Crystallochemical Study of Kaolinitic Minerals from Anambra And Ebonyi States of Southeastern Nigeria.

Anarado, C.J.O*, Eboatu, A.N, Anarado, C.E, Egwuatu, C.I..

1.Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Nnamdi Azikiwe University, PMB 5025, Awka, Nigeria.

Tel: +2348036695586

ABSTRACT

The major deposits of Kaolinitic mineral were sampled, with the aim of studying possible solid solution, ionic substitution, and thus, ultimately understanding the the nature and sizes of nanoparticles in the mineral deposits. Powder X-ray Diffraction Analysis, X-ray Flourescence analysis and Physical tests were used to study them. Kaolinite and Quartz were the major phases in the raw Anambra Kaolin, while the Ebonyi Kaolin had Kaolinite, Quartz, Cristobalite, Montmorillonite and Goethite as major phases. The quartz were deposited in hexagonal crystalline structure, with cell parameters : a- 4.91239A, b-4.91239A, c-5.40385A. The Kaolinite had Monoclinic structure, with cell parameters: a-5.16000A, b-8.95232A, c-7.39000A. Cristobalite had Cubic structure, with a,b,c,=7.16000A. Montorillonite had hexagonal structure, with a-5.21000A, b-5.21000A, c-22.00000A. Goethite had Orthorhombic structure, with a-4.61880A, b-9.95280A, c-3.02360A. The Specific Gravity of the Anambra deposite was 2.2, while that of Ebonyi was 2.6. Both had relatively low Moh's hardness value of 1.0. While the Anambra deposit showed white streak, the Ebonyi deposit showed Yelllowish brown streak. The Anambra deposit had the major oxides as $-Al_2O_3$ = 27.71%, SiO_2 = 65.76, giving a ratio of 2.37, while the Ebonyi deposit had Al_2O_3 =5.22, SiO_2 =77.05, with a ratio of 14.76. Both ionic substitution and solid solution occurred in the Ebonyi deposit. Montmorillonite has replaced some Quartz in its hexagon structure, instead of the usual Monoclinic structure. The Kaolinite also had a Triclinic structure instead of hexagonal structure expected.

The industrial application of these minerals would be significantly impacted by the nano-structural changes.

Key words: Mineral; Nano-particles; Streak; Solid Solution; Hexagonal; Triclinic ; Orthorhombic.

Introduction.

Minerals are naturally occurring inorganic substances that have distinctive chemical compositions and atomic structures, which usually form rocks (Robin, 1989; Read, 2005). Mineraloids may exist without a distinctive chemical composition and structure. Of the over two thousand minerals known, out of which only about a hundred and twenty are common, silicates are the commonest class (Read, 1980; Rafferty, 2012). This is surely due the high abundance of Silicon and Oxygen in the earth crust.

Abundance of minerals varies geographically and geologically, a great deal. Each region of the world therefore has certain peculiarities in mineral deposits. Africa, certainly has her good share of both native minerals and and salt minerals (Egbai, 2013).

The complex chemical reactions that occur in both the molten magmatic and hydrothermal fluids in the earth crust, under enormous and varying physical conditions are fairly known to scientists (Alexander, 1980; Read, 2005). As a result of these, a lot of phenomena are associated with minerals which end up affecting their physical and chemical properties. Atomic/ionic substitution, solid solution, isomorphism, pseudomorphism, polymorphism are some of the post-formation phenomena that affect these properties. The extent of these processes and their effect vary with deposits.

The physico-chemical properties of minerals affect their uses or otherwise. Diamond and Graphite, both polymorphous carbon minerals, have different atomic structures, physical properties, and different uses. Yet, cubic diamond has different properties from the hexagonal diamond. Again, even in the cubic diamond used for ornamental purposes, the twinned crystal diamond mineral posses great workability problems, thereby reducing its use and value (Deffeyes and Deffeyes, 2009).

Apart from the engineering applications of minerals, they are great sources of inorganic chemicals.

Background.

Nigeria has large deposits of many minerals. Most of these deposits are found in the north-central Nigeria, with the belts often crossing into the eastern Nigeria, obviously following the geologic formations (Arogunjo, 2007). In the eastern Nigeria, Ebonyi state has much more mineral deposits than all the four other political states of Anambra, Enugu, Abia, and Imo. The research looked at the Kaolin which is a clay deposit common to both Ebonyi and Anambra states, with a view to studying their crystallochemical characteristics. The exploitation of the minerals presently is largely informal.

Methods.

Two deposits in Anambra state, and one in Ebonyi state, were sampled for Kaolin, as the miners were mining.

Hand colour: The colours were noted after sensory observation.

Streak: The streaks were studied with streak plate method.

Hardness: The hardness of the samples were measured using the Moh's method. Specific gravity: The simple displacement method was used to measure the specific gravity of the samples.

Elemental Analysis: 0.46g, each of the samples were used to make 0.09g/cm^3 pellets, with which X-ray Flourescence analysis was carried out, using Canberra SL12170 model of spectrometer.

Crystallography: The Powder X-ray diffraction (XRD) study was used, with Bruker D8 Advance powder diffractometer, equipped with sealed x-ray tube (CuKα radiation, wavelength - 1.54178 Å).

Results.

Table 1. Results of the Physical tests on the Kaolin samples.

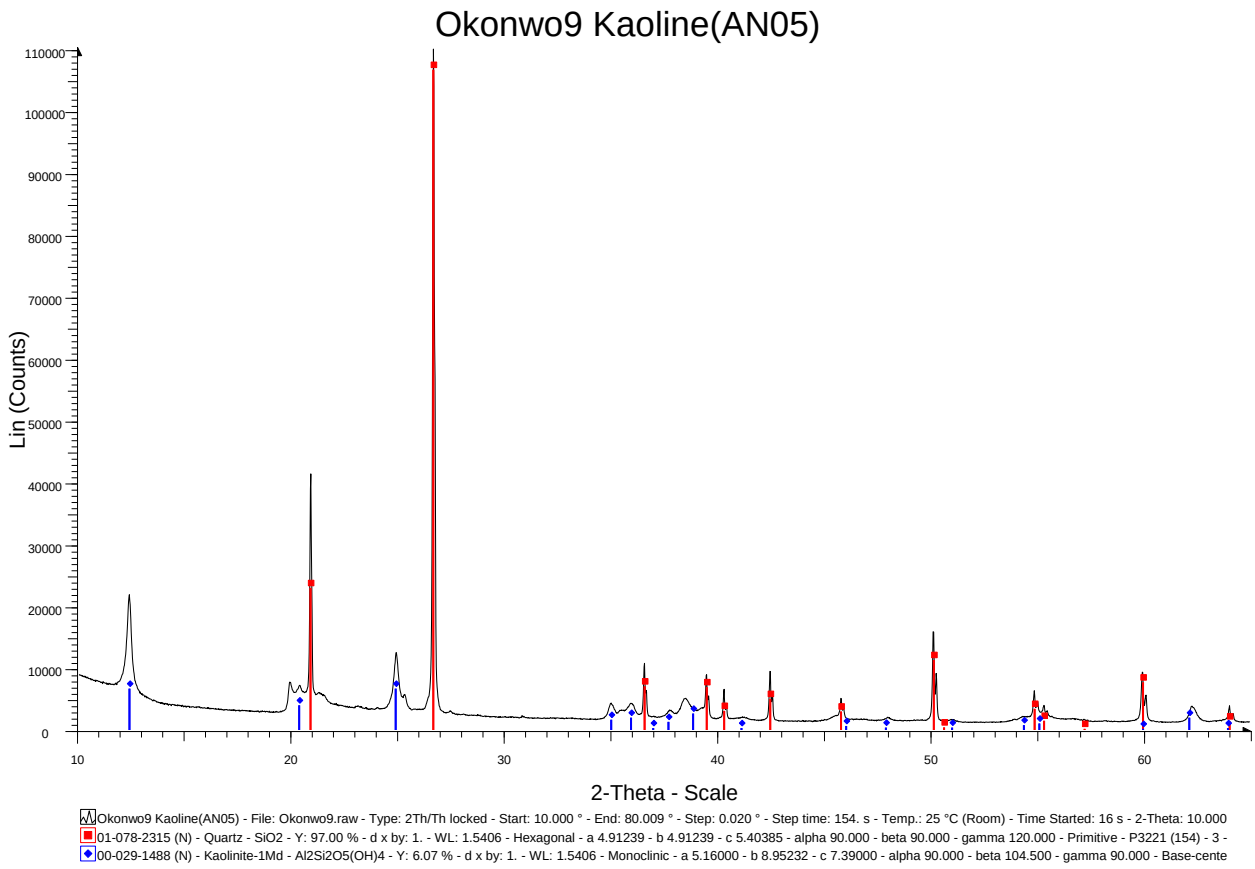
Test	Anambra 3	Anambra 5	Ebonyi 1			
Colour	Off white	Offwhite	offwhite			
Steak	White	white	Yellowish brown			
Hardness	1.O	1.O	1.O			
Sp Gravity	2.2	2.2	2.6			

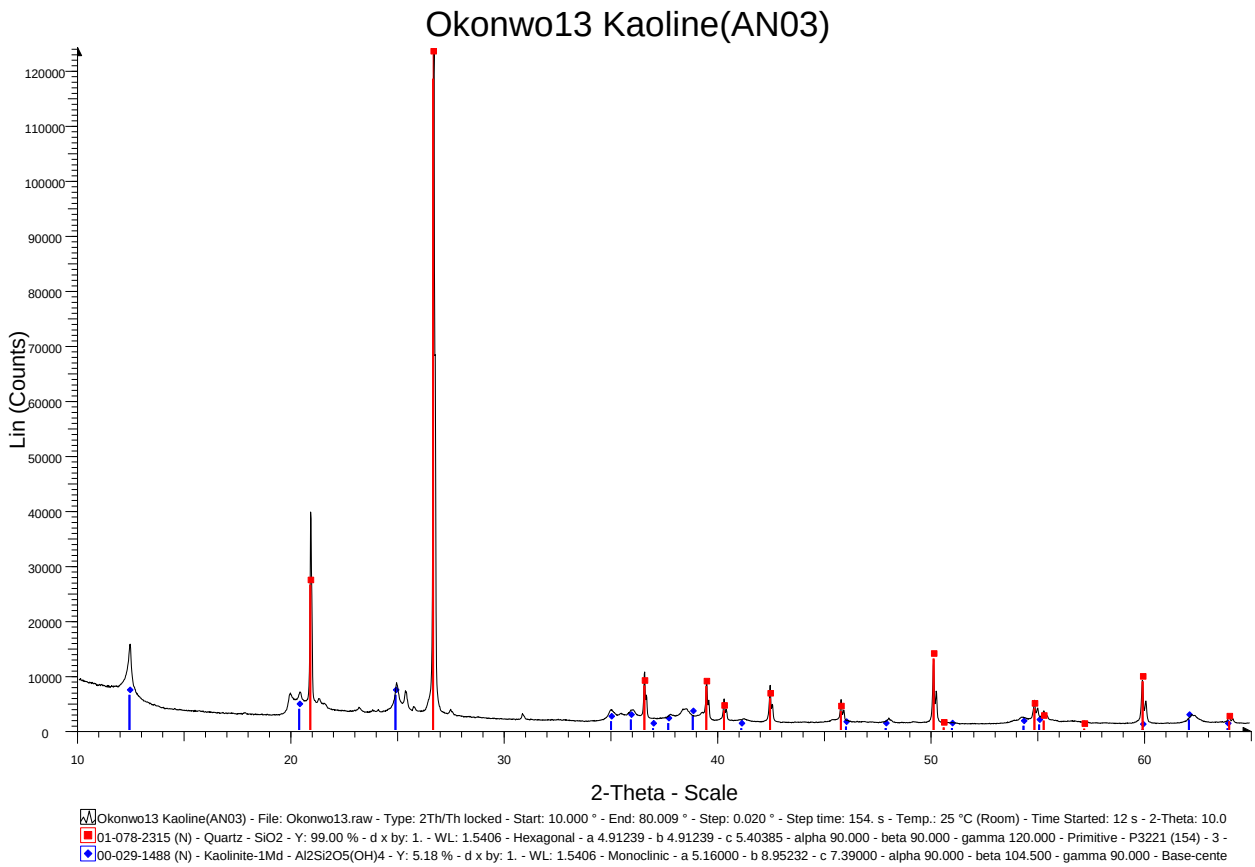
Table 2. Results of Elemental Analysus on the Kaolin samples.

Sample	Al%	Si%	Ca%	K%	Mn %	Ti%	Fe%	Cu%	Pb%	Zn%	Cr%	Co%
AN03-Kaolin	3.315	10.887	ND	0.565	0.766	11	7.77	ND	ND	0.141	1.31	0.482
AN05-Kaolin	14.665	30.739	ND	0.552	0.73	7.84	4.4	ND	ND	0.161	1.08	0.515
EB-Kaolin	5.56	18.811	2.075	1.758	0.898	2.78	8.74	ND	ND	0.13	1.23	0.362

Table 3. Oxides.

Oxide	Anambra 3	Anambra 5	Ebonyi
Al_2O_3	27.71	27.71	5.22
SiO_2	65.76	65.76	77.05
SiO_2 /Al_2O_3	2.37	2.37	14.76


Okonwo9 Kaoline(AN05)
Lin (Counts)
2-Theta - Scale
Okonwo9 Kaoline(AN05) - File: Okonwo9.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 80.009 ° - Step: 0.020 ° - Step time: 154. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 10.000
01-078-2315 (N) - Quartz - SiO2 - Y: 97.00 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.91239 - b 4.91239 - c 5.40385 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3221 (154) - 3 -
00-029-1488 (N) - Kaolinite-1Md - Al2Si2O5(OH)4 - Y: 6.07 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.16000 - b 8.95232 - c 7.39000 - alpha 90.000 - beta 104.500 - gamma 90.000 - Base-cente


Okonwo13 Kaoline(AN03)
Lin (Counts)
2-Theta - Scale
Okonwo13 Kaoline(AN03) - File: Okonwo13.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 80.009 ° - Step: 0.020 ° - Step time: 154. s - Temp.: 25 °C (Room) - Time Started: 12 s - 2-Theta: 10.0
01-078-2315 (N) - Quartz - SiO2 - Y: 99.00 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.91239 - b 4.91239 - c 5.40385 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3221 (154) - 3 -
00-029-1488 (N) - Kaolinite-1Md - Al2Si2O5(OH)4 - Y: 5.18 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.16000 - b 8.95232 - c 7.39000 - alpha 90.000 - beta 104.500 - gamma 90.000 - Base-cente

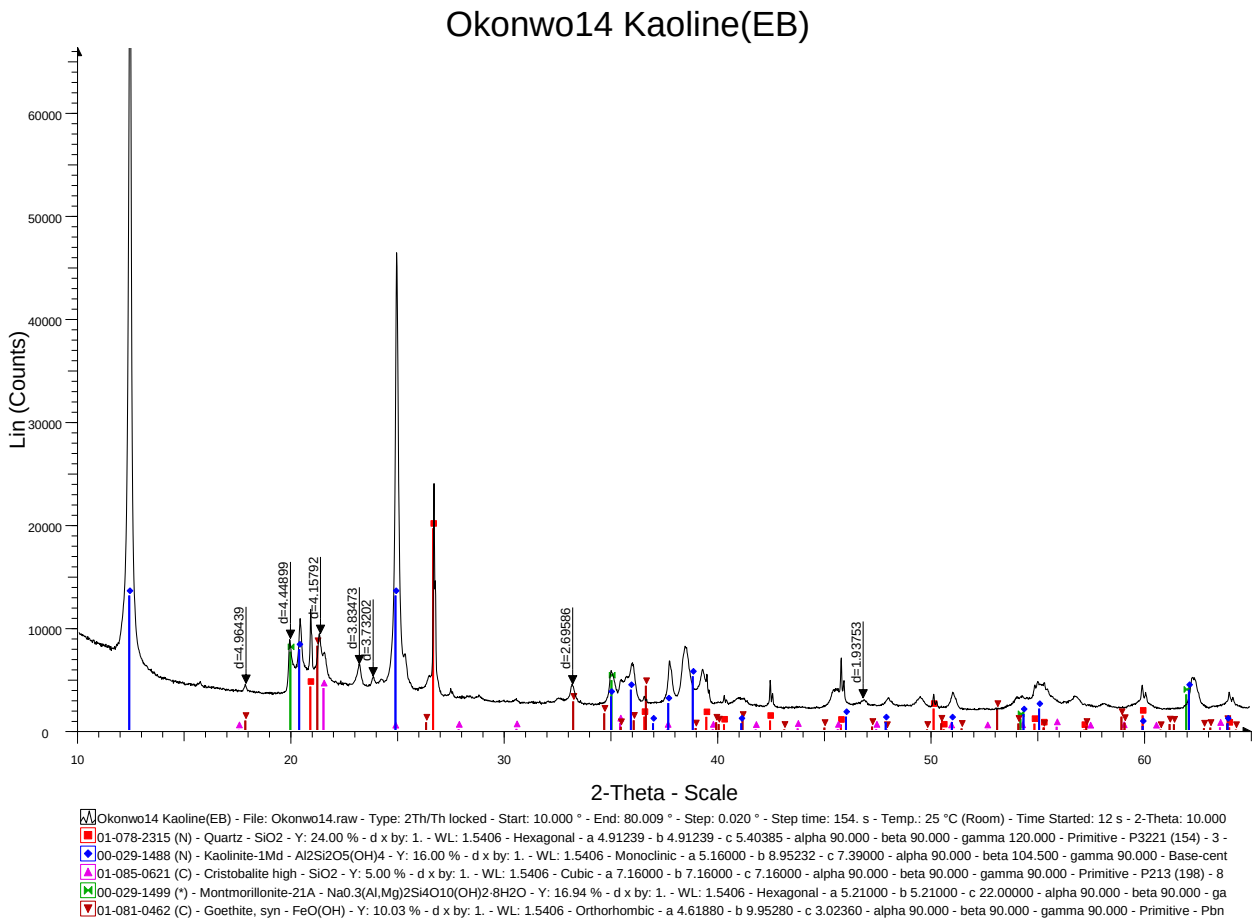


Table 4. Crystal parameters of the Anambra 03 sample.

Deposit	Mineral	Crystal Structure	a (Å)	B	C	A	β	Γ
Anambra 3	Qaurtz -SiO_2	P.Hexagonal	4.91239	4.91239	5.40385	90	90	120
	Kaolinite-$Al_2Si_2O_5(OH)_4$	BS.Monoclinic	5.16	8.95232	7.39	90	104.5	90

Table 5. Crystal parameters of the Anambra 05 sample.

Deposit	Mineral	Crystal Structure	a (Å)	B	C	A	B	Γ
Anambra 5	Qaurtz -SiO_2	P.Hexagonal	4.91239	4.91239	5.40385	90	90	120
	Kaolinite-$Al_2Si_2O_5(OH)_4$	BS.Monoclinic	5.16	8.95232	7.39	90	104.5	90

Table 6. Crystal parameters of the Ebonyi 1 sample.

Deposit	Mineral	Crystal Structure	a (Å)	b	C	α	β	Γ
Ebonyi 1	Qaurtz -SiO_2	P.Hexagonal	4.91239	4.91239	5.40385	90	90	120
	Kaolinite-$Al_2Si_2O_5(OH)_4$	Bc.Monoclinic	5.16	8.95232	7.39	90	104.5	90
	Cristobalite-SiO_2	pCubic	7.16	7.16	7.16	90	90	90
	Montmorilonite-$Na_{0.3}(AlMg)_2Si_4O_{10}(OH)_2.8H_2O$	Hexagonal	5.21	5.21	22	90	90	120
	Goethite-FeO(OH)	Orthorhombic	4.6188	9.9528	3.0236	90	90	90

Discussions.

Two clayey samples collected from Anambra States – one from Ukpor in Nnewi South Local Government Area, coded AN03, and the other one from Ozubulu, in Ekwusigo Local Government Area, coded AN05 – were identified as Kaolin stones. The two samples showed similar physical characteristics and chemical compositions. They had the hand colour of off-white, White streak, Moh's Hardness of 1.0. While AN03 had the Specific gravity of 2.6, AN05 had 2.2. They showed no form, and no magnetic properties. The characteristics are within the literature range of Kaolin deposits (Fakolujo *et al.*, 2012; Egbai, 2013). However, from the elemental analysis, as shown in Table 2, AN05 had higher Al, Si, and Fe contents than AN03. Given this fact, it would have been expected that AN05 would have higher specific gravity than AN03. The SiO_2/Al_2O_3 ratio which is higher for AN03 may give a clue to the observation. Some physico-chemical properties have been reported to vary with the silica/alumina ratio (Gil *et al.*, 2005). The ratio has been explained by same workers as being due to the existence of Al^{3+} in different polyhedra (tetrahedra and octahedra). Silicates have different structural arrangements, which would influence the packing in a mineral, and eventually, the density/specific gravity.

The two phases identified in the Kaolin samples, AN03 and AN05, were Kaolinite, $Al_2Si_2O_5(OH)_4$ and Quartz, SiO_2. In both samples, the Kaolinite was

deposited in Monoclinic crystal structure, with base-centered unit cell. The cell parameters and volumes were the same, as can be seen in Tables 4 and 5. The quartz in the two samples was deposited in the Hexagonal crystal structure, with similar unit cell parameters and volumes. While the two minerals have been reported to associatively occur, Kaolinite is reported to deposit in Triclinic crystal system (Mineral data Publishing, 2001). In this case, the Kaolinite is in Monoclinic crystal structure, with two angles of 90^{o} ($\alpha = \gamma = 90^{o}$). This structure corresponds to alternate layers of tetrahedra and octahedra. The silicon forms a tetrahedron with the oxygen atoms, as in the orthosilicate ion, SiO_4^{4-}, and forms a chain where the tetrahedra are linked at the oxygen ends. The silicon occupies the tetrahedral voids. The aluminum forms an octahedron with the apical oxygen atoms of the silicate and those of the OH^-, and also extends in a chain. The layer consists of one tetrahedral sheet linked to one octahedral sheet. The layers would then be held together by H-bonding. The tetrahedral sheet is bound to distort due to its misfit with octahedral sheet. Bish (Bish, 1993) actually showed that this distortion occurs, with axial compression on the a- and b- axes, away from the ideal tetrahedral values of 5.28 Å and 9.15 Å, respectively. The kaolinites here had a- and b- values of 5.16 Å and 8.9523 Å, respectively, showing the basal tetrahedral compression.

The quartz that was associated with kaolinite here was in hexagonal structure. Quartz is known to be an obdurate solid substance, not easily affected by small changes in temperature, pressure, etc.(Glinnemann *et al.*, 1992). In quartz, the four oxygen atoms of the silicate tetrahedron are bonded, each, to a silicon atom. Each oxygen is shared by two silicon atoms. Thus, one half of each oxygen "belongs" to a given silicon, thereby producing the empirical formula of SiO_2. This would lead to a network of Si—O bonds. This crystal is the same with literature reports for quartz. The bonds were reported as being wholly covalent (Yorder, 2006). The unit cell volume was 112.929 $Å^3$. This is within the range of quartz cell volume (Matsuzuka and Toriyama, 2010). The Kaolin collected from Ebonyi State was found to contain more inorganic compounds than the samples from Anambra State. It had the Kaolinite, $Al_2Si_2O_5(OH)_4$, Alpha Quartz, SiO_2; Montmorilonite, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.8H_2O$; Cristobalite, SiO_2; and Goethite, FeO(OH).

The Kaolinite, $Al_2Si_2O_5(OH)_4$, was as usual, in Monoclinic structure, with Base-centered unit cell of volume, 330.450 $Å^3$. The unit cell parameters are the same with the kaolinites found in the samples from Anambra.

The Quartz was in Hexagonal structure, with Primitive unit cell of volume, 112.929 $Å^3$.

The Montmorilonite, $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.8H_2O$, was deposited in Hexagonal structure, with Primitive unit cell of volume, 617.149 $Å^3$. In the structure, of this 2:1 phyllosilicate, tetrahedra are almost entirely SiO_4^{4-}, without substitution of Si^{4+} by Al^{3+}. The octahedra have two cation sites occupied by the Al^{3+} and Mg^{2+}, in addition to a vacancy. It is the octahedral sheet that develops the -1 charge which is balanced by the Na^+, in the interlayer. The Na^+ ions are hydrated by the water of crystallization. Petiti and co-workers (Petiti *et al.,* 2002) reported similarly charged type of montmorillonite from Germany, and the type with tetrahedral charge. The octahedral charge is believed to be due to the substitution of cations with different valency. ie $Mg^{2+(VIII)} \Longrightarrow Al^{3+(VIII)}$ (Fusova, 2009; Darehkordi *et al.,* 2012). The montmorillonite reported by Mineral Data Publishing (2001) had a monoclinic structure. The 8 molecules of water in this montmorillonite would have caused swelling and thus, elongation on the c-axis (a=5.21Å, c=22Å; as against the former's a = 5.17Å, b = 8.94Å, c = 9.95Å).

The Cristobalite, a silica (SiO_2) polymorph, formed at high temperatures, was in Cubic structure, with Primitive unit cell which had a volume of 367.062 $Å^3$. This volume is much bigger than those of the hexagonal quartz encountered in this work. High temperatures have been reported to cause tilting of the tetrahedra, by change in the Si-O-Si bond angles (Downs and Palmer, 1994). Two forms of cristobalite – α-cristobalite (or low cristobalite) and β-cristobalite (high

cristobalite) – are known. The β-cristobalite is said to be stable at temperatures of 1625ºC 1470ºC, and remains metastably in the form up to 225ºC when the reversible transition to the α-cristobalite occurs (Wright and Leadbetter, 2006; Withers *et al.*, 1989). The α-cristobalite crystallises in tetragonal system while the β-cristobalite crystallises in the cubic system (Downs and Palmer, 1994). This suggests that the cristobalite in this sample was crystallised at high temperature, since it was cubic. Like the quartz, the cristobalite is a tectosilicate, that is made of SiO_4^{4-} tetrahedra, where all the O ends are bonded to adjacent silicon atoms.

The Goethite had the orthorhombic structure, closely related to cubic structure of the cristobalite, with the angles being 90º. The Ebonyi Kaolin manifests the evidence of solid solutions. The trivalent Fe is bound to interact with the sites of the trivalent Al. Cation ordering is known to occur in this kind of situation. (Evstigneeva et.al., 2003). Orderring alters the electrical properties of minerals (Matsuzuka and Toriyama, 2010).

The Ebonyi deposit will be a better lublicant material than the Anambra deposits, due to the influence of montmorillonite.. The kaolin sample contained higher Fe (8.74%) than the other Kaolin samples (7.77% for AN03, and 4.4% for AN05), from Anambra state (Table 2(. The differences in the constituents of this sample from the other two Kaolin samples can be seen from the deeper streak of Yellowish-brown, as against the white streak of the latter.

Conclusions.

The Kaolin deposits have varying Crystallochemical properties. The difference in the contents of the Kaolin samples from Anambra and that from Ebonyi State showed that the same rock can vary in content according to the chemistry of the region of occurrence.

The changes in the crystal structures support the chances of inducing further structureal reordering, that can result in materials of higher values and uses.

References.

Alexander, B.R., (1980), The Science of the Earth, John Wiley and Sons Inc., New York, p15.

Arogunjo, A. M., (2007), Heavy Metal Composition of Some Solid Minerals in Nigeria and Their Health Implications to the Environment, *Pakistan Journal of Biological Sciences*, 10: 4438-4443.

Bish, D.L (1993), The 1:1 Clay Mineral Structure: Kaolinite and Its Relatives, *Clays and Clay Minerals,* 41: 738-744.

Darehkordi , A, Sadegh Hosseini, S.M, and Tahmooresi,M., (2012), Montmorillonite Modified as an Efficient and Environment Friendly Catalyst for One-Pot Synthesis, *Iranian Journal of Sc. and Engineering,* 9: 49-56.

Deer *et al.*, 1966)

Deffeyes, S.K and Deffeyes, S.E., (2009), Nanoscale: Visualising the Invisible World, Massachusset Institute of Technology Books, Massachusset, pp1-50.

Downs, R.T and Palmer, D.C., (1994), The Pressure Behavior of α-Cristobalite, *American Mineralogist,* 79: 9-14.

Egbai, J.C., (2013), Kaolin Quantification in Ukwu-Nzu and Ubulu-Uku, Using Electrical Resistivity Method, *International Journal Research and Review in Applied Sciences,* 14(3):

Evstigneeva , T.L, Rusakov, V.S and Kabalov, Y,K., (2003), Isomorphism in the Minerals of Stannite-Family, *New Data on Minerals. M,* 38: 65- 69.

Fakolujo, O.S, Olokode, O.S, Aiyedun, P.O, Oyeleke, Y.T, Anyanwu, B.U and Lee, W.E., (2012), Studies on the Five (5) Selected Clays in Abeokuta, Nigeria, *Pacific Journal of Science and Technology, 13(1): 83-90.*

Fusová, L., (2009), Modification of the Structure of Ca-Montmorillonite, *GeoScience Engineering, LV (1):* 27-32.

Gil, A, Vicente, M.A, and Konli, S.A, (2005),Effect of the Si/Al ratio on the structure and surface properties of silica-alumina-pillared, Journal of Catalysis, 229:1, 119-126.

Glinnemann , J, King, H.E Jr, Schulz, H, Hahn, T, La Placa, S.J and Dacol , F (1992), Crystal Structures of the Low-Temperature Quartz- Type Phases of $Si0_2$ and $Ge0_2$ at Elevated Pressure, *Zeitschrift für Kristallographie, 198:* 177 – 212.

Jewhurst *et al.*, 2006

Matsuzuka, N and Toriyama, T., (2010), Analysis for Piezoresistive Property of Heavily-Doped Polysilicon with Upper and Lower Bounds, *Journal of Applied Physics, 108:* 649021 - 6.

Mineral Data Publishing, (2001), www.mindwt.org, Accessed December 11, 2012.

Petiti, S, Caillaudi, J, Righi, D, Madejova,J, Elsass, F and Koster, H.M., (2002), Characterization and Crystal Chemistry of

an Fe-rich Montmorillonite from Ölberg, Germany, *Clay Mineralogy,* 37: 283-297.

Read, P.G (2005), Gemmology, Elsevier, Massachusset, pp29-67.

Robin, G., (1989), Chemical Fundamentals of geology, Unwin Hymann, London, p105

Withers, R.L, Thompson, J.G and Welberry, T.R., (1989), The Structure and Microstructure of α-Cristobalite and its Relationship with the β-Cristobalite, *Physics and Chemistry of Minerals,* 16: 517-523.

Withers, R.L, Thompson, J.G and Welberry, T.R., (1989), The Structure and Microstructure of α-Cristobalite and its Relationship with the β-Cristobalite, *Physics and Chemistry of Minerals,* 16: 517-523.

Yorder, H.C., (2006), Ionic Compounds: Application of Chemistry to Mineralogy, John Wiley and Sons, New Jersy, pp1-186.

Wright, A.F. and Leadbetter, A.J. (2006), The structures of the β-cristobalite phases of SiO_2 and $AlPO_4$, *Philosophical Magazine*, 31(6): 1391-1401.