23
Sr	9.5	12.2	35.6	18.2

Table 8 Trace elements analyzed in the Jamaican bauxite (Robinson, 1971).

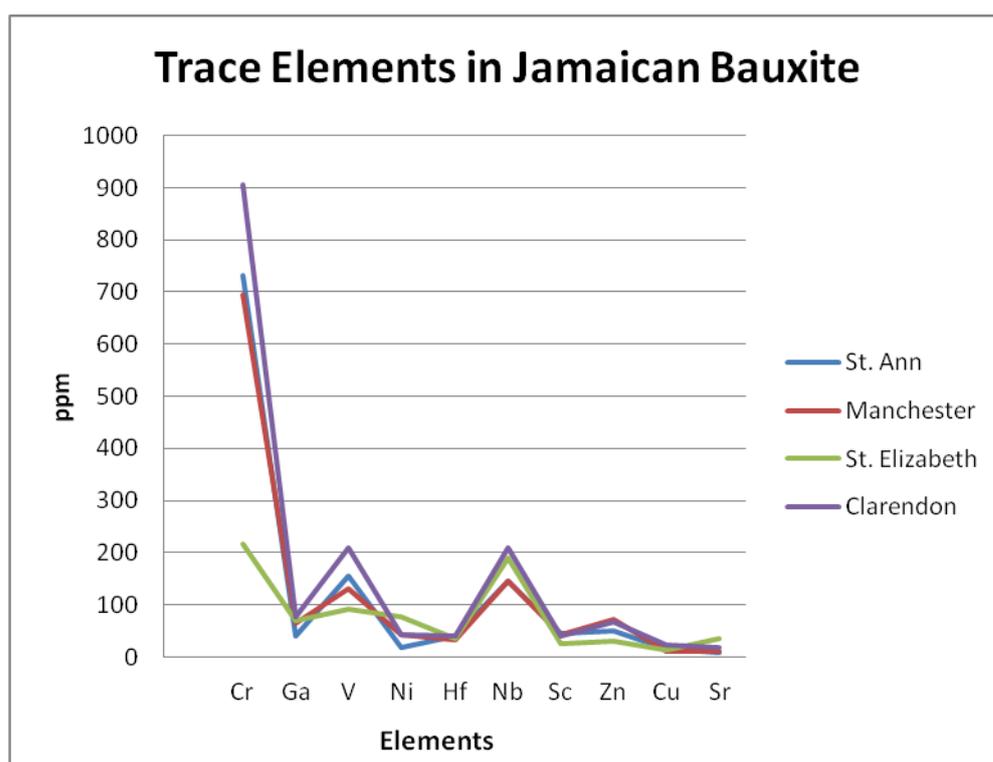


Figure 25 Distribution of the trace elements in the Jamaican Bauxite.

Chromium is the most abundant trace element found in Jamaican bauxite, concentrations across the four major locations show range from 216 to 905 ppm. This is followed by niobium with concentrations in the range of 156-254 ppm. Also in high amount is vanadium and zinc ranging from 92 - 209 ppm and 29.8 to 71.6 ppm

respectively. The other elements such as Ga, Hf, Sc, Cu and Sr are present but in concentrations below 100 ppm.

5.2.3 ALUMINUM IN JAMAICAN BAUXITIC ROCKS

Jamaican bauxite is relatively high in aluminum content. The Al_2O_3 content of Jamaican bauxites ranges from 45- 52% and an average of 45%. However, it takes roughly 4 tonnes of bauxite to produce 1ton of aluminum. Geochemical mapping done (by Lalor, et al) indicate that Jamaican bauxite has greater than 15 % aluminum in all locations, with some areas, of course, showing greater concentrations. Figure 26 below shows the bauxite deposits of Jamaica and its aluminum content.

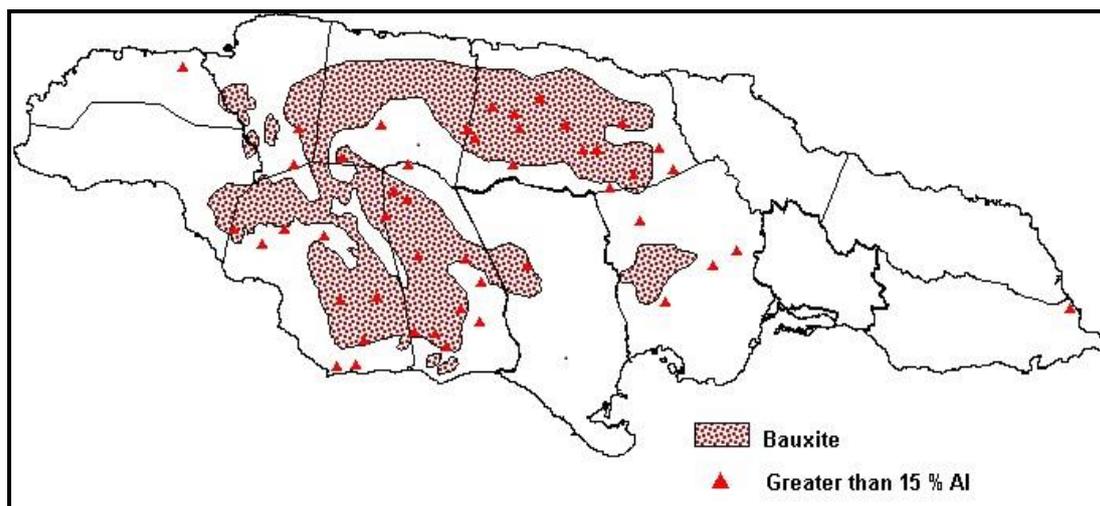


Figure 26 Aluminum content found in Jamaican bauxite (Lalor, 1996).

A more precise map illustrating the percentage concentration of aluminum in bauxitic soils across Jamaica is shown in Figure 27. This illustrates that bauxite deposits from St. Ann have the highest percentage concentration of aluminum 75 to >90% composition. Bauxite deposit from the Cockpit Country region also demonstrate a high aluminum percentage composition. Followed by Manchester, St. Elizabeth and Clarendon. The deposits of St. Catherine has the lowest aluminum concentration when compared to all the other major deposits.

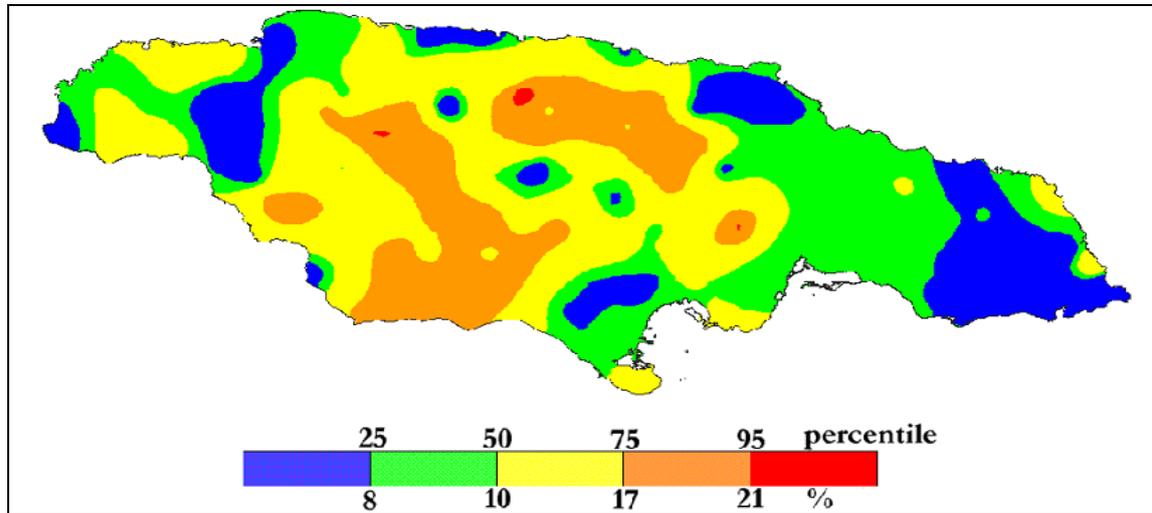


Figure 27 Aluminum concentration map Jamaica (Lalor et al., 1996).

6 GEO-ECONOMIC POTENTIAL OF BAUXITIC DEPOSITS IN PORTUGAL AND JAMAICA

6.1 HISTORICAL NOTE

Bauxite is the most important mineral resource for the aluminum industry. Annually, the quantity of bauxite produced is dependent on the demand for aluminum on the global market. Aluminum over the past few decades has risen to be an advent in the family of commercial metals. The unique physical and chemical properties have advanced the demand for the metal and its alloy over other materials, including other metals; in building construction, technology, food and beverage, and a host of other industries. However, this was not the case in just over a century ago.

In the pre World War I period, bauxite demand was relatively low as there were not many uses for the metal. The total world production in 1900 was considerably less than 500,000 tons. In 1914, total world production was approximately 1 million tons and the primary usage of the metal was for the manufacturing of stainless utensils. During this period the United States and France were the top producers of aluminum, followed by the USSR. After WWI, the commercialization of bauxite for aluminum smelting increased and Europe became a powerhouse with Italy, Hungary, Yugoslavia and Russia becoming major players, and together with France supplied almost all of the requirements in Europe.

After World War II, advances in technology increased the demand for aluminum, this encouraged the expansion in output of bauxite and production increased and peaked at 14 million tons per annum. This expansion was taking place at a much faster pace than world economic growth and new mines were developed in Haiti, Ghana, Sierra Leone, Dominican Republic, Jamaica, Australia, Brazil and Guinea. In the 1970s aluminum started replacing substitutes, including cast iron, rolled and galvanized steel, tinplates, cast zinc, copper wires and tubes, timber glass, cardboard and metalized paper.

Today, the demand for aluminum fluctuates from time to time and world prices dictate markets. Data released in 2013 illustrates that the current demand for the metal is just over 11 million tons. A decade ago the demand for the metal was significantly higher, at just over 20 million tons per annum. The decrease in demand on the world stage is due to competition, recycling and development of synthetic material that are used as good substitutes in several industries.

6.2 World Production

World bauxite reserves are estimated to be 5.8 billion tons with potential bauxite resources amounting to another 1 billion ton. The world top producers over the last 40 years have not changed much, since these are the countries with the highest concentration of commercially quantifiable grade. In 1972, Australia, Jamaica, USSR and Suriname held 60% of the world's market share.

These top four countries dominated the market for a very long time. In today's market share, Australia has increased its share of global output from 20-32% when compared to 40 years ago. On the other hand, Jamaica, Russia and Suriname are no longer on the list of major producers having been replaced by Brazil (15%), China (14%) and Indonesia (11%). Figure 28 shows the production of bauxite by major players globally (in 2011).

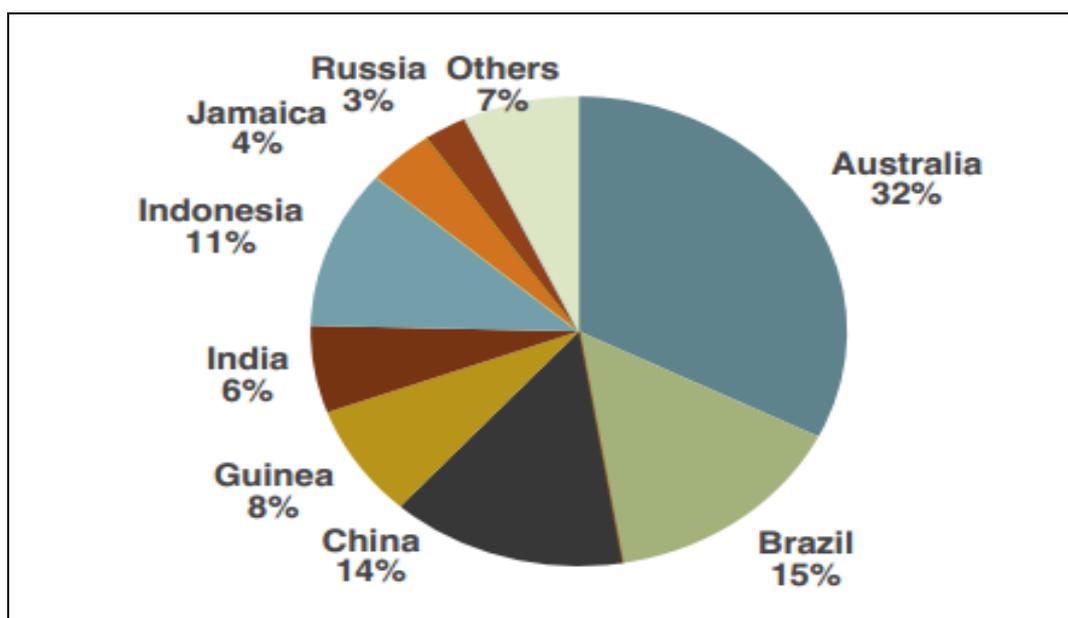


Figure 28 Bauxite production by major world producers (Napper, 2013).

On average, it takes approximately 4-7 tons of bauxite (depending on the composition and grade) to produce 2 tons of alumina. The Bayer process is used to convert the bauxite into alumina. The alumina is then converted into aluminum metal. It takes 2 tons of alumina to produce 1 ton of aluminum using the Hall-Héroult process.

Many countries that produce bauxite are unable to fully convert the raw bauxite to aluminum. The process is expensive and energy extensive. Therefore, smelting tends to take place in highly industrialized countries that have an abundant supply of

energy. In other parts of the globe, where energy is an issue the bauxite is shipped to one of these industrialized countries where it is converted to alumina and subsequently aluminum. Figure 29 shows the countries that are the top producers for alumina (in 2011). Alumina as a product is widely used in portland cements and used as flux for iron and steel making.

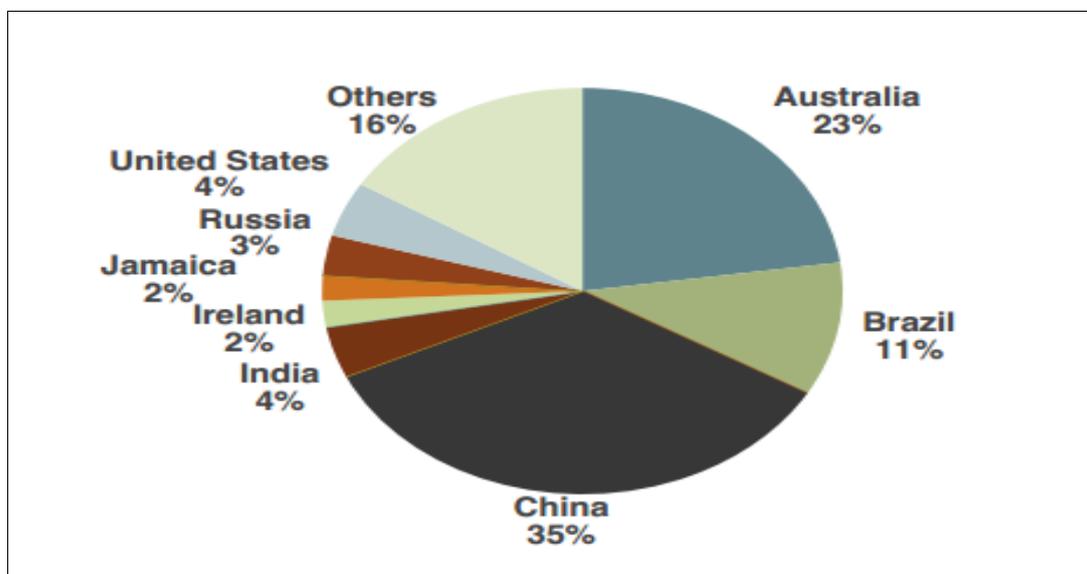


Figure 29 Alumina production by major world producers (Napper, 2013).

6.3 ALUMINUM USES AND CONSUMPTION

Aluminum has many and varied uses. The metal is consumed heavily by the transportation, engineering (mechanical and electrical), building and construction, and packaging industries. Figure 30 shows the world's top producers of aluminum metal.

- In transport, aluminum is used in cars (engine blocks, cylinder heads, transmission housings and body panels), trucks and buses (sheet and plate for bodies), in railway stock and in aircraft.
- In construction, aluminum is used in sheet products for roofing and wall cladding, in extrusions for windows and doors, and in castings for builders' hardware.
- In packaging, aluminum is used in the form of alloy sheet for beverage can bodies and tops, as foil for household and commercial wrap, and in manufactured packaging products such as cartons for fruit juice and packaging for pharmaceuticals.

- In the electrical sector, aluminum is used in the form of wire, normally reinforced with steel to form cables.

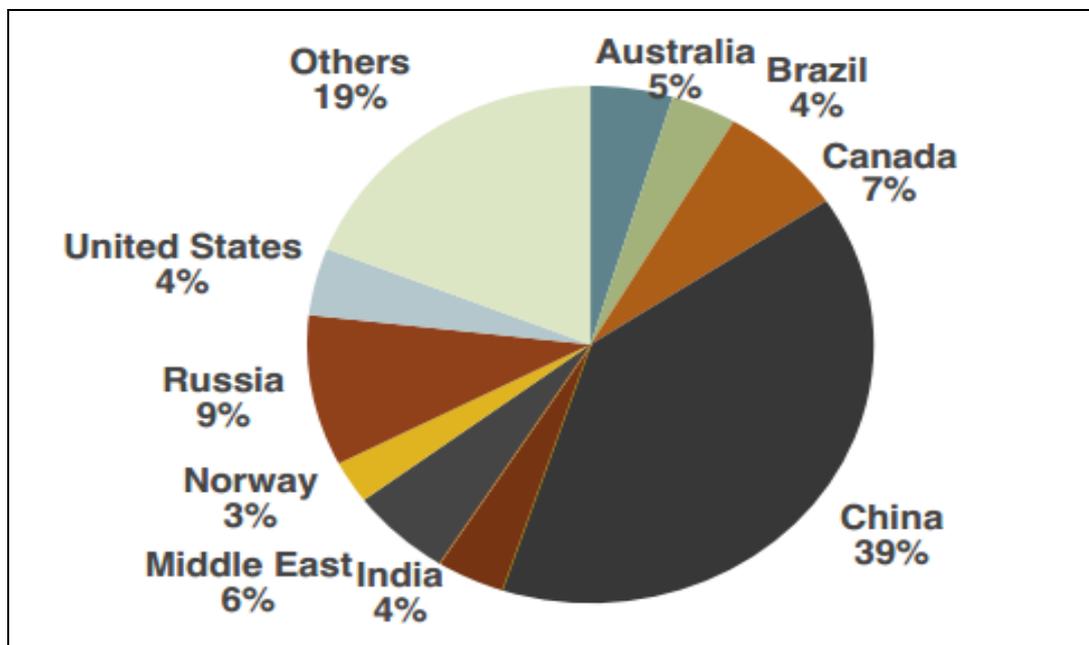


Figure 30 Aluminum production by major world producers (Napper, 2013).

Aluminum products are consumed the world over. However, countries with a higher population and an appetite for aluminum-based industries tend to consume a greater proportion of the metal. Data released by the European Aluminum Association in 2013, revealed that China is the world's largest consumer (20.3 million tons) and is followed by the rest of continental Asia (10.1 million tons). The total primary aluminum consumption in the world so far in 2013 is some 50.2 million tons. Europe accounts for just over 7.2 million tons followed by North America at 5.5 million tons and the rest of the world at 4.2 million tons (Fig. 31).

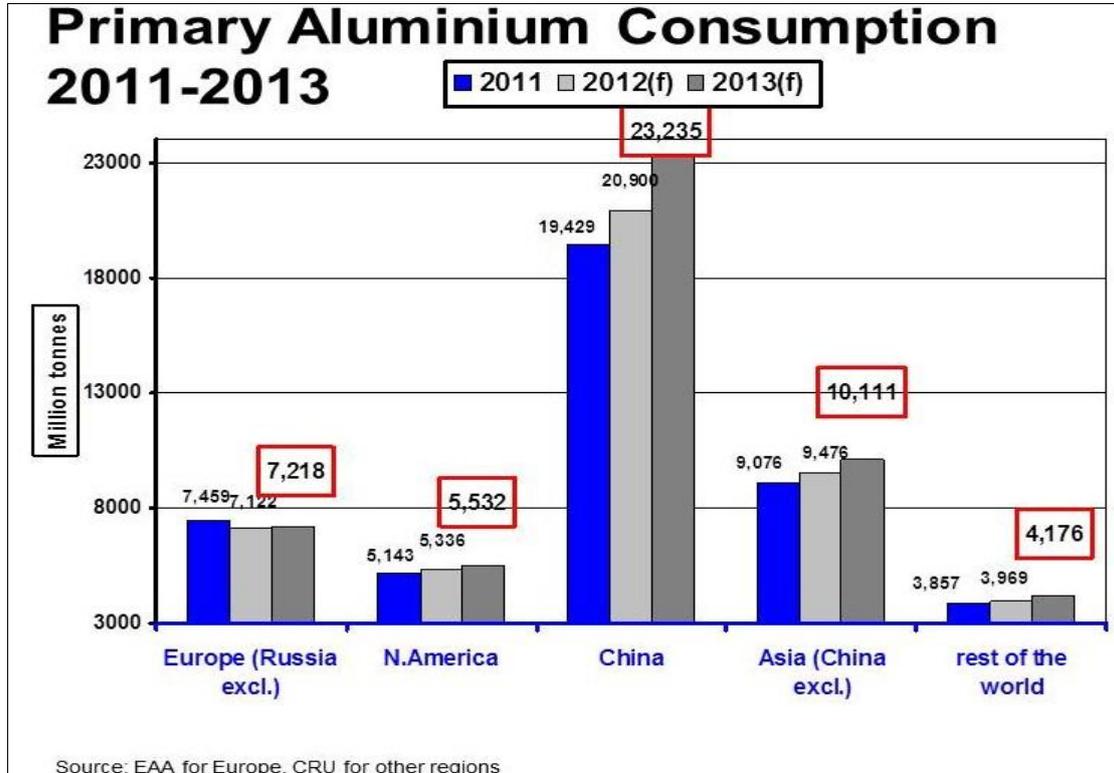


Figure 31 Chart showing primary aluminum consumption globally (EEA, 2013).

6.4 ECONOMIC OUTLOOK FOR PORTUGAL

Results obtained indicate that Portugal's bauxite is of limited commercial grade. Although, the Al_2O_3 content of the clays is over 30%, the high occurrence of kaolinite and phosphate-sulphate and quartz along with the free liberated limestone in mineable areas may inadvertently contaminate the bauxite during mining. Beneficiation of the grade in the Andorinha-Cantanhede region may not be cost effective as the bauxite is not readily amenable. In order for the Portuguese bauxite to be considered mineable, then there must be at least 300 million tons available.

There has been limited reconnaissance studies carried out in the area to determine the actual tonnage; work carried out in the past suggests that the tonnage is less than that required by international standard to be considered profitable. This is further compounded by the fact that, the geochemical studies proved that the grade is not of high gibbsitic content, but instead contains a higher bohemite and diaspore content with considerable silica due to high sandstone contact. Also, the deposit is not superficial, but exists in karstified sinks up to several meters deep and this can make mining costly and difficult.

Portugal is a well developed country with very good transportation routes and infrastructure. Therefore, having commercial quantities of high gibbsitic quality would not hinder the commercialization of bauxite mining for the aluminum industry. The Andorinha-Cantanhede region is linked to the major cities of Portugal, where the commercial ports are located, by several kilometers of roadways and highways. Transporting the bauxite or finished products to other areas in the country or globally would not be an issue. Also, there are many large rivers which provide cheap energy (hydro power) in Portugal along with wind and natural gases could be used to convert the bauxite into the metal.

The potential for Portugal to be a major player in the production of aluminum from its bauxitic resources is extremely improbable at this time. There are too many factors that are against the development of this industry. For this to be realized, the extractable alumina from the bauxite will have to be in the range of the ratio of around 2:6, roughly. Anything outside of this range will be unprofitable.

6.5 ECONOMIC OUTLOOK FOR JAMAICA

When bauxite mining was commissioned in Jamaica began in 1952, the country became a powerhouse soon after. In 1958, Jamaica was the world top producer, a position it held for a decade until it was surpassed in 1969; producing on average 8 million tons per annum. Jamaica's bauxite reserves are estimated to be in excess of 1.8 billion tons, and over 1.5 billion tons of this is commercially exploitable. The majority of the reserves are located within the southern Manchester, St. Elizabeth, St. Ann and the heavily forested region of the Cockpit Country.

Jamaica's bauxite is of a high grade. The geochemical report provided illustrate that bauxite contains up to >60 % of gibbsite in some areas, with lower concentrations of bohemite and goethite. Although in some areas, light minerals are in high concentrations, the beneficiation of the bauxite ensures that the quality of the gibbsite is not compromised. It takes approximately 5 tons of Jamaican bauxite to produce 2 tons of alumina and a ton of aluminum.

The bauxitic mining zones of the country are connected to the smelting plants by rails and some are located within close proximity to ports where the raw bauxite is shipped to Canada to be processed. Most of the bauxite mined in Jamaica is shipped as raw dirt whilst the other is shipped after being converted to alumina. Several companies such as Alcoa, Winalco, and Noranda (formerly Kaiser) have smelting plants located across the country. And, although many of the operations have scaled

down the country continues to produce a significant portion of the world's bauxite and alumina.

The reserves dictate that at the current pace, Jamaica will be producing bauxite for well over another 50 years continuously. The climate of the country, the large shallow surface deposits; which make mining simple and affordable, and proximity of the country to North America lend itself to prominence in the aluminum market globally.

7 CONCLUSION

Portuguese and Jamaican bauxitic rocks show very little similarities, if any. The similarities are shared mainly in physical properties. Weathering of Portuguese bauxitic rocks result in the hyperaluminous clays seen deposited on the surface and in the cavities of karst limestone which is concentrated in the Andorinha-Cantanhede region. The argillaceous and arkosic sandstone have a strong white kaolinite-rich band that is further weathered into aluminum hydroxides. Jamaican bauxite on the other hand, has been developed as a result of the chemical weathering of limestone; specifically the White Limestone across the country. There is also some evidence which suggest that bauxitic rocks in the central inliers of the country have been developed from igneous materials (volcanic ash). The commercial grades and significant quantities are located in three major parishes; St. Elizabeth, Manchester and St. Ann. None the less, large deposits are also found in St. Catherine, Clarendon and Trelawny.

Portuguese bauxitic rocks show a variety of mineralogy and chemical properties. The weathered hyperaluminous clays have a strong kaolinite and silica association from the Jurassic limestone and the grés Belasiano sandstone in the region. The bauxite is one that shows an autochthonous characteristic. Jamaican bauxite shows very strong correlation with the karst-type limestone on which it is situated. The bauxites of Jamaica are located on the surface and in cavities of the karst limestone. The deposits have at least 69% gibbsite, with Bohemite and goethite at smaller quantities. Portuguese bauxitic rocks produce just over 30% gibbsite and have a high kaolinite and silica content. Both bauxitic rocks have a strong presence of major and trace elements; hematite and magnetite are common with some rutile; in strong presence are Zr, Mn, Cr, and some strontium for Portuguese bauxite. In the Jamaican bauxite Ga, Nb, and Zn show strong occurrences.

Jamaican bauxitic resources have been contributing to the global aluminum and alumina industries for just over 50years. The country has been a world number one producer for several years before cheaper grades were found in China and Indonesia. The island continues to mine and export bauxite for the conversion into market ready products despite the closure of several plants across the island. Just over 1 billion tonnes of the resource have been calculated to be left in reserve. In contrast, in Portugal, the bauxite reserves are not of significant

quantity and quality. The hyperaluminous clays from the Andorinha region have been used locally in the past as a refractory material for bricks and ceramics. The mineralogical properties of the bauxite make it unattractive for the alumina and aluminum industries.

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