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Characterization of raw silica sand from the Ivorian sedimentary basin for silica glass making

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Abstract

The objective of this work was to characterize the sand of the Ivorian sedimentary basin and find out sands for the production of silica glass. The analysis of raw sand samples with the X-ray fluorescence spectrometer (XRF) revealed silicon oxide (SiO_2) contents ranging from 78.66% (Port-Bouët) to 97.41% (Maféré). Other oxides, such as alumina, iron oxide, sulphur oxide and potassium oxide are found in small proportions in all samples. The principal component analysis of the XRF data classifies the samples locations in three (3) groups, according to their chemical composition. Thus, the first group of sites, located in the eastern part of the basin, has silica contents higher than 96%. The second group, located in the West of the basin and in Abidjan, is characterized by silica contents lower than 92% and contains more impurities. Finally, the third group of sites, located at the extremities of the basin, presents intermediate characteristics to the two previous groups. The Maféré sand (group 1), belonging to the eastern zone, contains fine sand (66.8% of grains sizes are less than or equal to 500 microns), with rounded grains and very siliceous (97.41% SiO_2), is usable for soda lime glass making.

1. Introduction

Silicon oxide (SiO_2), also known as silica, occurs in nature in crystalline form, of which quartz is the most common and best-known form [1, 2]. The term silica also refers to sedimentary geological deposits enriched with quartz grains [3]. For example, siliceous geological formations that can be a natural silica resource are found in detrital deposits [3-5], where quartz grain richness is the result of continuous deposition as sediments through natural processes such as weathering, remobilization and transport [6, 7].

Silica is mainly used by photovoltaic energy factories ($SiO_2 > 99.99\%$) and glassmaking companies for the production of soda-lime glass ($SiO_2 > 95\%$ and $Fe_2O_3 < 1\%$ $Al_2O_3 < 4\%$) [8-10].

In France, sand from the Paris Basin (Beauchamp and Fontainebleau) and the Aquitaine Basin is quarried for an estimated production of 9.3 million of tons in 2018 (USGS 2019). The silica sands from these quarries are of high purity ($SiO_2 > 95\%$, with low Fe_2O_3 and Al_2O_3 contents) [10].

In Africa, silica sand production is low. It is attributed to the Maghreb countries, including Algeria, which in 2008 produced 498.035 tons with SiO_2 contents higher than 90%, coming from sand deposit areas [11].

Two major geological groups occupy the Ivorian territory a Precambrian basement and a sedimentary domain located in the south along the coast. This sedimentary basin is the site of the accumulation (deposition) of detritus resulting from the alteration of the Precambrian basement rocks and drained by the various rivers that flow into the sea [12-14]. Despite these assets, Côte d'Ivoire, like the sub-Saharan countries, imports large quantities of glass every year [15].
In order to reduce this import, the production of glass based on local silica would be an interesting alternative. It is in this context that the question "Could the Ivorian sedimentary basin contain sand adapted to the needs of the glass industry? "is of particular importance. In order to answer this question, the present study is therefore undertaken to characterize the sand of the Ivorian sedimentary basin. Specifically, the aim is to determine the content of silica and other oxides in the sand of the Ivorian sedimentary basin on the one hand, and the other hand the granulometry and morphology of the sand grains with the highest silica content.

2. Material and Methods

2.1. Collection and preservation of samples

The search for sand containing silica at a high rate on the Ivorian territory led us to carry out sampling in the onshore part of the Ivorian sedimentary basin, between the coastal town of Fresco in the west and the border with Ghana in the east (Figure 1). For this purpose, fifteen (15) artisanal quarry sites belonging to the continental shelf were selected for the prospection phase.
Samples were taken with an auger at a depth of 50 cm using the method described by Fournier J. et al and Ph. Rocher [16, 17]. Three (3) spot samples of 350 grams each were taken at random on each site. Then, a composite sample of 1050 grams is obtained from the point samples in order to give a better representation of each site. The samples obtained were placed in sterile bags free of any contamination and then transported at room temperature to the laboratory.

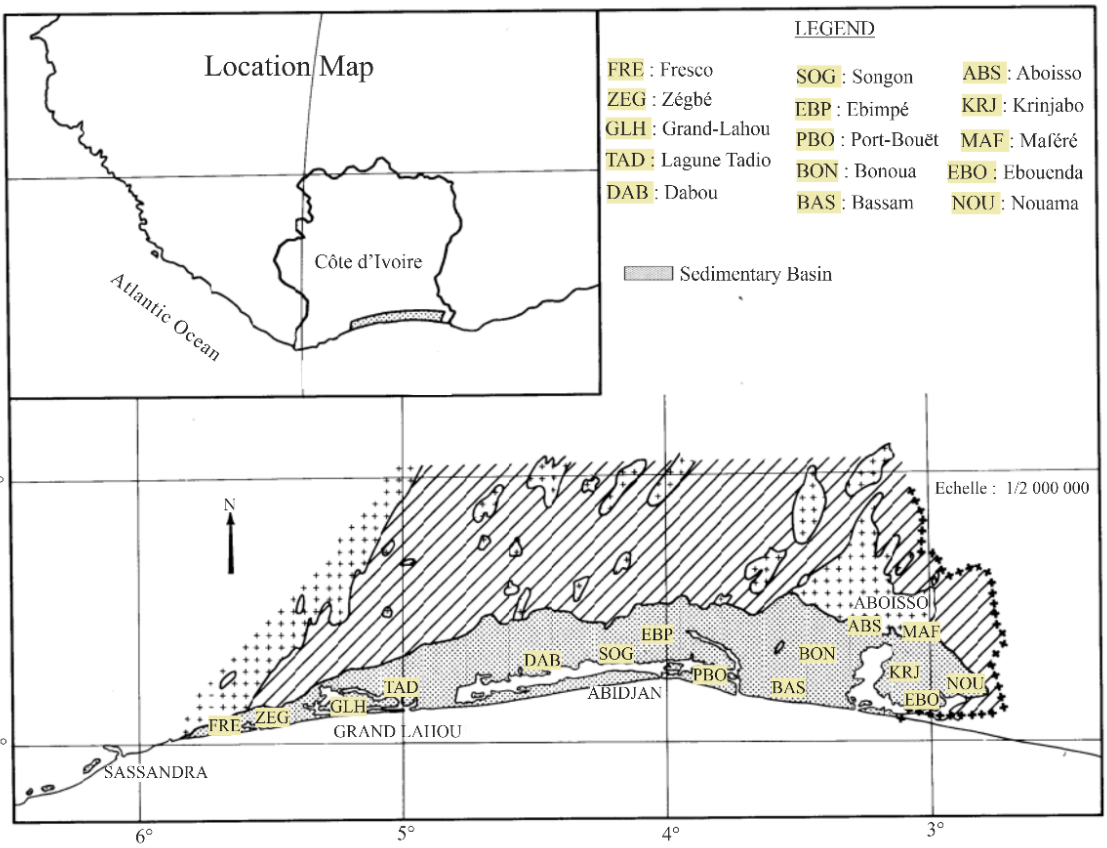


Figure 1: Sand Samples Collection map ([13] _amended).

2.2. Sample preparation for the analysis phase

Once in the laboratory, the samples were transferred to cloth bags and placed on grids to allow the residual water to drain off by gravity. After draining, the canvas bags containing the samples were oven-dried. Drying was carried out to a constant mass at 105 degree Celsius to completely remove the water contained in the sand samples. After cooling in a desiccator, a first fraction of 50 grams of each sample was taken and then crushed (LM2 disc mills with internal mortar) to obtain grindings with a particle size below 75 micrometers. These grindings are intended for analysis by X-ray fluorescence spectrometer [18] for the determination of the content of silica and other oxides. A second fraction of 950 grams of sand from each sample is taken for particle size analysis.

2.3. Sample Analysis

The silica content was determined by analysing the chemical composition of the samples. Thus, 15 grams of grind per sample was placed in the cups of the 8000 Oxford Instruments X-Supreme Spectrometer [18]. The samples were irradiated with a beam of X-rays having sufficient energy, so that the atoms thus ionized emitted fluorescence radiation also in the X-ray range intrinsic to each atom. The intensity and energy of these X-rays were measured by the spectrometer, which then quantifies the elemental chemical composition of each sample [19].

The particle size analysis was performed using a vibrating sieve shaker according to Fournier [16]. In this method, the sieves used, of the AFNOR type, were arranged in decreasing order of sieve mesh diameter size from 630 microns to 80 microns. The observation of the shape of the grains was carried out by micrography.

Principal Component Analysis (PCA) was performed using the results of the XRF to classify the sampling sites according to the proportions of chemical compounds (including silica content) present in the samples. It was performed on a data matrix consisting of fourteen (14) variables (the chemical compounds) and fifteen (15) observations (sampling sites distributed along the sedimentary basin, (Figure 1). The XLSTAT version 2016.02.27444 statistical software was used to perform this statistical analysis.

3. Results and discussion

3.1. Chemical composition of sedimentary basin sand

Figure 2 below shows the proportions of silica contained in each sample. The analysis of Figure 2 shows that the silica contents range from 78.60% at Port-Bouët to 97.41% at Maféré. The sand of Ebimpé, Bonoua, Krinjabo, Ebouenda, and Maféré have silica contents higher than 96%. These results are similar to those obtained by Marteau et al. in the Fontainebleau sand with silica contents between 95% and 99% [1, 10, 17].

In view of the results below (Figure 2) and according to British Standards: 2975 (1958 & 1988) and U.S. specifications (Norton, 1957), the sand of Bassam, Bonoua, Ebouenda, Krinjabo, Ebimpé and Maféré would be usable for the production of amber quality glass. Indeed, this quality of glass requires more than 95.0 % silica [20].

The quality of a silica-based glass is influenced by the presence or absence of other chemical compounds contained in the silica sand. The determination of these impurities is important for the choice of raw material for glass manufacture.

Indeed, the XRF analysis also revealed other chemical compounds contained in the samples. These are alumina (Al_2O_3), iron trioxide (Fe_2O_3), sulphur trioxide (SO_3), potassium oxide (K_2O), titanium dioxide

(TiO_2) and magnesium oxide (MgO), which are considered impurities in glass production. The contents of these constituents are shown in Figure 3.

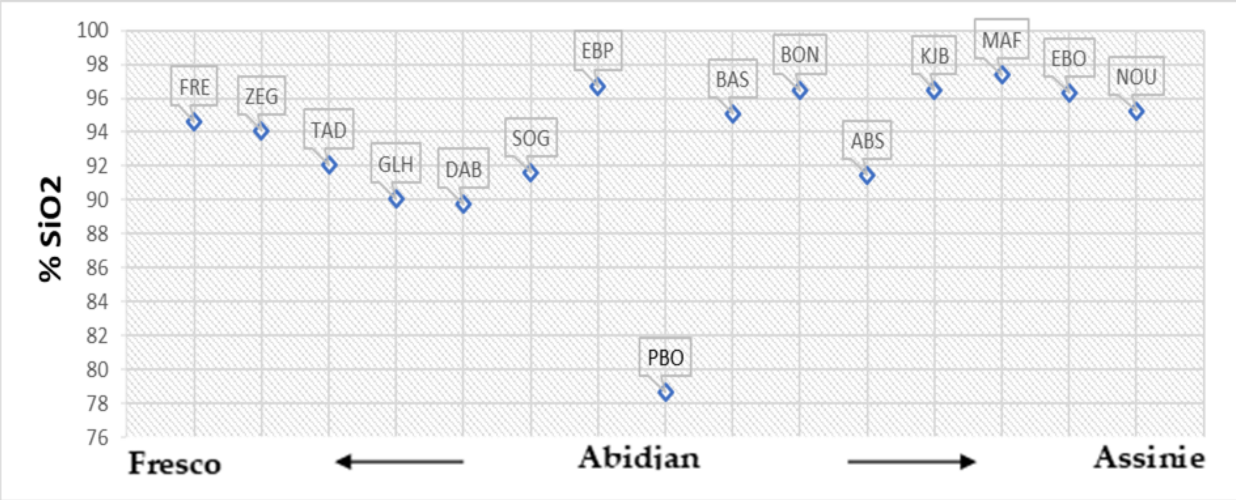
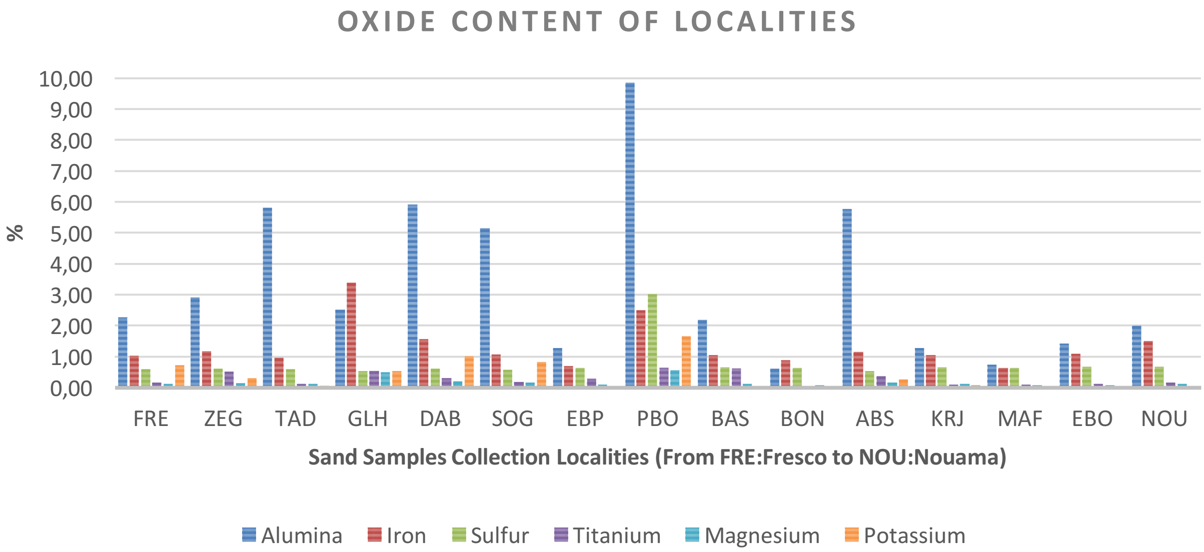


Figure 2 : SiO_2 content of the sand of the Ivorian sedimentary basin.

Legend: FRE: Fresco - ZEG: Zégbé - TAD: Lagune Tadio - GLH: Grand-Lahou - DAB: Dabou - SOG: Songon - EBP:Ebimpé - PBO : Port-Bouët - BAS : Bassam - BON :Bonoua - ABS : Aboissou - KRJ : Krinjabo - MAF : Maféré - EBO : Ebouenda - NOU: Nouama



Legend: FRE: Fresco - ZEG: Zégbé - TAD: Lagune Tadio - GLH: Grand-Lahou - DAB: Dabou - SOG: Songon - EBP:Ebimpé - PBO : Port-Bouët - BAS : Bassam - BON :Bonoua - ABS : Aboissou - KRJ : Krinjabo - MAF : Maféré - EBO : Ebouenda - NOU: Nouama

Figure 3: Proportion of alumina, iron oxide, sulphur oxide, titanium oxide, magnesium oxide and potassium oxide contained in the samples.

Figure 3 shows the levels of impurities in the sand samples. Of all the minor oxides obtained, alumina has the highest value in each sample, with a maximum content at Port-bouet (9.85%). In addition, the Port-Bouët site contains the highest levels of sulphur oxide and titanium oxide among all the samples. The poor quality of the sand at this site, located on the seafront, is believed to be related to anthropogenic activity as well as to the continuous flow of waste water and the disposal of household waste to the site. Sites with a silica content of more than 96% contain between 1% and 1.5% aluminium oxide. This observation is valid for the Bonoua site and the sites east of Aboisso. This proportion of alumina is much lower than that of the sand of Cambodia, Malaysia and Bangladesh, which are respectively 5.61%, 6.02%

[21], and 10.62% [22]. However, the XRF spectrometer analysis of the silica sand from Biskra (Algeria) indicates a value of 0.4% less alumina [23] than all our samples.

All the samples from the Ivorian basin contain less ferric oxide than the sand from the Padma River (Bangladesh), whose content is 3.398% according to the work of Rafi et al [22]. On the other hand, the lower ferric oxide content of 0.7% at the Ebimpé site (Anyama) is higher than that of Cambodia, Malaysia and Biskra (Algeria) estimated at 0.35%, 0.41% and 0.5% respectively [21, 23]. The samples analysed contain less than 0.7% sulphur oxide, except for the Port-Bouët sample, which contains 3% sulphur oxide. The Krinjabo, Maféré and Bonoua quarries contain traces of titanium oxide. The highest levels of this oxide are found at Bassam (0.30%), Grand-Lahou (0.53%) and Port-Bouët (0.63%).

We also note the presence of trace oxides in the samples such as: phosphorus oxide (P_2O_5, 0.18% on average), calcium oxide (CaO, 0.17% on average) and sodium oxide (Na_2O, 0.12% on average).

Subsequently, the correlation between silica and impurities detected by X-ray fluorescence spectrometry was evaluated by Principal Component Analysis.

3.2. Statistical analysis of XRF data

The Principal Component Analysis (PCA) correlation matrix shows in Table 1 quantifies the correlations between the different variables (chemical compounds). In this matrix, the values reflect the degree of correlation and their sign indicates its positive or negative nature. In our case, the PCA matrix reveals that silica is negatively correlated with other chemical compounds except phosphorus. Thus, a sample with a high silica content is low in other oxides and vice versa.

Table1: Correlation matrix between the variables of the XRF analysis.

	SiO_2	Al_2O_3	Fe_2O_3	SO_3	P_2O_5	Cl	TiO_2	MgO	CaO	K_2O	Mn_2O_3	SrO	Na_2O	Cr_2O_3
SiO_2	**1**													
Al_2O_3	**-0.912**	**1**												
Fe_2O_3	**-0.672**	0.397	**1**											
SO_3	**-0.816**	**0.660**	0.421	**1**										
P_2O_5	**0.857**	**-0.644**	**-0.692**	**-0.832**	**1**									
Cl	**-0.809**	**0.541**	**0.743**	**0.861**	**-0.940**	**1**								
TiO_2	**-0.609**	0.474	**0.594**	0.456	**-0.536**	**0.530**	**1**							
MgO	**-0.870**	**0.626**	**0.913**	**0.692**	**-0.899**	**0.904**	**0.688**	**1**						
CaO	**-0.844**	**0.571**	**0.896**	**0.709**	**-0.913**	**0.925**	**0.596**	**0.980**	**1**					
K_2O	**-0.880**	**0.787**	**0.551**	**0.695**	**-0.719**	**0.680**	0.462	**0.730**	**0.768**	**1**				
Mn_2O_3	-0.176	-0.083	**0.794**	-0.106	-0.361	0.382	0.342	**0.594**	**0.584**	0.095	**1**			
SrO	**-0.944**	**0.771**	**0.700**	**0.853**	**-0.873**	**0.888**	**0.597**	**0.883**	**0.901**	**0.926**	0.211	**1**		
Na_2O	**-0.897**	**0.661**	**0.727**	**0.913**	**-0.953**	**0.974**	**0.578**	**0.917**	**0.933**	**0.783**	0.291	**0.945**	**1**	
Cr_2O_3	**-0.759**	**0.635**	**0.828**	0.489	**-0.598**	**0.650**	**0.768**	**0.822**	**0.725**	**0.542**	0.473	**0.706**	**0.668**	**1**

This result shows that except for phosphorus pentoxide the higher the silica content the lower the content of the other oxides. These results could be explained by the fact that sediments always settle with organic particles (probable origin of phosphorus). It could also be contamination after deposition by plant or animal debris. The first factorial plane represented by factors F1 and F2 accounts for 86.07% of the total inertia (Table 2). This plane (F1 and F2) then expresses most of the global information. Figure 4 below shows the projection of the variables (oxides) and observations (sampling sites) into the first factorial plane.

Table 2: Variance as a function of eigenvalues

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14
Eigenvalues	10.19	1.86	0.88	0.53	0.27	0.19	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.00
Variability (%)	72.76	13.31	6.31	3.79	1.95	1.35	0.29	0.14	0.04	0.03	0.01	0.01	0.00	0.00
% cumulated	72.76	86.07	92.38	96.18	98.13	99.47	99.77	99.91	99.95	99.98	99.99	100.00	100.00	100.00

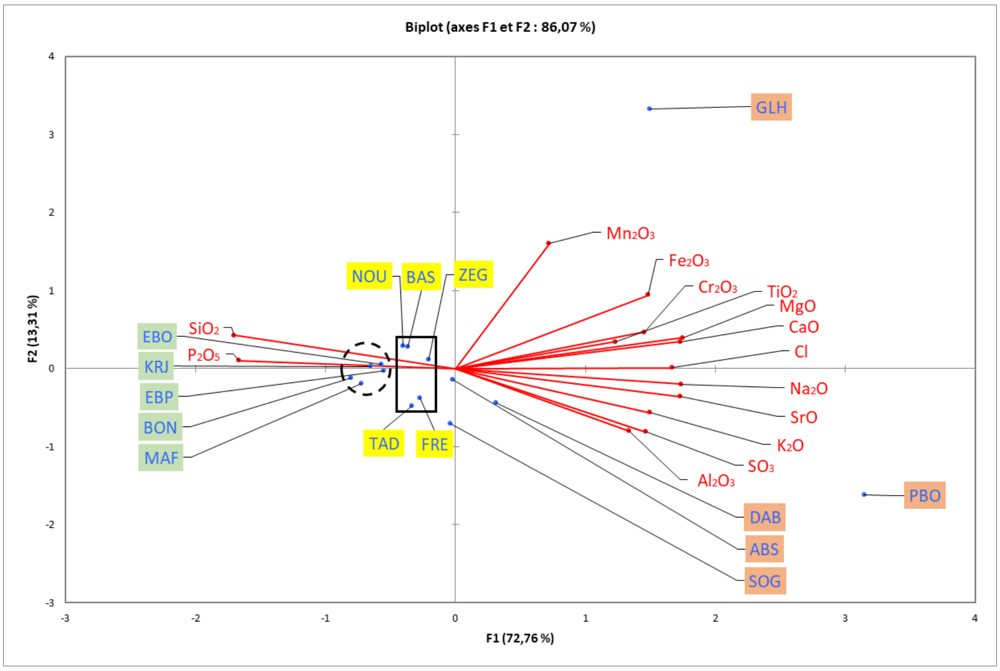


Figure 4: Projection of chemical composition and sampling sites on the factorial foreground

Legend: FRE: Fresco - ZEG: Zégbé - TAD: Lagune Tadio - GLH: Grand-Lahou - DAB: Dabou - SOG: Songon - EBP:Ebimpé - PBO : Port-Bouët - BAS : Bassam - BON :Bonoua - ABS : Aboissou - KRJ : Krinjabo - MAF : Maféré - EBO : Ebouenda - NOU: Nouama

Group 1:		*Rich in SiO_2 (>96%) and contain the same amount of P_2O_5 (0.2%). (sites located in the East of the basin)*
Group 2:		*Contains more impurities and less silica compared to other sites and is located in the west of the basin and in Abidjan.*
Group 3:		*Includes low-pollution sites located at the extremities of the basin and containing more than 92% silica.*

The factor 1 expressing 72.76 % of the variance pits silica and phosphorus oxide against the other oxides in the samples. The proportions of phosphorus and silica are closely related and move in the same direction but differ by a factor of 2. which expresses 13.31% of the variance.

Three groups can be identified using the PCA biplot (Figure 4). Thus, group 1 sands with a silica content greater than 96% contain approximately the same proportion of phosphorus oxide (0.20% on average) and low levels of other oxides. These sands are mainly located in the east of the basin. These sands (group 1) with the highest silicon oxide content (97.41%) are located in a zone that is only slightly affected by anthropic action which would justify the low levels of impurities in these sands. Indeed, agricultural activity generates impurities through the use of crop protection products [24]. The group 2 is characterized by a silica content of less than 92% and contains more impurities and trace amounts of phosphorus oxide (0.14% on average). However, these sand samples contain less strontium, less manganese, less chromium and the same proportion of chlorine on average than the Padma rivers sands [22]. The sites in this group are the most polluted by urbanization and domestic waste. The sites in the third group are located at the extremities of the basin and have an intermediate composition between the other two groups. The granulometric analysis as well as the grain morphology of the silica sand of Maféré (better quality sand of group 1) was carried out.

3.3. Particle size distribution and grain shape

Figure 5 below shows the results of the granulometric study of Maféré sand (97.41%). The analysis of Figure 5 shows that the Maféré sand is of fine grain size with 66.8% of the grains having a size less than or equal to 500 microns. This fine granularity is ideal for a silica sand intended for the production of silica glass. Such grain sizes are consistent with those used by the glass-making industry [22, 25]. Furthermore, the sand of the Padma River Delta (Bangladesh) is finer with 72% of the grains having a granularity lower than 500 microns. Those of Fontainebleau (France) are also finer with 50% of the grains having a size ranging from 100 microns to 150 microns and those of Beauchamp (France) are finer with 50% of the grains having a size lower than 140 microns. [17, 22]. Moreover. the micrograph of Maféré sand shows mostly rounded and not very elongated grains (Figure 6). The shape of the Maféré quartz grains is the same as that of the silica sand of the sand quarries of France [1, 10].

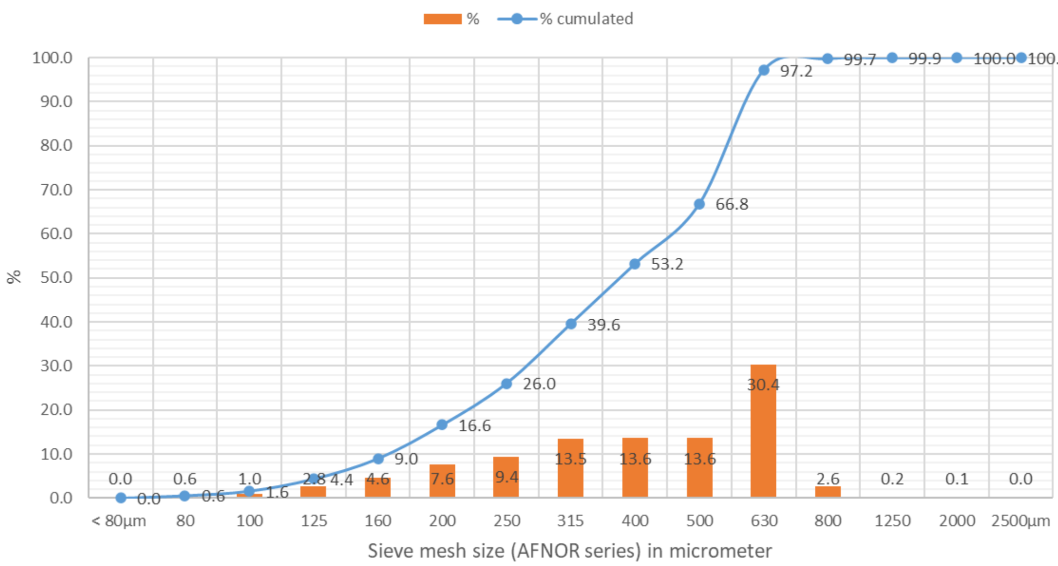
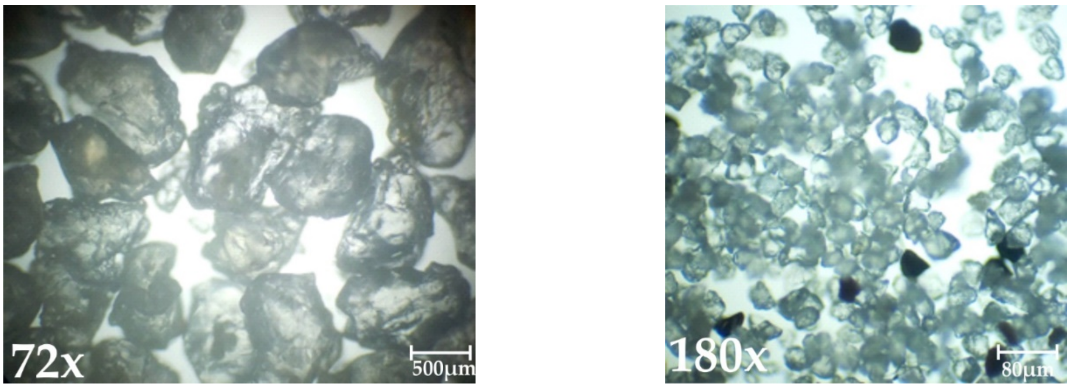


Figure 5: Granulometry of Maféré Sand



(a) **(b)**

Figure 6: Micrograph of 500 microns (a) and 80 microns sand (b)

This is evidence of a long transport since the break-up of the bedrock. In fact. the agents of erosion move the detritus from the bedrock to the basin. where the sediments are deposited.

Conclusion

The objective of this study was to characterize the sand of the Ivorian sedimentary basin in order to provide solutions for the production of soda-lime glass from local silica. Sampling and analyses of sand from the Ivorian sedimentary basin made it possible to identify three groups of sites occupying the entire extent of the basin from west to east. They reveal that this sand is rich in silicon dioxide (SiO_2). The silica highest concentrations are located in the east of the basin towards the border with Ghana. North of Abidjan there are sites with high silica content (such as the locality of Ebimpé) but these are under the effect of anthropogenic activities pollution. The sand from the Maféré site containing 97.41% silicon oxide with 66.8% of grains sizes less than or equal to 500 microns can be used for soda-lime glass making.

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