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KAOLINIZATION PROCESSES IN THE RHYOLITIC ROCKS OF KEFALOS, KOS ISLAND, AEGEAN SEA, GREECE.

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ABSTRACT

Kaolin occurrences in the South Kefalos peninsula, Kos island, Aegean sea, Greece, are products of hydrothermal alteration of rocks of rhyolitic composition. The chemical, mineralogical and textural characteristics of kaolin occurrences were investigated by X-Ray diffraction (XRD), Analytical scanning electron microscopy (SEM) and bulk rock chemical analyses. Attempts have been made to correlate the primary with secondary mineral assemblages and to establish the factors controlling the stepwise character of the transition from the fresh rhyolitic to kaolinized rocks. The kaolinization processes follows two main alteration pathways: I) K-feldspar → Mixed-layer kaolinite-smectite → kaolinite → dickite. II) Na-plagioclase → kaolinite → dickite.

KEY WORDS: Kos Island; kaolinite; hydrothermal activity; dickite; mixed-layer kaolinite-smectite; rhyolite;

1.INTRODUCTION

The kaolin occurrences of the Kefalos peninsula SW Kos island (fig.1) are associated with rhyolitic rocks of Pliocene age (Paraskevopoulos, 1960; Boven et al, 1987; Dalabakis, 1987; Kelepertsis and Reeves, 1987; Triantaphyllis, 1994;). These rocks exhibit perlitic texture and are mainly composed of quartz, Na-plagioclase, K-feldspar and volcanic glass. The kaolin occurrences are white in color commonly stained reddish by iron oxides and extend over an area of about 0,5Km^2. This study aims at revealing the kaolinization processes of the rhyolitic rocks of the area.

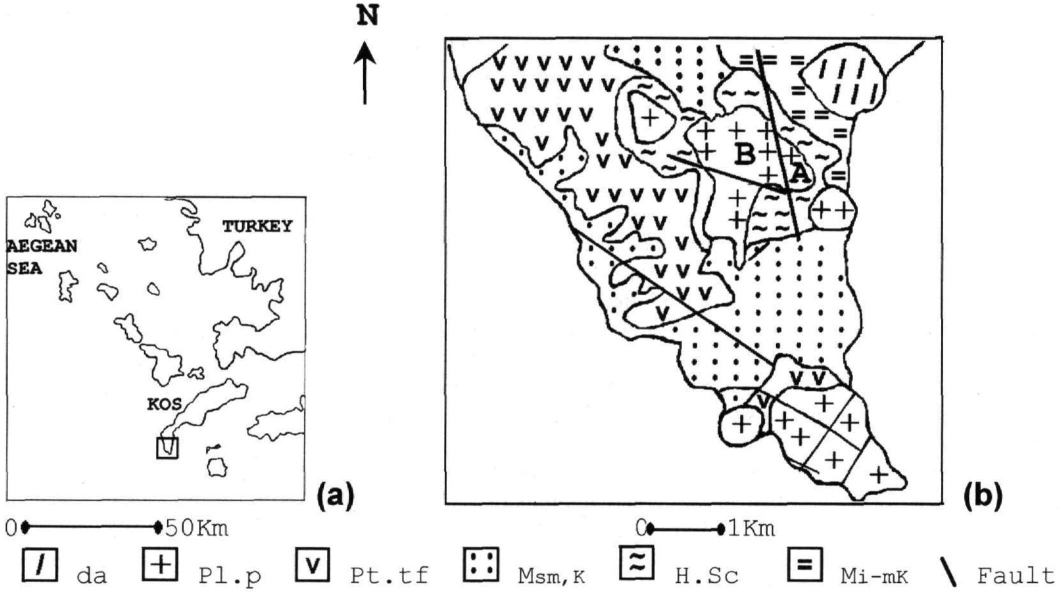

Figure 1.(a)Location of south Kefalos peninsula, Kos island. (b) Geological sketch map of South Kefalos peninsula, Kos island (Triantaphyllis, 1994) showing sample locations A and B.
da: Dacitic domes, Pl.p: Pliocenic rhyolitic domes, Pt.tf: Volcanic tuffs, Msm,K: Lacustrine deposits, H.Sc: Scree, Mi-mK: Neritic marine deposits.

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2. ANALYTICAL TECHNIQUES

The altered rhyolites outcrop on both sides of the NW-SE fault (fig.1(b)). Forty samples were collected from outcrops A and B, east and west of the above fault respectively (1(b)). Samples were collected in order to represent different stages of alteration from the unaltered rhyolites occurring away from the NW-SE fault to completely altered rhyolites near the fault.

Mineralogical analyses of bulk-rock and clay-fraction (<2μm) samples were performed by XRD, using a Philips PW1050/25, diffractometer with Ni-filtered CuKa radiation. Powders from oriented specimens were scanned (1^0 2θ/min) from 3 to 60 ^{0}2θ. Clay minerals were identified using three XRD patterns per sample (air-dried at 25^{0}C, ethylene-glycolated, and heated at 490^{0}C for 2h) of the clay-sized fraction (<2μm).

The size and form of submicroscopic clay minerals and their assemblages with other minerals and the elemental compositions were determined by a scanning electron microscope (SEM) equipped with EDS (Jeol S250MK3 and JSM 6300) operated at 20 kV. The detection limit was 0.01%.

The degree of kaolinite crystallinity or structural disorder was estimated by defining two crystallinity indices (i) R_2 Liιtard's test, determined on the (131) and (131) reflections, which is exclusively sensitive to the presence of stacking faults by translation of ±b/3 (Liιtard, 1977) and (ii) test L_{002} related to the number of the layer-stacking faults along the c* axis and is determined by the enlargement at mid-height of the reflection L_{002} (Guinier, 1956). Hinckley index (Hinckley, 1963) has not been determined because the reflections which are used for this index are forming a band and also because the presence of cristobalite affects the reflections intensity at $20^0 - 23^0$ 2Θ.

Chemical analyses of both major oxides and minor elements were carried out using the I.C.P. method on $HClO_4$/HF solutions. SiO_2 was determined by XRF after $LiBO_2$ fusion. Zircon was measured by the xylenol orange colorimetric method.

3. RESULTS AND DISCUSSION

Five clay mineral phases were detected by XRD in the altered rhyolite: kaolinite, dickite, mixed-layer kaolinite-smectite, smectite and illite. Cristobalite and quartz are also present in most of the samples in considerable amounts. Kaolinite content increases from the unaltered rhyolite to completely kaolinized rocks. From the X-Ray Diffraction patterns it is evident that dickite growths progressively at the expense of kaolinite. Mixed-layer kaolinite-smectite is an intermediate stage in the kaolinization process of feldspars (fig.6, table 6). Smectite and illite are present in few samples and in small amounts. Traces of barite, alunite, pyrophyllite and NaCl were identified in few samples from SEM micrographs and microprobe analyses.

The texture of Kos kaolin is typical of a kaolin produced by hydrothermal alteration (Keller, 1976). The porosity of kaolin is low and it's bulk density is high. Space for the growth of the kaolinite was restricted to all directions. As a result, characteristically tightly packed crystals of kaolinite are formed (fig. 2). Kaolinite is not well-crystallized and it is a product of alteration of feldspars. The results of the crystallinity indices are listed in Table 1. It is evident from the data presented in Table 1 that kaolinite shows layer-stacking faults along the c*-axis because $6<L_{002}<9$ (Cases et al, 1982) and a few stacking faults by translation of ±b/3, (Liιtard, 1977). SEM observations show c*-axis disorder of kaolinite and stacking faults by translation of ±b/3 (fig. 3). This is attributed to the limited space available for kaolinite crystals growth due to the removal of silica and K-feldspars in solution during the incongruent dissolution of feldspars and not to substitutions occurring in the octahedral sites as it is commonly observed (e.g. Cases et al, 1982, Tsolis-Katagas and Mavronichi, 1989). The electron microprobe analyses of representative kaolinite crystals listed in Table 2, which show inconsiderable amounts of Fe_2O_3, K_2O, TiO_2, MgO, CaO, Na_2O, SrO and BaO, support the above interpretation.

Books of dickite are shown in fig.4. Electron microprobe analyses of representative dickite crystals given in Table 3 show the presence of small and equal amounts of BaO (0,11%) and SO_3 (0,10%). In fig.5 a sceletal barite crystal is shown (confirmed by EDS spectrum) decomposing as a result of hydrothermal alteration. These observations, combined with the presence of BaO and SO_3 in dickite, indicate that decomposed barite, "intergrowths" with newly formed dickite as a result of the limited space available during the alteration processes.

SEM observations show the presence of partly altered feldspars (fig. 6). A series of quantitative electron microprobe analyses of partly altered feldspar crystals show that the feldspars are altered to mixed-layer kaolinite-smectite in a small distance from the center of the crystal and to kaolinite in the margins, forming a kaolinite rich zone. The results of XRD analysis and electron microprobe analyses (Table 6) show that the mixed-layer phase is composed of 80-85% kaolinite and 15-20% smectite (Newman, 1987). In the most altered samples kaolinite is altered to dickite forming a dickite rich zone; in this zone pyrophyllite is present in trace amounts. The coexistence of dickite and pyrophyllite suggests that the temperature of formation was probably lower than 280^{0}C '(Inoue, 1995)

Major element and trace element analyses of two slightly altered rhyolite and ten altered samples with different degree of kaolinization are given in Table 4. The lowest K, Ca, Na and Ba and the highest Al and LOI content is found in samples in which the alteration process is more advanced (samples K6, K12, K11, K9).

Table 1. Results of R_2 Liitard's test and test L_{002} of kaolinite of Kos.

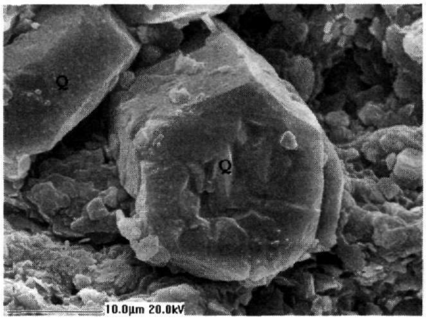
SAMPLE	R_2	L_{002} (mm)	SAMPLE	R_2	L_{002} (mm)
K5	0.99	7	K11	1.15	9
K6	1	7	K12	0.91	6
K8	1.14	8	K13	1.05	8
K9	0.88	8	K18	1.14	8
K10	1.08	6			

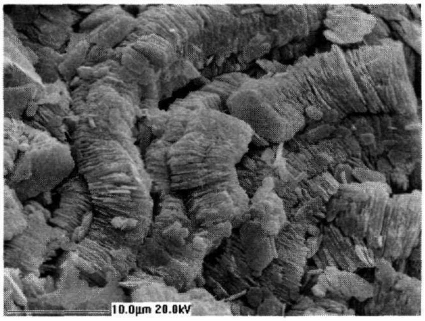
Table 2. Basic statistics of quantitative electron microprobe analyses of Kaolinite from four different samples.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SrO	BaO	SO_3	Total
Minimum	44.87	0.00	37.70	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.03
Maximum	46.79	0.01	39.64	0.17	0.06	0.06	0.05	0.05	0.00	0.26	0.08	86.77
Mean	45.71	0.00	38.84	0.12	0.02	0.02	0.02	0.02	0.00	0.08	0.02	84.86
St.Dev.	0.80	0.00	0.64	0.04	0.02	0.02	0.02	0.02	0.00	0.11	0.03	1.23
n	6	6	6	6	6	6	6	6	6	6	6	6

The correlation coefficient of LOI-K_2O is –0.84, of Na_2O-LOI is –0.92, of K_2O-Na_2O is +0.95, of Ba-K_2O is +0.77 and of Ba-Na_2O is +0.76 (Table 5). The high correlation coefficients found between K, Na and Ba shows that they decrease in the more altered samples following the same geochemical pathway. The high negative correlation coefficient found between K and LOI shows that LOI increases in the more altered samples following the opposite geochemical pathway. These relations indicate that kaolinite, is alteration product produced during the breakdown of K-feldspars and Na-plagioclases. A minor amount of kaolinite could also originate from the alteration of volcanic glass, as it has been observed in few thin sections.

The correlation coefficient of Sr and Al_2O_3 is +0.88 (fig. 7) and of Sr–P_2O_5 is +0.88 (fig. 8). The most altered samples show high amount of Al_2O_3, Fe_2O_3, Sr and P_2O_5 and low amount of SiO_2. The correlation coefficient of P_2O_5-Al_2O_3 is +0.85 (fig. 9), Fe_2O_3-SiO_2 is –0.87 (fig. 10), Zn-Fe_2O_3 is +0.98, Cu-Fe_2O_3 is +0.91 and Cr-Fe_2O_3 is +0.90. The high positive correlation coefficients found between Fe_2O_3, Al_2O_3 and P_2O_5 show that the amount of Fe_2O_3, Al_2O_3 and P_2O_5 increase in the more altered samples, following the same geochemical pathway. From the above relations it is concluded that Fe_2O_3 P_2O_5 and Sr increase in amount with advancing kaolinization by enrichment (the negative correlation coefficient of Fe_2O_3-Sr is attributed to the low Sr values in the oxidized samples K7, K12). The elements Cr, Cu and Zn are strongly correlated with Fe_2O_3 and not to kaolinization process (Table 5). The amounts of Fe_2O_3, Sr, Zn, Cu and Cr are increasing in the most altered samples more radically than the other elements suggesting that hydrothermal fluids may add Fe_2O_3 and Sr (Thorpe, 1982), Zn, Cu and Cr to the altered rhyolite. Varnavas and Cronan (1991) in their investigation of the submarine hydrothermal field off Kos, reported Fe, Sr, Cu and Zn concentrations in the submarine hydrothermal waters from Kefalos Bay 14, 10.2, 1.1 and 1.4 μg/l





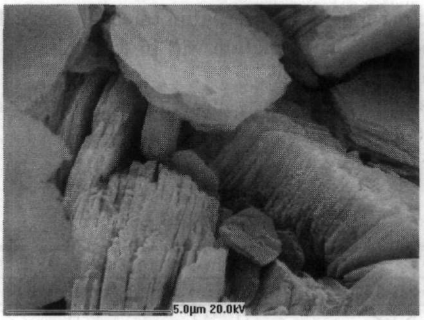


Figure 2.

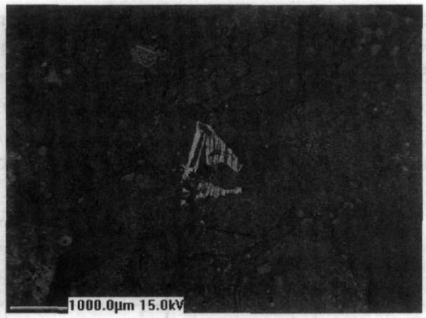


Figure 3.

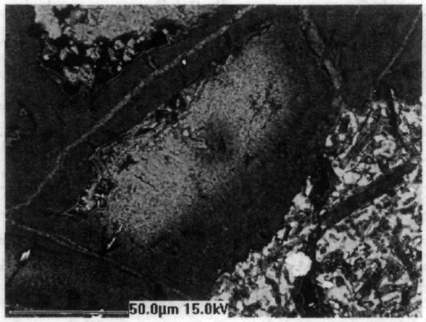


Figure 4.

Figure 5.

Figure 6.

Figure captions

Figure 2: SEM micrograph, showing books and flakes of tightly packed kaolinite and euhedral Quartz (Q) crystals. Figure 3: SEM micrograph of kaolinite books with c*-axis disorder and small stacking faults by translation of ±b/3. Figure 4: SEM micrograph of dickite crystals. Figure 5: SEM micrograph of sceletal barite crystal. Figure 6: SEM micrograph of partly altered Feldspar forming zones, A: altered Feldspar, B: single plates and thin packets of plates of mixed-layer kaolinite-smectite, C: kaolinite rich zone.

Table 3. Basic statistics of quantitative electron microprobe analyses of Dickite.

respectively. These hydrothermal waters show no enrichment in S over normal seawater (Varnavas and Cronan, 1991; Dando et al, 1999).

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SrO	BaO	SO_3	Total
Minimum	44.75	0.00	37,97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.26
Maximum	46.64	0.02	39,91	0.15	0.07	0.12	0.09	0.06	0.10	0.59	0.87	86.77
Mean	45.63	0.01	38,81	0.07	0.04	0.03	0.06	0.04	0.04	0.11	0.10	84.91
St.Dev.	0.53	0.01	0,61	0.05	0.02	0.04	0.03	0.02	0.05	0.18	0.27	1.12
n	10	10	10	10	10	10	10	10	10	10	10	10

Table 4. Major and trace element analyses of parent rocks (rhyolite slightly enriched in SiO_2), oxidized rock# and kaolinized rocks listing with increasing degree of alteration, from Kefalos, Kos island.*

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	H_2O	L.O.I.	TOTAL
K14*	78.80	10.63	0.17	0.01	0.59	4.26	3.85	0.15	0.02	0.01	0.10	0.80	99.39
K15*	77.50	11.71	0.83	0.09	0.62	4.45	3.91	0.14	0.02	0.06	0.13	0.46	99.92
K7#	30.63	7.24	48.10	0.14	0.22	0.06	0.08	0.32	0.06	0.05	2.59	10.88	100.37
K8	66.21	14.99	0.97	0.05	0.12	0.26	0.26	0.63	0.11	0.01	3.80	12.46	99.87
K18	71.49	15.12	0.50	0.03	0.12	0.07	0.90	0.57	0.09	<0.01	0.93	10.11	99.93
K5	67.71	16.98	1.60	0.74	0.10	1.11	0.01	0.48	0.08	<0.01	2.06	9.49	100.36
K10	70.86	17.05	3.32	0.04	0.13	0.14	0.03	0.54	0.13	<0.01	0.61	7.41	100.26
K13	59.89	17.83	3.73	0.03	0.12	0.19	0.96	0.56	0.13	<0.01	2.30	14.46	100.20
K6	63.95	19.66	1.95	0.05	0.14	0.12	0.01	0.64	0.13	0.10	2.62	11.33	100.70
K12#	42.96	21.73	19.16	0.01	0.12	0.08	0.51	0.35	0.17	<0.01	0.69	14.09	99.87
K11	60.44	25.83	1.13	0.02	0.09	1.13	0.14	0.19	0.19	<0.01	0.75	11.94	100.85
K9	55.16	26.04	5.20	0.03	0.10	0.07	0.47	0.42	0.14	0.06	0.59	12.55	100.83

Sample	Ba	Co	Cr	Cu	Li	Nb	Ni	Sc	Sr	V	Y	Zn	Zr	La	Ce	Nd
K14*	931	16	10	4	20	14	7	1	83	4	7	11	61	17	34	14
K15*	965	14	10	3	14	14	7	1	79	6	11	22	72	19	36	17
K7#	79	21	137	51	5	9	38	5	139	135	15	181	69	17	39	19
K8	130	17	25	10	3	11	36	9	806	67	8	12	115	15	38	15
K18	194	7	18	4	20	11	6	10	439	83	4	7	53	18	42	13
K5	142	7	18	4	3	9	10	25	318	100	5	16	92	36	82	30
K10	150	7	25	4	3	10	8	14	439	94	44	17	91	50	139	49
K13	244	9	38	16	5	10	18	27	759	104	4	12	98	16	45	18
K6	781	11	22	13	3	11	20	8	467	75	5	15	115	19	38	20
K12	320	11	132	43	3	8	22	20	885	225	3	47	68	39	89	36
K11	339	4	23	7	5	4	7	14	1087	107	1	10	35	62	160	58
K9	469	5	48	6	3	9	10	10	1106	109	1	9	85	10	21	11

***Explanatory notes:** H_2O=loss at 110 ^0C, LOI=loss at 1000 ^0C, oxides and LOI %, trace elements in ppm*

Table 5. The most significant correlation coefficients of major and trace elements from parent rocks and kaolinized rocks of Kefalos, Kos island.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	LOI	Ba	Sr	Y	Zr	Cu	Zn	Co
Cr	-0.93	-0.11	-0.08	0.90	0.04	-0.11	-0.23	-0.39	-0.33	0.21	0.14	0.44	-0.37	0.12	-0.02	-0.13	0.97	0.79	0.27
Co	-0.12	-0.04	-0.84	0.46	0.13	-0.17	0.41	0.25	0.31	-0.64	0.30	-0.27	0.04	-0.59	0.01	-0.01	0.39	0.54	
Zn	-0.78	-0.20	-0.51	0.98	0.22	0.05	0.03	-0.16	-0.18	-0.22	0.26	0.10	-0.30	-0.33	0.16	-0.14	0.83		
Cu	-0.91	-0.07	-0.21	0.91	0.09	-0.11	-0.17	-0.34	-0.30	0.13	0.28	0.41	-0.32	0.00	-0.05	-0.07			
Zr	0.07	0.72	-0.03	-0.15	0.34	0.18	-0.23	-0.20	-0.28	0.02	0.66	0.23	-0.07	0.01	0.18				
Y	0.13	0.13	-0.31	0.11	-0.11	-0.06	0.06	-0.01	-0.09	-0.12	-0.11	-0.29	-0.21	-0.35					
Sr	-0.28	0.23	0.88	-0.18	-0.19	-0.29	-0.68	-0.62	-0.52	0.88	0.08	0.75	-0.33						
Ba	0.47	-0.50	-0.09	-0.35	0.53	-0.26	0.77	0.76	0.77	-0.42	-0.46	-0.67							
LOI	-0.63	0.58	0.55	0.24	-0.12	-0.04	-0.91	-0.92	-0.84	0.79	0.53								
H_2O	-0.31	0.65	-0.17	0.23	0.13	0.23	-0.45	-0.47	-0.54	0.10									
P_2O_5	-0.36	0.34	0.86	-0.07	-0.19	-0.23	-0.80	-0.77	-0.71										
K_2O	0.53	-0.64	-0.45	-0.26	0.07	-0.20	0.95	0.95											
Na_2O	0.57	-0.66	-0.49	-0.27	0.11	0.05	0.96												
CaO	0.43	-0.68	-0.59	-0.08	0.22	-0.13													
MgO	0.05	0.09	-0.12	-0.01	-0.13														
MnO	-0.13	0.01	-0.05	0.17															
Fe_2O	-0.87	-0.16	-0.37																
Al_2O_3	-0.08	0.16																	
TiO_2	-0.01																		

Table 6. Basic statistics of quantitative electron microprobe analyses of mixed-layer kaolinite-smectite.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SrO	BaO	SO_3	Total
Minimum	48.02	32.29	2.16	0.02	0.23	0.00	0.01	BDL	BDL	BDL	85.11
Maximum	51.20	34.96	3.34	0.18	0.44	0.07	0.11	0.11	0.45	0.11	88.12
Mean	50.03	33.12	2.84	0.09	0.32	0.02	0.06	0.04	0.12	0.04	86.71
St.Dev.	1.03	0.87	0.43	0.05	0.06	0.02	0.03	0.03	0.18	0.05	1.03
n	10	10	10	10	10	10	10	10	10	10	10

BDL: below detection limit, TiO_2: BLD.

Figure 7. y=0.006x-0.042

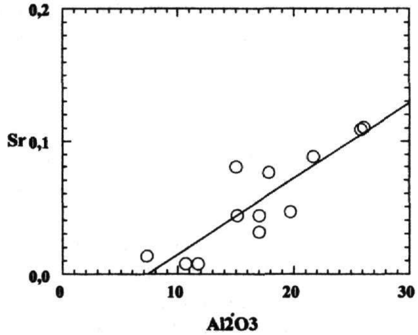
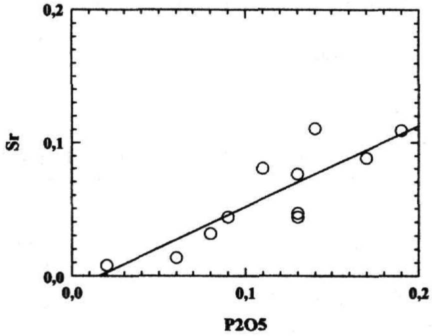


Figure 8. y=0.609x-0.009



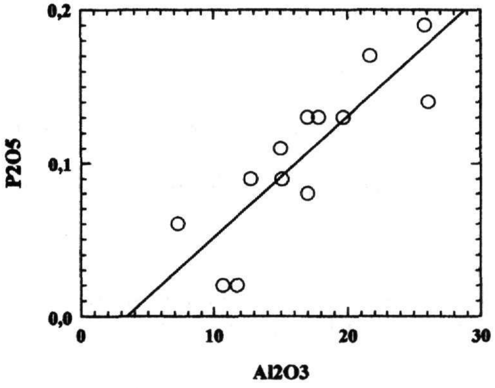


Figure 9. y=0.008x-0.027

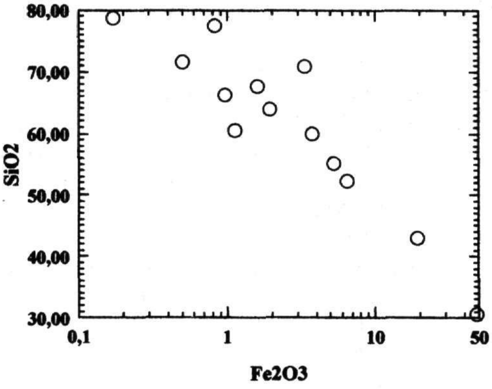


Figure 10. y=0.609x-0.009

Figure 7,8,9,10. Variation diagrams of selected major and trace-elements of kaolinized rocks from Kefalos, Kos island.

4. CONCLUSIONS

1.The kaolinization process of Kos island rhyolites seems to follow two main alteration pathways:

I) K-feldspar ? Mixed-layer kaolinite-smectite ? kaolinite ? dickite.

II) Na-plagioclase ? kaolinite ? dickite.

A minor amount of kaolinite could also originate from the alteration of volcanic glass.

2. Kaolinite shows layer-stacking faults along the c*-axis and a few stacking faults by translation of ±b/3. This is attributed to the limited space available for kaolinite crystals growth due to the removal of silica and K-feldspars in solution during the incongruent dissolution of feldspars and not to substitutions occurring in the octahedral sites.
3. The texture of kaolin is typical of a kaolin produced by hydrothermal alteration.
4. The degree of kaolinization is increasing from the parent rock to completely altered near the fault.
5. Hydrothermal fluids add to the altered rhyolite significant amounts of Sr, Cr, Cu, Zn and Fe. Relative to the volcanic rock (rhyolite), the kaolinitic zone is characterized by depletion of Si, Na, K, Ca, Ba and enrichment of Al, Sr, P and Fe.
6. The presence of dickite and pyrophyllite in the most altered samples indicate that the temperature of hydrothermal alteration was probably lower than 280^0C.

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