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Structural Order of Clays from Gounioube's Deposit (Ivory Coast): Study by Electron Paramagnetic Resonance Spectroscopy

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Abstract Cristallinity in kaolin samples from Gounioube's deposit is studied. For this purpose, the behavior of iron and electronic defects related to irradiation damage in these clays is examined by using Electron Paramagnetic Resonance spectroscopy measurements, which point out the presence of structural defects in these materials. A deep inspection carried out by comparison of raw and bleached samples also confirms poorly cristallized samples kaolinite.

Keywords: *clays, kaolin, epr, cristallinity, iron status, structural defects*

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1. Introduction

Clay materials are part of many non-metallic mineral resources in Ivory coast. Among the sites containing these materials, there is Gounioube's deposit. Clays mined from this deposit were previously characterized to determine their potential technological applications since it is well established that clay materials may be used in several domains as ceramic floor tiles [1,2], bricks [3,4], roof tiles [5,6], dinner wares [7], sanitary wares [8], and glasses [9]. At this end, the investigations were carried out through standard methods as Differential Thermal Analysis, X-Ray Diffraction, Mössbauer, UV-visible and InfraRed spectroscopies, which allowed to determine mineralogical and physico-chemical properties of these clays. It is in such context that cristallinity studies were performed. It should be noted that cristallinity is a feature that is very sensitive to the subtle environmental changes [10]. A same mineral clay may show different degrees of crystallinity in vertical and lateral profiles [11]. During alteration, the crystallinity of particular mineral phases develops. It begins with the nucleation and crystalline growth as controlled by many internal (structural) and external (environmental) conditions. Crystallinity changes may also result from recrystallization, which can be either spontaneous or induced. Cristallinity studies carried out on Gounioube's kaolin samples seem indicate that clays from this site present structural defects at long-distance [12]. The validity of this hypothesis is elucidated through the present work, which will also allow to extend the analysis to short-distance level. For this purpose, the Electron Paramagnetic Resonance (EPR) spectroscopy measurements are used to study the behavior of iron and electronic defects related to irradiation damage in these clays. This path will consist to deepen the investigation of the effects of iron statutes on the structural order of Gounioube's deposit clays.

2. Materials and Methods

2.1. Materials

The present work is concerned fourteen kaolin samples. These clays have been collected in different pits (Figure 1), at different depth on the Gounioube's deposit (City of Anyama) located at 30 km from Abidjan in the south of Ivory Coast [13,14] and referenced from G1 to G14. The field is mainly out of a detrital sandy-clay plateau from the terminal continental level (Miocene-pliocene), resulting from a ferrallitic alteration of the basal rocks under humid tropical climate [13,15,16].

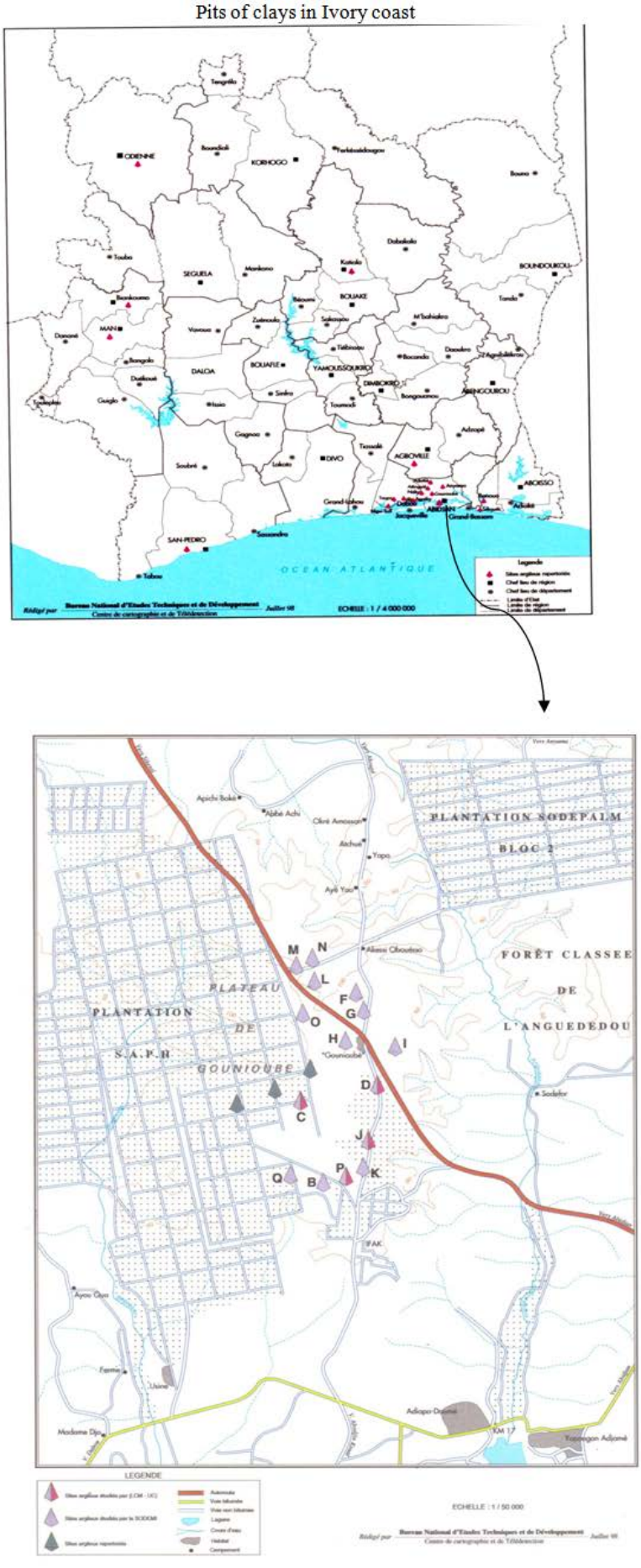

Figure 1. Map showing different pits of Gounioube's deposit (city of Anyama, Ivory Coast)

2.2. Experimental Method

The kaolin samples were analyzed by EPR spectroscopy in an ESP300E spectrometer, using X band (9.422 GHz) at room temperature, with a gain of 8.10^3 for overall samples and 2.10^4 for defaults. Magnetic field calibration was performed with the DPPH standard (g = 2.0037 ± 0.0002). Calibrated silica tubes (suprasil grade) were filled to a depth of 15 mm with a known amount of dry powdered sample (about 40 mg) prior to analysis. There is currently no standard to measure the concentrations of the various paramagnetic species found in natural kaolinites. The comparisons between samples are therefore made by determining either the surface area or the intensity of the experimental signals, which gives a relative estimation of the concentrations of the corresponding paramagnetic species. Thus, the EPR spectra were recorded in the form of a signal derived from the absorbance whose intensity varies as a function of the applied magnetic field and calibrated with respect to a standard (DPPH) which allow to determine the accurate position, in energy of the bands. The effect of reducing/chelating treatment on the kaolin samples was analysed through CBD method [17,18,19,20]. The chemical and mineralogical compositions obtained by Inductively Coupled Plasma (ICP) and X-Ray Diffraction (XRD) techniques respectively indicated that the major minerals of theses clays are kaolinite, quartz and mica [21]. Mössbauer spectroscopy allowed to observe the iron role during thermal transformations and showed that iron is found in various forms such as Fe^{3+}, Fe^{2+} in octahedral substitution into the kaolinite network according to types of iron oxyhydroxides (hematite and / or goethite) and ferric gels [12]. It appears that Fe^{3+} is one of the most common impurities in the kaolinite structure and a low cation exchange capability is generally attributed to this mineral [22].

Table 1. Cristallinity indexes of kaolin samples from Gounioube's deposit where R1 and R2 indexes are deduced according Liétard [24] definition, DC(001) is angular width at half intensity of the (001) line of kaolinite, P1 and P2 indexes are evaluated according to Liétard [24] and Cases *and al.* [25] definition.

Samples	R1	R2	DC(001)	P1	P2
G1	-	-	143	-10×10^{-4}	0.758
G2	0.90	0.98	135	-42×10^{-4}	0.806
G3	0.58	1.09	119	-16×10^{-4}	0.715
G4	0.65	1.08	119	-19×10^{-4}	0.762
G5	0.48	0.81	149	-17×10^{-4}	0.745
G6	0.92	0.66	132	-33×10^{-4}	0.772
G7	0.75	0.65	132	-29×10^{-4}	0.791
G8	-	-	140	-33×10^{-4}	0.769
G9	0.67	1.07	163	-49×10^{-4}	0.823
G10	0.76	1.05	145	-6×10^{-4}	0.765
G11	-	-	132	-13×10^{-4}	0.776
G12	-	-	132	-7×10^{-4}	0.691
G13	-	-	119	-20×10^{-4}	0.720
G14	0.55	0.68	140	-33×10^{-4}	0.758

The experimental cristallinity indexes of the fourteen kaolin samples are also previously [23] determined and are listed in Table 1. In these data, R1 and R2 indexes evaluated according to Liétard [24] definition and DC(001) corresponding to the angular width at half intensity of the (001) line of kaolinite are deduced from X-Ray Diffraction measurements whereas P1 and P2 indexes determined according to Liétard [24] and Cases *and al.* [25] definition are recorded from Infra Red spectroscopy technic.

3. Results and Discussion

Figure 2(a-d) show the EPR spectra of the fourteen kaolin samples. These results are distributed according different pits of Gounioube's deposit. All spectra exhibit similar shape and their appearance is characteristic of natural kaolinites [23,26]. Such curves result from the superimposition of various signals described in the literature [27,28,29,30], which can be distinguished into two kinds of Fe^{3+} ion domains.

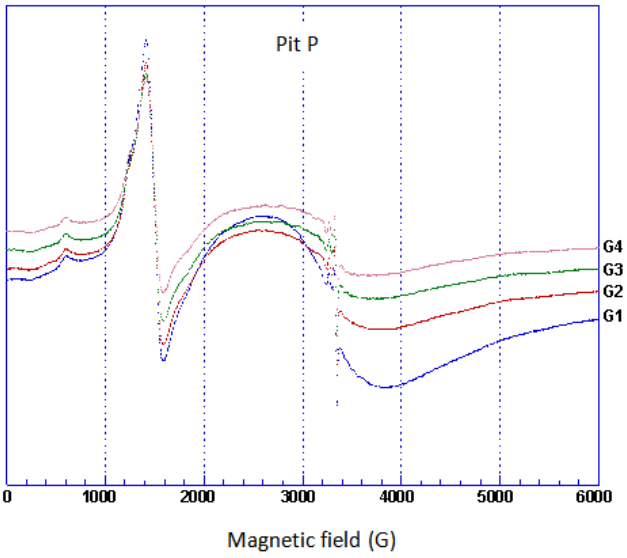

Figure 2(a). EPR Spectra of four kaolin samples from pit P of Gounioube's deposit

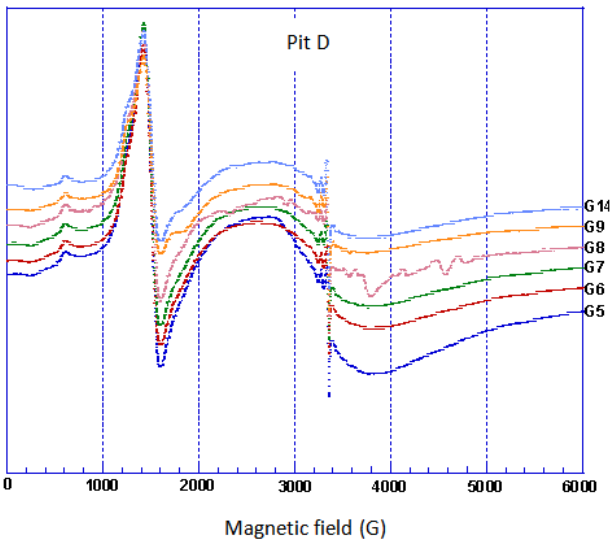

Figure 2(b). EPR Spectra of six kaolin samples from pit D of Gounioube's deposit

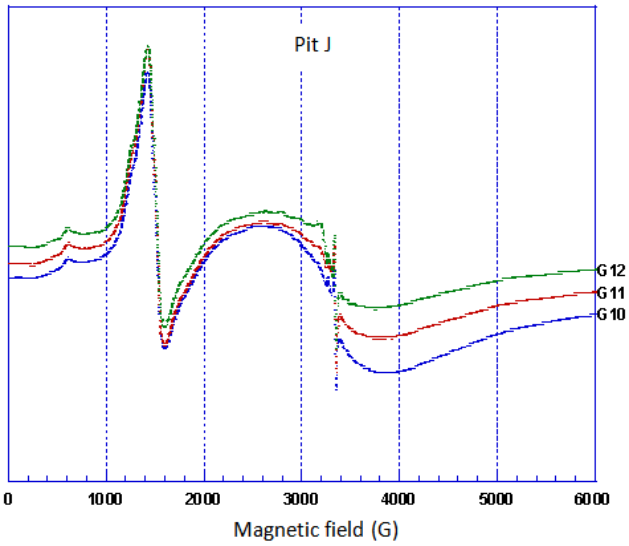

Figure 2(c). EPR Spectra of three kaolin samples from pit J of Gounioube's deposit

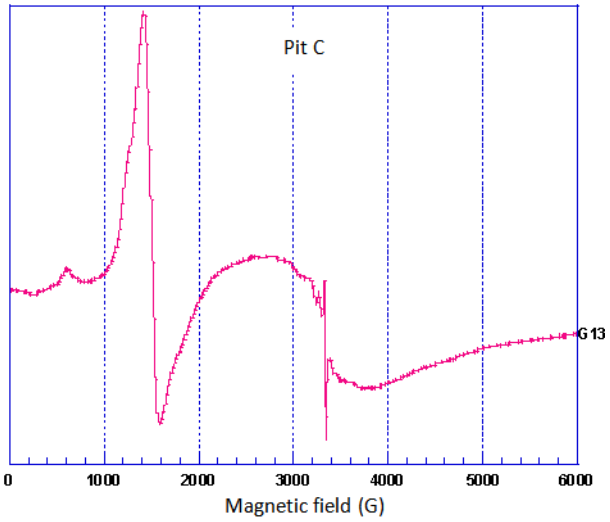

Figure 2(d). EPR Spectra of kaolin samples from pit C of Gounioube's deposit

The first one located at low magnetic field ranged between 1200 and 2000 Gauss, is diluted domain, showing a complex signal due to ferric iron as an impurity in kaolinite. This is attributed to isolated Fe^{3+} ions occupying Al^{3+} sites of the kaolinite structure. It can be due to both of distinct sites referenced Fe(I) and Fe(II) [22,27] localized in diluted domain and showing different distortions [31]. The other domain governed by non-homogeneously broadened lines and by magnetic dipole-dipole interaction among Fe^{3+} ion centers is referred to concentrated domain. In this area, the large signal based on 2500 G is due to oxyhydroxides of iron associated to the kaolinite whereas the strait intense signal centered on 3300 G is assigned to electronic defects located into the kaolinite network. This former can be explained either to spin-spin interactions among irons in the oxy-hydroxides adsorbed to the mineral indicated or to ferric gels [32,33]. Its relative large amplitude in Gounioube's kaolin samples indicates sufficiently high concentration of Fe(I) probably due to the existence of strait structural connections taking place between oxyhydroxides of iron and the kaolinite. Furthermore, the contribution of electronic defects to this signal can also involve the surface properties of kaolinite and govern the behavior of its processing. By comparison of these spectra to those of well cristallised kaolinites in literature as Georgia clays [34], these signals are characteristic of crystalline defects at high-distance. This behevior is in good agreement with the cristallinity indexes that are deduced from Infra Red and X-Ray diffraction spectra [23] and summarized in Table 1. Indeed, these indexes correspond to values of P1 negative and P2 less than 1, a signature of poor cristallinity. On the X-ray diffraction spectra recorded in the same context, the diffractograms showed that the different peaks are weakly resolved [23]. In addition, the apparent coherent domain of these kaolin samples appears significantly different from what is expected for well crystallized kaolinites. All of these experimental methods emphasize a poor cristallinity in kaolinites, meanning a structural desorder in Gounioube's clays. Moreover, in the framwork of a previous work [12], the study of Fe-role during thermal transformations and all phases containing iron through Mossbauer spectroscopy technic showed low mechanical strengths for the kaolinite samples from Gounioube's deposit. Such situation was due to the fact that a part of Fe-content is located outside the clay structure and does not contribute to the clay densification process, so that the mechanical strengths of the clays were found low [12].

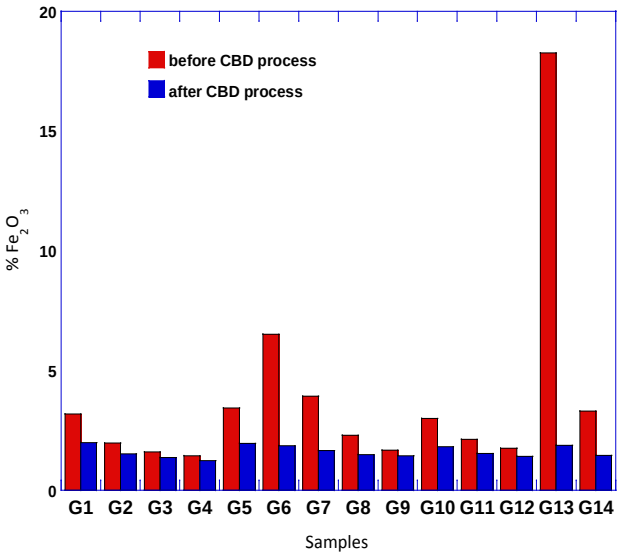

Figure 3. Comparison of content of ferric ion in kaolin samples of Gounioube's deposit before and after CBD treatment

CBD treatment that consists to clays bleaching is carried out to remove the iron oxyhydroxides locacted in clays. Figure 3 shows the comparison of Fe-content between the samples before and after this treatment. As showed on the histograms, the plots show a decrease of Fe-content after CBD process for all studied samples. It appears clearly that the bleaching is widely efficient for G13 for which the magnitude of Fe_2O_3 varies from 18.27% to 1.87%, a value that is almost common for the other samples investigated. This content still remains relatively high meaning that a certain Fe-content could not be eliminated by the CBD treatment. This certainly corresponds to Fe incorporated in the crystal structure of the native clay. CBD treatment shows that most of the Fe contained in Gounioube's kaolin samples is included in

iron minerals, intimately associated with kaolinite what is a usual occurrence. In order to distinguish the iron under occlusion status from that one located inside the clay structure, the data recorded after CBD treatment are compared to that one evaluated in RPE spectra.

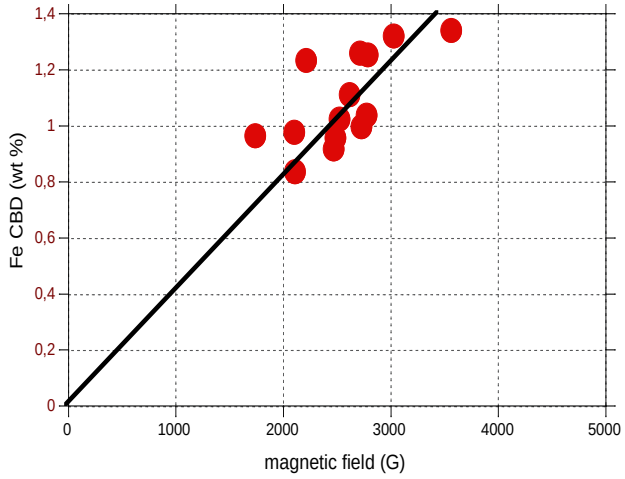

Figure 4. Evolution of iron after CBD treatment as a function of magnetic field for the fourteen Gounioube's clays

The results are displayed in Figure 4, which shows the evolution of residual amount of iron after CBD treatment as a function of magnetic field. As can be seen on the plot, there is a low dispersion of the distribution of the ferric ion but no correlation with magnetic field in particular at low field since correlation coefficient is found relatively low. By comparison of these data to RPE Spectra in Figure 2, Figure 4 shows the disappearance of signals at low magnetic field ranged between 1200 and 2000 G and also the strait intense signal centered on 3300 G. This indicates that the ferric Fe referenced as Fe(I) and Fe(II) is under a non-occluded status between the kaolinite leaflets. Thus, the plot in Figure 4 is only due to nanoscopic iron oxyhydroxides intercalated between the layers of the kaolinite as observed also by others authors [35,36].

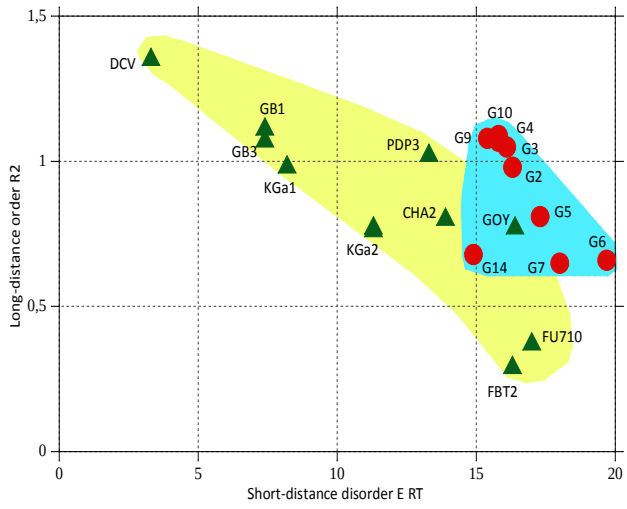

Figure 5. Comparison of order-desorder between kaolin samples from Gounioube's deposit and reference clays retrived from literature [37,38]. Red circles =kaolinites from Gonioube's deposit. Green traingles = reference clays

The indexes of cristallinity listed on Table 1 established that kaolin samples from Gounioube's deposit are characterized by a structural disorder. An inspection of this feature is carried out to provide a better understanding of its behavior. At this end, few clays for which the order-disorder properties are well established and available in litterature [37,38], are considered as references in order to make comparison with our data. Figure 5 exhibits all of these data in which the references are exhibited in yellow zone whereas our experimental values are indicated in blue domain. The kaolin samples that are not displayed in this Figure have a value of zero R2 (see Table 1). In comparison to our data, the distribution of reference clays is characterized by a large dispersion for which various degrees of order and disorder can be distinguished. These may be described by three kinds of regime. Clays nominated as DCV, GB1, GB3 and KGa1 are governed by an order at long-distance and a disorder at short-distance while it occurs for references FU710 and FBT2 a disorder at short-distance. Gounioube's clays behave as PDP3, CHA2, KGa2 and GOY, the third group of references. Their location on the plot indicates a structural disorder at both of short and long distances. Our data are so in good agreement with the indexes retrieved from X-Ray Diffraction and InfraRed spectroscopy meaurements, which predicted a poorly cristallized structure in kaolin samples from Gounioube's deposit.

4. Conclusion

The present study allowed to investigate the structural order of kaolin samples from Gounioube's deposit. The iron status in raw materials before and after bleaching by CBD treatment underlines the structural defects in which it appears an desorder at high and short distances. This result confirms thus the hypothesis concerning a lack of cristallinity in Gounioube's clays.

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