Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1051-1060

Kaolinization of Tertiary Volcanic Rocks in the Biga Peninsula (Lapseki-Çanakkale), Turkey

DAVUT LAÇIN
Department of Geological Engineering, Faculty of Engineering
Istanbul University, 34850, Avcilar, Istanbul, Turkey
E-mail: ilginkur@istanbul.edu.tr

This study presents preliminary results on the kaolinization of tertiary magmatic units in the Biga Peninsula. Volcanic and intrusive rocks of tertiary age crop out in the vicinity of the Harmancik and Üçpinar villages of Çanakkale country, Lapseki town. Volcanic rocks consist of andesites, basalts and rhyolites, whereas intrusive rocks consist of granitic plutons. The granitic intrusions cut the volcanic rocks. Kaolin deposits appears to form within the andesitic rocks. The kaoline deposit is located at nearly 3 km northeast of Üçpinar village. Outcrops of the deposit extends along a north-south trend with a width of 200-250 m and a length of 600-700 m, reaching 10-15 m in thickness. The presence of clays minerals accompanied with feldspars and kaolinite indicates that the solutions from which the clay minerals precipitated were enriched in some alkali and alkali-earth ions. This implies weak kaolinization. Besides, sudden and sharp temperature fluctuation of the solution due to seasonal rainfall seems to have prevented mobile silica movement upwards and resulted high amount of finely dispersed α-quartz ($SiO_2 > 75$ %) within the kaolin deposits. As a result, the dissolved silica did not replace and silicify the main rocks and therefore, a "silica-gossan" did not develop. This can also be considered as an another evidence for weak kaolinization. It is argued that the kaolinization within the study area was formed by hydrothermal fluids circulating through the faults.

Key Words: Kaolinite, Hydrothermal fluid, Lapseki.

INTRODUCTION

Kaolinite, which is one of kaolin group minerals, due to its important physical and the chemical characteristics, has wide applications in the industry and the ceramic sector. Therefore, a lot of researchs examined the origin rock and the formation conditions of the kaolinite mineral. There are a lot of the kaolin deposits in countries such as France, New Zeland Mexico, China and Turkey.

Many studies associated with the formation of the kaolinite mineral were proposed. For example, White[1], Ellis and Wilson[2] proposed that meteoric water which goes to the deep with hot rocks near to magma source and by getting connects directly with the steams which comes from the magma and magmatic steams makes hot the meteoric waters (generally between 100 and 300 ºC) and finally, they claim that the kaolinite mineral forms by this way. Exley[3] claimed that the kaolinization is essentially the event of the H-metasomation and the maphic minerals which passed to hydrogen-metasomatism alter first to montmorillonite, and then montmorillonite changed to the kaolinite mineral as the effect of the hydrogen metasomatism increases. Harrey and Murray[4] proposed that Maungaperarua deposit which is located in northern of New Zeland was formed by the hydrothermal effect of the rhyolites of Plio-quaternary age.

As seen, the kaolinite mineral can form in different environments and therefore, different ideas are associated with its formation.

In studied area, tertiary magmatic units crop out in the vicinity of Harmancik and Üçpinar villages of Çanakkale country, Lapseki town. Volcanic rocks consist of andesites, basalts and rhyolites, whereas intrusive rocks consist of granitic plutons. The granitic intrusions cut the volcanic rocks. Kaolin deposits appears to have formed within the andesitic rocks. The kaolin occurrences was altered to the kaolinite and can be named as alkali-bearing kaolin.

The aim of the study is to discuss the suitability of kaolin occurrences which can be named as the alkali-bearing kaolin formed in the andesitic rocks for ceramic industry.

EXPERIMENTAL

The studied area is located at nearly 3 km northeast of Üçpinar village in the vicinity of Çanakkale country, Lapseki town, in the Biga Peninsula of Turkey.

Sampling and methods: Nineteen samples were collected from the kaolin deposits, along vertical and horizantal profiles from the quarry faces. Samples were collected at depth 20-25 cm from the surface to minimize the effect of weathering and contamination, caused by mixing of material during excavation operations on active faces. The mineralogy was examined by X-ray powder diffraction (Philips diffractometer with a PW-1730 at 36 kV and 30 mA, using Ni-filtered CuK_α-radiation). Scanning speed was for all samples was 1º/min. Clay mineralogy was determined on less than 2 µm material prepared by sedimentation, after soaking in distilled water overnight. The clay particles were dispersed using ultrasonic vibration for 10 min, after addition of Na-hexametaphosphate deflocculant. The less than 2 µm fraction was seperated using sedimentation, spread on glass slides and allowed to dry under atmospheric conditions. The dried clay samples were saturated with ethylene-glycol vapour at 55 ºC for 17 h and X-rayed immediately.

The more information associated with the sedimentation times and dispersion is getting from the studies[5-11]. Semi quantitative analyses of the gylcolated clay fractions were obtained using the methods of Reynolds[12]. The chemical analysis was done from samples dried at 55 ºC for 2 h by the XRF method. Scanning electron microscope analysis (SEM) of the kaolin samples were done by covering with the carbon at the apparatus (Jeol JSM-T330 model).

Geology, mineralogy, morphology and mineral chemistry of the kaolin deposits: The most oldest rocks in the study area comprise andesites, basalts, rhyolites and granitic intrusions. Alkali-bearing kaolin occurrence is located within the andesitic rocks.

Andesite: The weathered surfaces of this rokcs are brownish grey in colour (Fig. 1). The fresh surfaces are grey and gren in colour. Felsic minerals (*i.e.* feldspars) as well as maphic minerals (biotite and hornblende) are also observed within the andesitic rocks with porphyric texture (Fig. 2). As a result of the alteration, the kaolinization was weakly developed.

Fig. 1. Field appearences of andesitic rocks

Basalt: This rocks appear at Yukari Kir Hill at west of the study area. The weathered surfaces are blackish grey in colour and the fresh surfaces of this rocks are also black in colour and hard.

Granite: In the south of the study area appear. The weathered surfaces are light grey in colour and the fresh surfaces are white in colour. The feldspar, biyotite, hornblende and quartz minerals were observed with eyes.

Rhyolite: The weathered surfaces are light grey and blackish grey in colour. The fresh surface also grey and greyish black in colour (Fig. 3). It is fairly hard and the broken surface is concoidal.

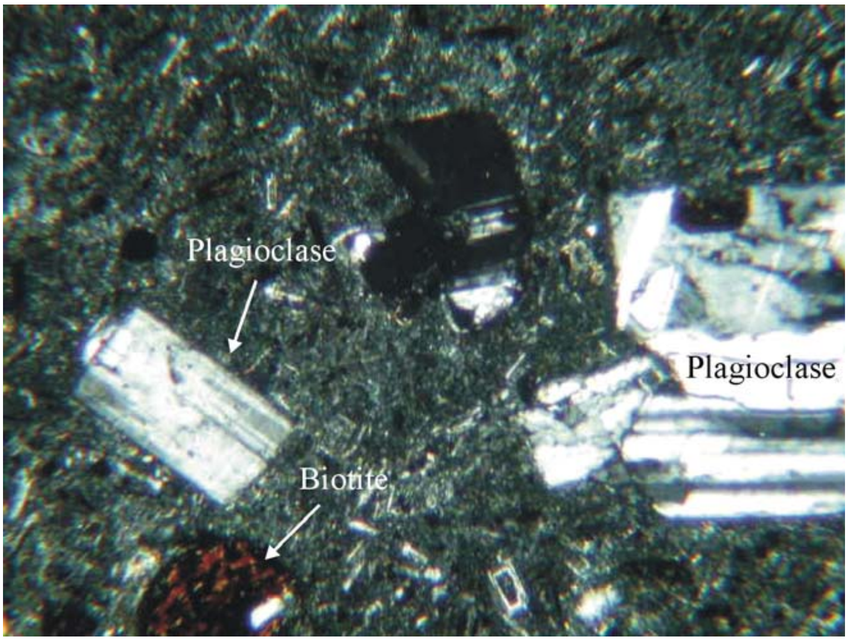

Fig. 2. Microscope appearences of andesitic lavas

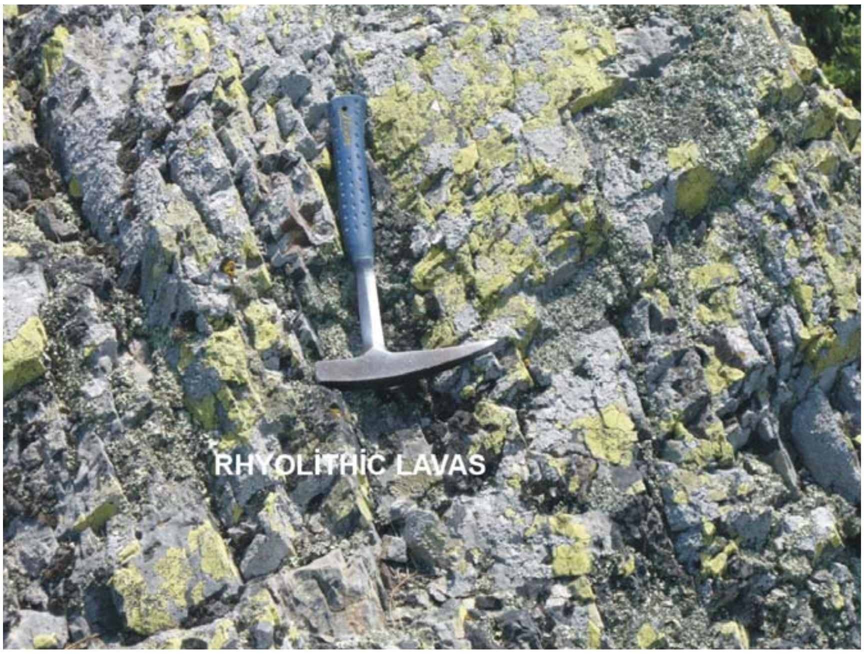

Fig. 3. Field appearences of the rhyolithic lavas

Kaolin: The kaoline deposit is located at nearly 3 km northeast of Üçpinar village. Outcrops of the deposit extends along a north-south trend with a width of 200-250 m and a length of 600-700 m, reaching 10-15 m in thickness.

The weathered surfaces are yellowish white and beige in colour. In regions where the iron-bearing solutions is circulating is yellowish brown in colour (Fig. 4).

Fig. 4. Field appearences of kaolin deposits

Nineteen samples were collected from kaolin deposits. Their places determined by the GPS apparatus (Global Position System) of the samples collected from the kaolin deposits. SEM images are shown in Fig. 5, the unoriented XRD pattern on Fig. 6. The results of the chemical analyses on the Table-1 and the results of the physical test are presented in Table-2.

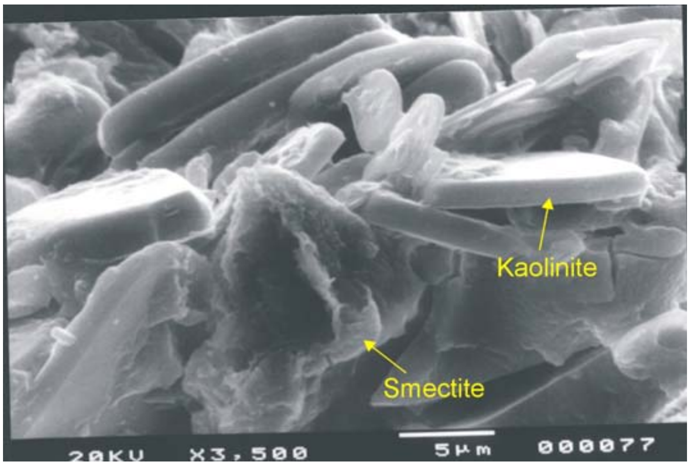

Fig. 5. SEM image for the kaolinite and smectite minerals

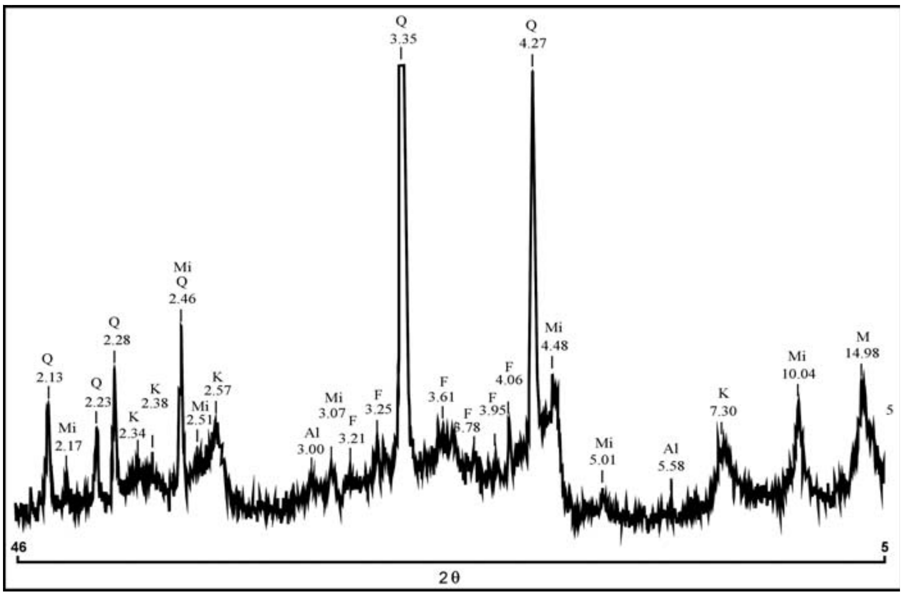

Fig. 6. Unoriented XRD pattern of the kaolin deposit (M = Montmorillonite, Mi = Mica, K = Kaolinite, Al = Alunite, Q = Quartz, F = Feldspar)

TABLE-1
CHEMICAL ANALYSES OF SAMPLES COLLECTED FROM THE STUDY AREA
(CHEMICAL ANALYSES WAS DONE BY THE XRF METHOD)

Sample	Major element oxides (%)									
	AZ	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_4
N-1	2.07	72.95	15.57	0.19	0.75	0.15	0.01	3.10	5.20	0.26
N-3	1.93	73.54	14.94	0.16	1.19	0.11	0.01	3.05	4.98	0.25
N-4	2.33	74.93	14.64	0.18	1.14	0.14	0.01	1.53	5.05	0.24
N-5	3.08	75.25	15.14	0.17	0.77	0.14	0.01	0.63	4.79	0.25
N-10	2.14	73.87	16.22	0.18	0.77	0.13	0.01	2.26	4.42	0.23
N-11	2.50	74.31	15.96	0.17	0.73	0.11	0.01	2.26	3.95	–
N-12	2.19	74.49	15.70	0.17	0.80	0.12	0.01	2.07	4.46	–
N-13	2.50	73.86	16.01	0.17	0.72	0.14	0.01	2.11	4.48	–
N-14	2.70	72.23	17.02	0.17	0.72	0.14	0.01	1.97	5.05	–
N-15	1.84	71.48	16.97	0.18	0.71	0.15	0.01	3.87	4.77	–
N-16	2.35	71.97	17.05	0.19	0.71	0.10	0.01	2.77	4.84	–
N-17	2.01	71.93	16.88	0.19	0.66	0.10	0.01	3.34	4.83	–
N-18	1.95	72.00	16.63	0.17	0.96	0.15	0.01	3.31	4.83	–
N-19	2.59	68.40	18.55	0.31	1.42	0.17	0.12	1.57	6.82	–

TABLE-2
PHYSICAL TEST RESULTS OF SAMPLES COLLECTED FROM THE STUDY AREA

Sample no.	Fir. Temp. (ºC)	Water absorb. (%)	Firing small (%)	Density (g/L)	Visco. (cps)	Firing colour (L)
N-1	1180.000	–	–	–	–	–
N-2	1180.000	–	–	–	–	–
N-3	–	3.980	8.830	1616,00	180,000	51,530
N-4	–	5.880	7.890	1522,00	220,000	61,190
N-5	1180.000	7.640	4.170	1512,000	1100,000	80,950
N-6	1180.000	–	–	–	–	–
N-7	1180.000	8.480	5.060	1578,000	335,000	74,880
N-8	1180.000	–	–	–	–	–
N-9	1180.000	9.360	5.320	1553,000	2600,000	78,240
N-10	1180.000	8.070	6.720	1603,000	1480,000	75,220
N-11	1180.000	10.490	5.180	1606,000	1540,000	82,190
N-12	1180.000	–	–	–	–	–
N-13	1180.000	6.970	5.820	1559,000	1524,000	75,470
N-14	1180.000	7.250	6.760	1581,000	3140,000	80,680
N-15	1180.000	0.540	10.700	1564,000	160,000	60,720
N-16	1180.000	7.240	6.820	1597,000	170,000	73,310
N-17	1180.000	3.800	8.730	1613,000	385,000	70,900
N-18	1180.000	2.990	9.310	1637,000	730,000	63,970
N-19	–	0.710	10.380	–	–	56,130

RESULTS AND DISCUSSION

The tectonism developed depending on North Anatolia Fault System gives rise to the faults in the study area. It is considered that kaolinization within the study area were formed by hydrotermal fluids originated from meteoric and/or magmatic sources and moved through the faults. White[1], Ellis and Wilson[2] reported that the meteoric waters directly contacted with the hot rocks near to the magmatic sources and/or the steams derived from the magmatic sources were heated (generally 100-300 ºC).

The hydrogen-metasomatism is the phenomena in which small and the active hydrogen ions replace the iron, magnesium, sodium, calcium, potash and silicium ions by effecting to the minerals of the main rocks. In this way, the newly formed clay minerals, due to the increase of the hydrogen ions within the fluids, give rise to an increase of the analytic water amount within the rocks.

The hydrolic leaching reactions of feldspars was explaned by Hemley and Jones[13] as follows:

$$Na_2CaAl_4Si_8O_{24} + 4H^+ + 2H_2O \rightarrow 2Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+ + Ca^{2+}$$

This environments have generally the vast temperatures and less alkaline + K^+ ion/H^+ an activity ratios. During the hydrolysis of the silicate minerals, in small acid environment that the hydrogen ions formed by increasing the dissolution of Al_2O_3 and SiO_2 and give rise to kaolinite within the solution. With the result that, the silica minerals (for example; low-crystoballite and α-quartz) which was much observed within the kaolin deposits and silica-gossans show that the solutions is rich in H_4SiO_4. This can be formed in conditions of low-alkali + K^+ ion/H^+ and in this way, according to the K_2O-Al_2O_3-SiO_2-H_2O equilibrium diagram proposed by Garrels and Christ[14], kaolinite forms.

If the dissolved potash, sodium and calcium ions quickly away from the solution, the kaolin derives from directly plagioklas and potash-feldspar.

If dissolved potash, sodium and calcium ions didn't quickly away from the solutions, alkali + toprakalkali/H^+ activity ratios increase. If hydrogen-metasomatism isn't too much to form kaolin minerals and there are alkali and kalalkali ions in solutions, smectite group clays, illite and mixed-layered clay minerals are formed. The balance of smectite group clay minerals (*e.g.*, montmorillonite) by effecting of the incongruent dissolution will be altered. Particularly, montmorillonite crystals will be transformed to illite minerals as the authigenic by increasing of K^+-ions in the solutions. Ylogan *et al.*[15], explain that illite formations are similar in Ponza iceland of Italy. Montmorillonite and illite occurrences were also observed in studied area.

The chemical analyses results of samples which were collected from kaolin deposits (Table-1); SO_4 content is 0.23-0.26 and with the result that, roasting losses are also fairly low (1.57-2.76). Ideally, kaolinit composition has ratios as follows:

$$SiO_2;\ 46.5\ \%,\ Al_2O_3;\ 39.5\ \%\ \text{and}\ H_2O;\ 14\ \%$$

Whereas, Al_2O_3 ratio of kaolin deposits in the study area is around 18.55 % and SiO_2 ratio is also around 75 %. This also shows that extra silis in the environment is transformed to silica minerals.

Moreover, Fe_2O_3 ratios is also low (0.66-1.19). 1.19 Ratio is only observed in sample N-3. The reason of this situation is the effect of painting of the iron-rich solutions. The reason is that the iron which is located in structure of the mafic minerals such as biyotite and hornblende is first mobilized during the hydrogen-metasomatism and the later is dissolved partly and the remaining iron is transformed to hematite and goethite minerals by the oxidation. Thus, kaolin deposit is altered to yellowish and pinkish in colour. The total alkali ratios of the samples is located between 6 and 8 and is the named as alkali-bearing kaolin.

When examined the results of the physical tests of the samples (Table-2), L-ratios of samples except for N-3, N-4, N-15, N-18 and N-19 samples are high and the firing colours are white and whitish.

When examined scanning electron micrographs of samples, it is fairly observed the texture of the porosity. Intercrystalls porosity is also high. Hexagonal-shaped kaolinite crystalls have the book texture of infrequent structure (Fig. 5). This shows that the kaolinization isn't formed at too depths, therefore, the pressure isn't high. When examined the unoriented XRD patterns of samples, it is observed that the sample consist of montmorillonite, mica, kaolinite, alunite, quartz and feldspar minerals.

Conclusion

It is considered that kaolinization within the study area were formed by hydrotermal fluids originated from meteoric and/or magmatic sources and moved through the faults.

The presence of the other clays minerals accompanied with feldspars and kaolinite indicates that the solutions from which the clay minerals precipitated were enriched in some alkali and alkali-earth ions. This situation implies weak kaolinization. During the kaolinization of the parent rocks, at first iron, later alkali and alkali earth metals and finally silica removed from the environment. Despite of an intense kaolinization, the kaolin occurrences contain high amount of finely dispersed low-cristobalit and α-quartz ($SiO_2 > 75$ %), resulting in low Al_2O_3 values (up to 18.55 %). Whereas, the kaolinization of the main rocks represents the desilication. This phenomena, could be the result of the temperature fluctuation of the hot water depending seasonal rainfalls. And as a results, the dissolved silica did not replace and silicify the main rocks and therefore, a silica-gossan did not develop. This can also be considered as an another evidence for weak kaolinization.

In hydrothermal kaolin deposits, it is expected that the kaolinization is to be rich and therefore, Al_2O_3 ratios will also be increased. Al_2O_3 ratios (14.31-18.55 %) of alkali-bearing kaolines in the study area are low. Owing to the fact that the iron contents is also low (0.40-1.14 %) and firing colours is white (L = 75.47-82.19), it can be used at the ceramic industry.

ACKNOWLEDGEMENT

This work is part of the Project "The origin of the effective kaolinization formed depending on Tertiary volcanic rocks within the Çanakkale country boundaries" supported by the Research Fund of Istanbul University, Project No: 437/13092005. Therefore, I would like to thank to the Research Fund of Istanbul University.

REFERENCES

1. D.E. White, *Geol. Soc. Am. Bull.*, **68**, 1637 (1957).
2. A.J. Ellis and S.H. Wilson, *N.Z.J. Geol. Geophys.*, **3**, 593 (1960).
3. C.S. Exley, *Clay Miner.*, **11**, 51 (1976).
4. C. Harrey and H. Murray, The Geology, Mineralogy and Exploitation of Halloysite Clays of Northland, New Zealand; in ed.: Keller, Kaolin Symposium, Kaolin genesis and Utilization, Pub. Clay. Mineral Soc., pp. 233-248 (1990).
5. C.B. Taner and M.L. Jackson, *Proc. Soil. Soc. Am.*, **12**, 60 (1947).
6. M.L. Jackson, Soil Chemical Analysis-Advanced Course, Published by the Author, Department of Soil Science, University of Wisconsin, Madison, Wis., USA (1956).
7. M.L. Jackson, Soil Chemical Analysis, Prentice-Hall Inc., Englewood Cliffs, New Jersey, USA (1958).

8. M.L. Jackson, in eds.: C.I. Rich and G.W. Kunze, Soil Clay Mineralogical Analysis, in Soil Clay Mineralogy, Universty of North Carolina Pres, Chapell Hill, North Carolina, USA, Ch. 8, pp. 245-295 (1964).
9. H. Van Olphen, Introduction Clay Colloid Chemistry, John Wiley and Sons, New York, London (1963).
10. H. Van Olphen, Introduction Clay Colloid Chemistry, John Wiley and Sons, New York, London (1977).
11. G.W. Kunze, Pretreatment in Mineralogical Analysis, in Methods of Soil Analysis, American Society of Agromony, Madison, Wis., USA, Part 1, pp. 568-577 (1965).
12. R.C. Reynolds, in eds.: D.R. Pevear and F.A. Mumption, Principles and Technics of Quantitative Analysis of Clay Minerals by X-Ray Powder Diffraction, In CMS Workshop Lectures, 1. Quantitative Mineral Analysis of Clays, Evergreen, Colorado: The Clay Minerals Society, pp. 4-36 (1989).
13. J.J. Hemley and W.R. Jones, *Economic Geol.*, **59**, 539 (1964).
14. R.M. Garrels and C.L. Christ, Solutions, Minerals and Equilibria: Harper and Row, New York, p. 450 (1965).
15. F.R. Ylogan, S.P. Altener and A. Pozzuoli, *Clays Clay Miner.*, **48**, 610 (2000).

(*Received*: 12 December 2007; *Accepted*: 19 September 2008) AJC-6874