GEOCHEMISTRY OF CLAY FORMATIONS FROM THE ISLAND OF AEGINA*

BY

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Περίληψις. Ἡ παροῦσα μελέτη ἀφορᾶ εἰς τὴν γεωχημείαν τῶν κυρίων στοιχείων καθὼς καὶ τῶν ἰχνοστοιχείων τῶν ἀργιλλικῶν σχηματισμῶν τοῦ βορείου τμήματος τῆς νήσου Αἰγίνης.

Τὰ κύρια χαρακτηριστικὰ τῆς χημικῆς των συστάσεως εἶναι ἡ ἐπικράτησις τοῦ ἀσβεστίου ἔναντι τοῦ μαγνησίου, τοῦ καλίου ἔναντι τοῦ νατρίου καὶ ἡ παρουσία τοῦ σιδήρου κυρίως ὑπὸ τὴν τρισθενῆ μορφήν. Παρετηρήθη ἐπίσης ὅτι αἱ κυριώτεραι μεταβολαὶ εἰς τὴν χημικὴν σύστασιν τῶν δειγμάτων συνδέονται γενικῶς μὲ τὴν ὀρυκτολογικὴν τοιαύτην.

Ἡ γεωχημεία τῶν κυρίων στοιχείων εὑρέθη νὰ ἐλέγχεται : κυρίως ἀπὸ τὸ κλαστικὸ (detrital) περιεχόμενον τῶν δειγμάτων (Al, Si, Ti, Fe) καὶ ὀλιγώτερον ἀπὸ ὀρυκτὰ ὅπως τὰ ἀνθρακικὰ (ἀσβεστίτης, δολομίτης) τὰ ὁποῖα πιστεύεται ὅτι εἶναι τὸ κυριώτερον μέσον διὰ τοῦ ὁποίου εἰσῆλθε ὑλικὸν ἐν διαλύσει.

Ὅσον ἀφορᾶ εἰς τὴν γεωχημείαν τῶν ἰχνοστοιχείων, εὑρέθη ὅτι μία μεγάλη ἀναλογία ἀπὸ τὰ στοιχεῖα Rb, V, Ni, Zr, Ti, εἶναι συνδυασμένη εἰς τὴν δομὴν κλαστικῶν ἀργιλικῶν ὀρυκτῶν, ἐνῶ στοιχεῖα ὅπως τὸ Sr, Ba εἰσῆλθον εἰς τοὺς σχηματισμοὺς ἐν διαλύσει.

Abstract. This study concerns the major and trace element geochemistry of the clay formations occuring in the north part of Aegina island.

The significant features of the chemical composition are the dominance of calcium over magnesium, potash over soda and the presence of iron mainly in the ferric state. The major variations in chemical composition are generally related to mineralogy.

The major element geochemistry is considered to be controlled firstly by the detrital fraction (Al, Si, Ti, Fe) and secondly by minerals such as carbonates (calcite, dolomite) which are believed to be the main means by which material was incorporated into the sediment from solution.

A large proportion of the contents of the trace elements Rb, V, Ni, Zr, Ti appears to be structurally combined in detrital clay minerals ; entry in solution is shown by elements such as Sr, Ba.

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* ΠΑΝΑΓΙΩΤΑ ΤΣΩΛΗ - ΚΑΤΑΓΑ, **Γεωχημεία τῶν ἀργιλικῶν σχηματισμῶν τῆς νήσου Αἰγίνης.** Ἀνεκοινώθη κατὰ τὴν Ἐπιστημονικὴν συνεδρίαν τῆς 2ας Δεκεμβρίου 1976.

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1. INTRODUCTION

The clay formations studied in this investigation occur in the northwerst part of Aegina island. They are of of marine origin and on the basis of microfossils their age was found to be Upper Miocene-Lower Pliocene (CAILLERE and TSOLI, 1972). Cretaceous limestones and Quaternary sediments are also found. The limestones occupy the north and northeast part, the clays are found to the south of this area, though the younger sediments occupy the north coast. The rest of the island is composed of volcanic rocks. PE (1971), based on their chemistry, distinguished four cycles of eruptions.

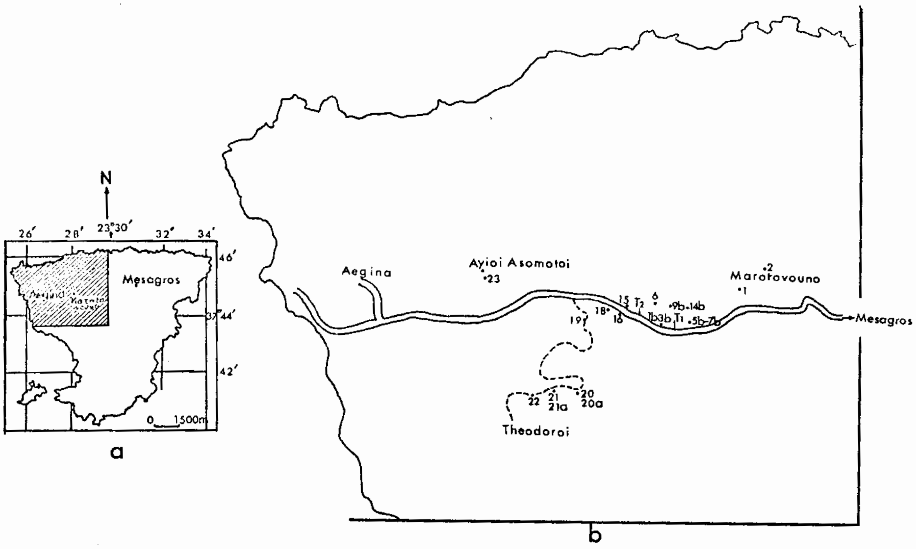

Fig. 1. a) Aegina island (shaded area shows area of study).
b) Location of samples within shaded area.
T_1, T_2. Two vertical sectiona, 5 m thick.

In the present paper 9 volcanic rocks and 30 clay material samples were collected from the northwest part of Aegina and analysed for major and trace elements contents. Figure 1 shows their localities.

In the following, data will presented on the distribution of major and trace elements in bulk samples and in the 1 micron fraction (between 1 - 2 microns) and the relationships of the abundance of the elements and certain minerals of the samples will be examined.

TABLE 1.

Quantitative mineralogical composition of clay samples from Aegina island as computed from chemical analyses (per cent.).

Sample No.	Illite	Saponite	Montmorillonite	Calcite	Dolomite	Quartz	Plagioclase	Goethite	Hematite	Gypsum
5	6.2	7.7		7.5	57.3	9.7	5.6	4	1.8	0.4
5b	14.5	17.8	3	20	7.5	26	6.8	5.8		0.4
7b	10	19	3.4	23	21	12	4	3	1.3	0.4
4b	11.2	16	3.8	18	30	11	5.8	2	2.6	0.4
7	17.2	10		3.2		27	34	8		1.4
8	13	16.5		38		16.5	6	4	1.6	1.4
9	16	18.8		33.6		15.2	7.5	5.3		2.8
10	16.2	18.5		30		21	2.5	6	1	2.4
16	16	20		30		22.5	5.7	4.8		0.4
3b	17	23		6	8	31	7.4	5.8	4	0.4
12	19	21	10	3		31	7	4	4.3	0.5
13	18	18.5	7	2.5		37	7.5	6	2.3	0.9
14	15	17		27		26	8	4.8	1	1.6
15	4	1	9	70		10		2.2		3.3
16	3.5	7		60		13	7	3.5		1.8
19	12	26.2		34.2		8	14	4.7		0.7
20	7	6	4.5	34	29	9.5	4	2	2.6	0.9
21	7.5	10	3	12	44.6	7.5	11	2	1.3	1.4
22	4			81		1	7		1	1
23	2	0.5	2.5	87		4			1	1.4

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2. ANALYTICAL METHODS

X-ray Fluorescence analysis.

Nine volcanic rocks and sixteen clay material samples (whole rock) were subjected to XRF analysis of major element content, using a PHILLIPS RW 1540 manual X-ray fluorescence spectrograph and standard procedures employed in the department of Geology, Manchester University (BROWN et al., 1973). Six specimens of clay material from the east part of Aegina previously analysed by wet chemistry were also run as extra standards (Table 1).

Analyses for trace element contents were also carried out by XRF techniques for thirty clay material samples and five samples from the east part of Aegina. The analytical and data reduction and correction procedures for both major and trace elements are similar to those given by the authors referred to.

3. MAJOR ELEMENTS ANALYSES

Clay material.

i) Bulk Samples.

The chemical composition of the samples can be conveniently represented by a plot in which the logarithms of the weight ratios of

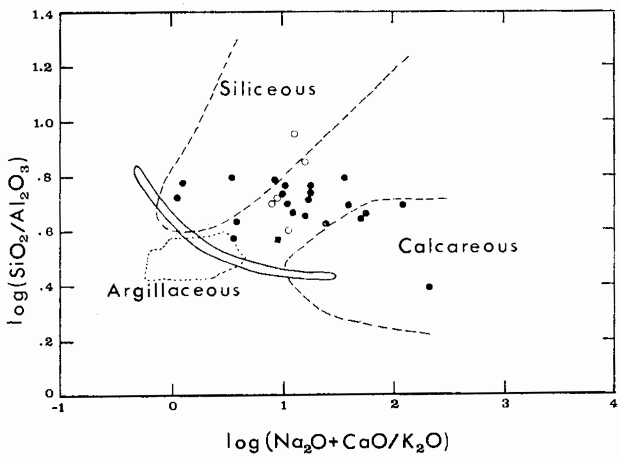

Fig. 2. Chemical composition of samples from Aegina plotted as a function of log (SiO_2/Al_2O_3) and log $(Na_2O/CaO)/K_2O$. The banana shaped area denotes the range in composition of igneous rocks, the stippled area shows the approximate range in composition of argillaceous sediments. (After GARRELS and MACKENZIE, 1971).

● — present study ○ — TSOLI (1972)

■ — average of the volcanic samples 3, 4 and 17.

TABLE 2.

Average chemical compositions of siliceous - argillaceous, intermediate and carbonate groups of samples from Aegina.

	siliceous - intermediate	intermediate	carbonate	average sediment *
SiO_2	59.99	38.72	20.58	44.5
Al_2O_3	12.64	7.02	4.21	10.9
Fe_2O_3	7.51	5.56	3.52	4.0
MgO	2.92	5.71	6.98	2.6
CaO	3.19	17.99	29.32	19.7
Na_2O	1.90	0.79	0.81	1.1
K_2O	2.10	1.66	0.64	1.9
SO_3	0.61	0.53	0.74	
H_2O	8.10	6.50	4.02	
CO_2	1.33	14.90	28.94	13.4
TiO_2	0.59	0.27	0.06	
MnO	0.06		0.01	
P_2O_5	0.16		0.05	0.1
Total	101.10	99.65	99.88	100.0

siliceous - argillaceous	(average four samples, 7, 11, 12 and 13)
intermediate	(average ten samples 1b, 3b, 4b, 5b, 7b, 8, 9, 10, 14 and 19)
carbonate	(average five samples, 5, 15, 16, 20 and 21)

* after Poldervaart, 1955.

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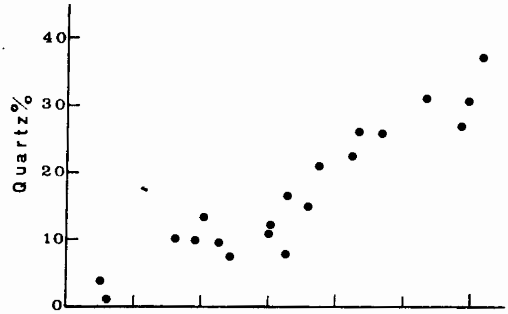
SiO_2 / Al_2O_3 and $(Na_2O + CaO) / K_2O$ from the co-ordinates of the graph (Fig. 2). The former ratio provides a numerical representation of the distinction between samples which are relatively high in silica, and samples, which are more aluminious. The later ratio provides an estimate of the argillaceous or calcareous nature of sediment. An argillaceous sediment has a low $(Na_2O + CaO) / K_2O$ ratio because of its mineralogical composition of quartz, clay minerals and feldspars, whereas a carbonate sediment has a high ratio, reflecting its relatively high CaO and low K_2O content.



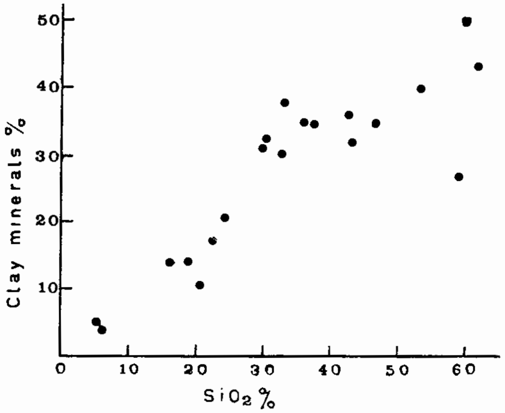


Fig. 3. Quartz versus SiO_2 content.
Fig. 4. Clay minerals versus SiO_2 content.

Geochemical variations.

Table 2 shows the average chemical composition for siliceous-argillaceous, intermediate and carbonate sediments from Aegina.

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Silicon.

The SiO_2 content varies roughly sympathetically with the quartz and clay mineral content (Fig. 3 and 4) and ranges from 58 to 62 wt % for the siliceous-argillaceous samples, from 30 to 53 tw % for the intermediate group of samples and 16 to 24 wt % for the carbonate group. In the samples SiO_2 occurs in the following locations: in smectite, illite, detrital quartz and in subsidiary amounts in detrital plagioclase.

Aluminium and Titanium.

The fact that the Ti content (being higher in the siliceous-argillaceous samples) varies sympathetically with Al_2O_3 (Fig. 5) suggests that these elements are closely related paragenetically. The calcareous samples 22 and 23 being extremely poor in Ti and Al are not considered in this plot.

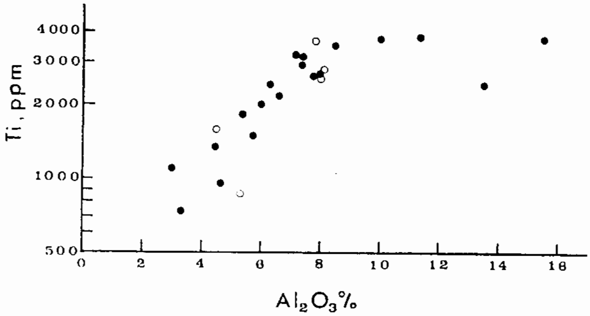


Fig. 5. Titanium versus Al_2O_3 content.

Since the principal enviroment of clay mineral formation is the weathering zone, it is obvious that the relationship between Al and Ti is established during the development of alluvium and is subsequently preserved during the mechanical redeposition of the clays in the terminal discharge basins.

Some other relationships are depicted in figures 6, 7 and 8; silica and iron are shown plotted against alumina, and iron against silica. In each case note that there is an approximately linear relationship passing nearly through the origin. This means that the inter-oxide ratios are relatively constant over the whole range of absolute values.

The range of absolute values is primarily a function of type of material: siliceous-argillaceous samples are relatively rich in these elements, carbonate samples are relatively deficient, while the intermediate group of samples have values in between these two. Thus it is suggested

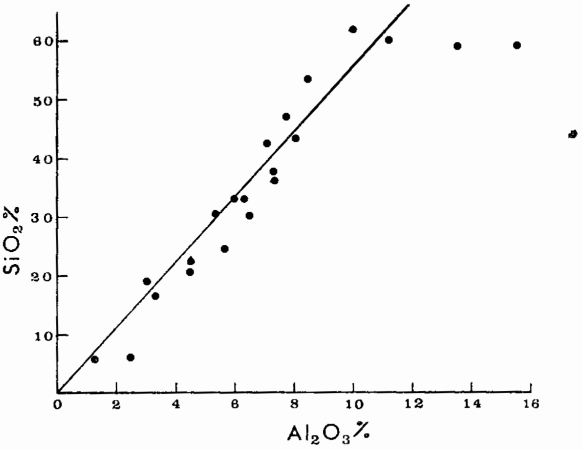


Fig. 6. SiO_2 versus Al_2O_3 content.

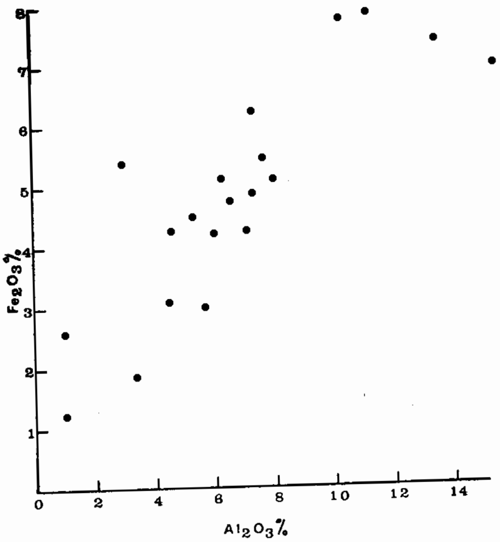
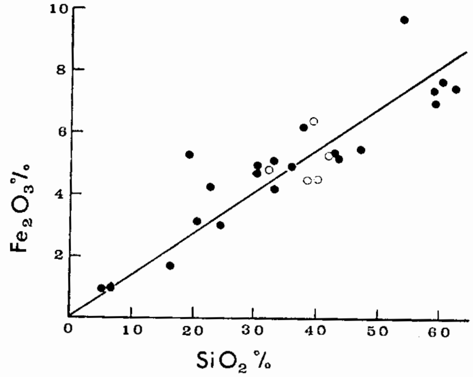


Fig. 7. Fe_2O_3 versus Al_2O_3 content.

that the original supplied material probably had certain specific ratios of oxide pairs (characterised by high absolute amounts), and that dilution by increasing amounts of carbonates, decreased the absolute amounts without changing the relative amounts of these elements.



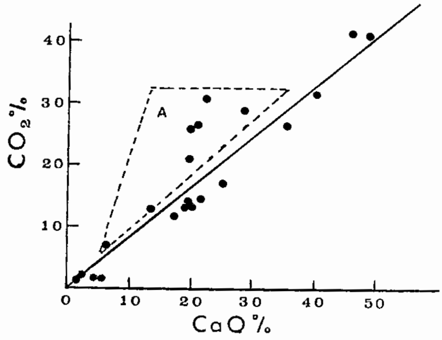


Fig. 8. Fe_2O_3 versus SiO_2 content.
● — present study ○ — TSOLI, 1972.

Fig 9. CO_2 versus CaO content.
A—high CO_2 relative to CaO, due to presence of dolomite.

It is significant however that any change, mineralogical or chemical, that took place involved a rearrangement of these elements (and Ti from figure 5) but no gain or loss on a whole rock basis.

Calcium.

Calcium can probably occur in four main positions in the samples: a) as calcium carbonate, b) as calcium sulphate, c) in smectite, d) in Na, Ca plagioclases.

The variation diagram in figure 9 for CO_2 and CaO indicates the importance of $CaCO_3$ as the home mineral of much of calcium in the samples. Samples 5, 20, 21, 3b, 4b, 5b and 7b containing dolomite in addition to calcite plot off the line defined by the calcite bearing samples, because of the higher CO_2/CaO ratio in dolomite.

After substraction of CaO to satisfy CO_2 and SO_3, the CaO content of the samples averages 1.76 wt $^0/_0$, excluding sample 8 which shows a value for residual CaO of 3.64 wt $^0/_0$; this may reflect inaccuracy in the CO_2 determination. VAN MOORT (1973) gave values between 0.02 $^0/_0$ and 4.32 $^0/_0$ for the CaO content of Australian sediments after carbonates subtraction. The higher CaO (residual) content found in Aegina sediments (more than 1.5 $^0/_0$) may be related to a source area rich in CaO.

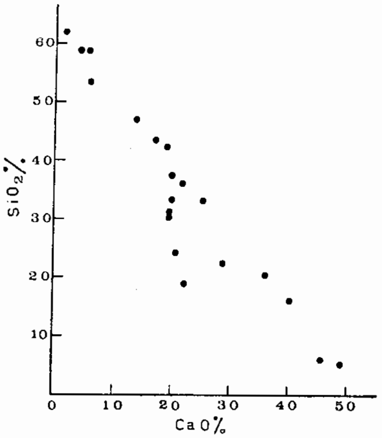


Fig. 10. SiO_2 versus CaO content.

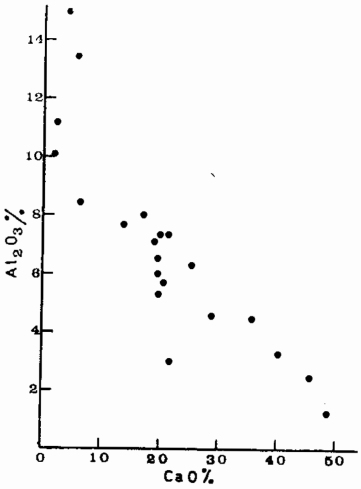


Fig 11. Al_2O_3 versus CaO content.

Figures 10 and 11 show SiO_2 and Al_2O_3 plotted against CaO content. A strong negative correlation is observed between CaO and SiO_2, CaO and Al_2O_3. This is well in agreement with the mineralogy. A high carbonate content is correlated with low quartz and smectite content (assuming that SiO_2 enters mainly these minerals) and low illite content (assuming that most of the Al_2O_3 enters illite).

Magnesium.

A high MgO content, 13.85 wt $^0/_0$, in the samples seems to be consistent with the dolomite content. After subtraction of MgO to form dolomite, the average MgO for the samples is 3.06 $^0/_0$ with considerable variation from 5.12 $^0/_0$ to 0.15 $^0/_0$.

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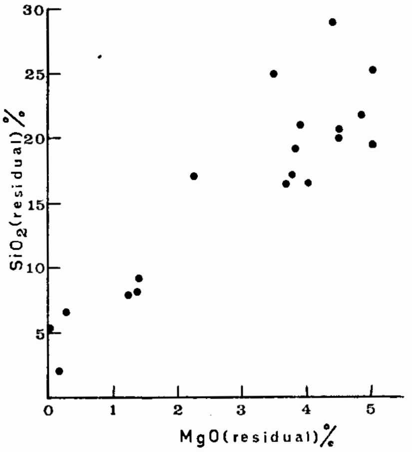
The constancy of the MgO residual / SiO_2 residual ratio supports the above hypothesis (Fig. 12).

Sodium and Potassium.

The alkali metal content is generally high in the samples having a high aluminium content. K_2O shows a better correlation with Al_2O_3 than does Na_2O (Fig. 13). Most of the potassium and much of the sodium is present in clay minerals. The distribution of potassium is undoubtedly related to the illite content of the samples. The Na_2O is always lower than the K_2O content except in samples which contain sodium chloride.



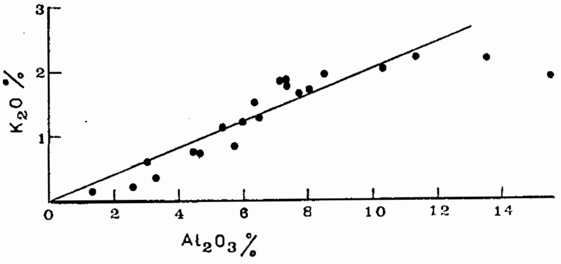


Fig. 12. SiO_2 (residual) versus residual MgO content.

Fig. 13. K_2O versus Al_2O_3 content.

4. TRACE ELEMENTS ANALYSES

Trace elements contained in sediments may be of detrital or nondetrital origin. The nondetrital material enters the basin of deposition

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TABLE 3.

Trace Elements Analyses for Clay Material from Aegina (Bulk Samples) in ppm.

Group of Samples	Siliceous-argillaceous				Intermediate												
Sample No.	7	11	12	13	1b	3b	4b	5b	7b	8	9	10	14	19	B_1	B_4	B_9
Rb	107	67	120	104	n. a.	n. a.	n. a.	n. a.	n. a.	74	87	102	90	58	98	38	91
Cu	78	43	30	31	17	42	3	35	16	78	65	78	55	46	52	38	32
Sr	411	510	150	176	298	165	172	250	206	391	455	423	246	495	321	385	226
Ba	530	592	189	231	n. a.	n. a.	n. a.	n. a.	n. a.	134	147	155	n. d.	134	138	142	117
Zn	57	92	92	79	70	104	57	76	58	59	69	70	80	68	81	86	85
Sc	11	14	4	4	n. a.	n. a.	n. a.	n. a.	n. a.	84	70	66	52	63	43	53	44
Y	27	19	21	25	n. a.	n. a.	n. a	n. a.	n. a.	18	22	24	31	15	17	13	15
La	12	11	20	30	n. a.	n. a.	n. a.	n. a.	n. a.	8	5	13	11	6	5	16	17
Ce	49	58	82	41	n. a.	n. a.	n. a.	n. a.	n. a.	52	53	59	61	49	43	46	60
Nd	24	20	28	30	n. a.	n. a.	n. a.	n. a.	n. a.	20	23	24	20	18	18	19	20
V	113	71	127	122	72	49	45	47	38	92	76	95	86	64	96	66	122
Cr	84	32	457	390	516	477	126	244	115	299	266	296	293	200	365	282	366
Ni	127	138	455	393	516	751	239	224	222	298	256	276	277	194	404	259	327
Zr	162	148	107	132	77	85	43	91	49	96	120	120	104	67	98	85	93
Ti	3,828	2,438	3,840	3,788	3,258	3,559	2,197	2,767	1,848	2,435	2,948	3,184	2,662	2,023	3,690	2,589	2,786

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Table 3 (continued)

Group of Samples	Carbonate									
Sample No.	5	15	16	18	20	21	22	23	B_6	B_8
Rb	30	15	24	45	33	35	10	3	52	29
Cu	37	91	85	34	46	26	92	n. d.	4	10
Sr	341	548	573	285	328	327	603	799	205	197
Ba	133	96	142	143	11	131	8	n. d.	102	318
Zn	70	48	54	74	65	75	56	50	77	67
Sc	64	155	132	60	85	63	181	204	36	36
Y	12	4	5	17	16	14	5	3	14	7
La	2	n. d.	5	6	n. d.	n. d.	n. d.	n. d.	6	n. d.
Ce	35	40	38	31	32	30	27	21	42	29
Nd	15	16	19	18	16	18	14	18	15	15
V	20	8	26	80	26	40	n. d.	n. d.	71	21
Cr	236	28	109	108	256	84	27	37	231	116
Ni	373	30	103	181	146	137	35	34	273	131
Zr	12	24	67	36	63	50	51	75	51	35
Ti	1,117	721	1,354	1,172	965	1,511	195	156	1,581	370

B_1, B_4, B_6, B_8, B_9 = samples from the east part of Aegina
n. a. = not analysed
n. d. = not detected

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in solution and may be incorporated into the sediment by a variety of processes such as direct precipitation, co-precipitation, adsorption and reaction with organic material. A number of trace elements are transported partly in suspension and partly in solution. The ratio of amounts of an element in suspension and in solution varies considerably for different elements.

The bulk samples have been analysed for the following trace elements: Zr, Sr, Rb, Y, V, Ti, La, Zn, Ni, Ce, Nd, Cu, Sc, Cr and Ba. Their values are listed in table 3.

For convenience in describing the variations in element contents found, the 15 trace elements will be grouped as follows:

1) Rb, 2) Copper, 3) The alkaline earths, Sr and Ba, 4) Zinc, 5) Scandium and Yttrium, 6) La, Ce, Nd, 7) The ferride elements, V, Zr and Ni, 8) Zr and Ti.

1. **Rubidium (Rb).**

The Rb content of the samples ranges between 3 and 120 ppm; the higher values were found in the siliceous-argillaceous and the lower in the carbonate samples.

In wethering, like igneous activity, rubidium is closely linked with potassium. HORSTMAN (1957) has shown that K/Rb ratio decreases during weathering, indicating a relative concentration of Rb.

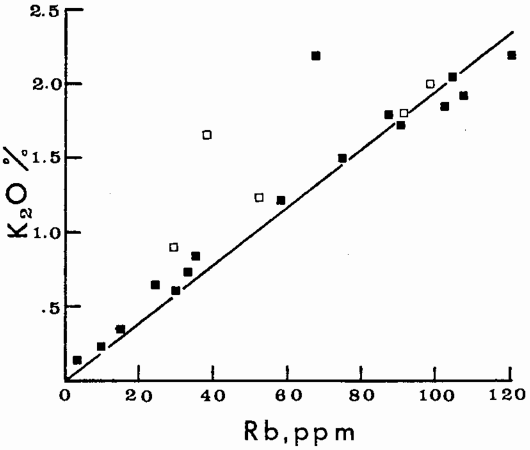

Fig. 14. K_2O against rubidium content.
■ — present studz □ — TSOLI, 1974.

When the Rb content of the samples is plotted against K_2O % (Fig. 14) a general linear correlation is observed and because concentration of potassium is directly related to illite composition in sediments, rubidium concentration in the samples from Aegina varies with illite content.

The Rb/K ratio is nearly constant within the samples analysed. This may suggest that the distribution of Rb seems to be related primarily to weathering in source areas rather than to the physico-chemical properties of the environment of the sedimentation. So most of the Rb is probably detrital in origin arriving at the site of sedimentation in solid particles of the mineral illite. The extent to which this element has been sorbed onto the clay fraction from sea water is not known.

2. Copper (Cu).

The copper content of the siliceous-argillaceous samples ranges from 31 ppm to 46 ppm with a mean value of 37 ppm. The intermediate group shows a much wider spread of values, in which the highest content reported is 78 ppm and the lowest 3 ppm. The carbonate group has higher contents of Cu reaching up to 91 ppm and with a mean value of 47 ppm.

The increase in relative concentration of this element from the siliceous-argillaceous to carbonate group of samples can be due to a sharp increase in the role of solution in its migration (STRAKHOV, 1969). The nature of the source rocks may well explain the entry of Cu in solution. Lack of correlation between Cu and the major elements supports the hypothesis that most of the Cu was brought into solution rather than structurally combined in silicate minerals.

If we examine the concentration of Cu in the 1 micron fraction of the three samples 9, 10 and 12 (fig. 15) we observe that this element is considerably enriched in the clay fraction. Its values range between 176 ppm and 352 ppm. This is taken to indicate: a) either that copper was sorbed onto clay minerals and probably replaced magnesium in smectite, or b) the preference of this element to accumulate in the fine fraction of suspended material during transportation.

3. The alkaline earths, strontium (Sr) and barium (Ba).

The Sr content of the samples from Aegina is highly variable and ranges between 150 ppm and 799 ppm with the higher values occuring in the carbonate group.

When the strontium content of the samples from Aegina is plotted against the $CaCO_3$ $^0/_0$ a positive correlation is observed (Fig. 16). The samples having low $CaCO_3$ contents have low Sr values and the amount

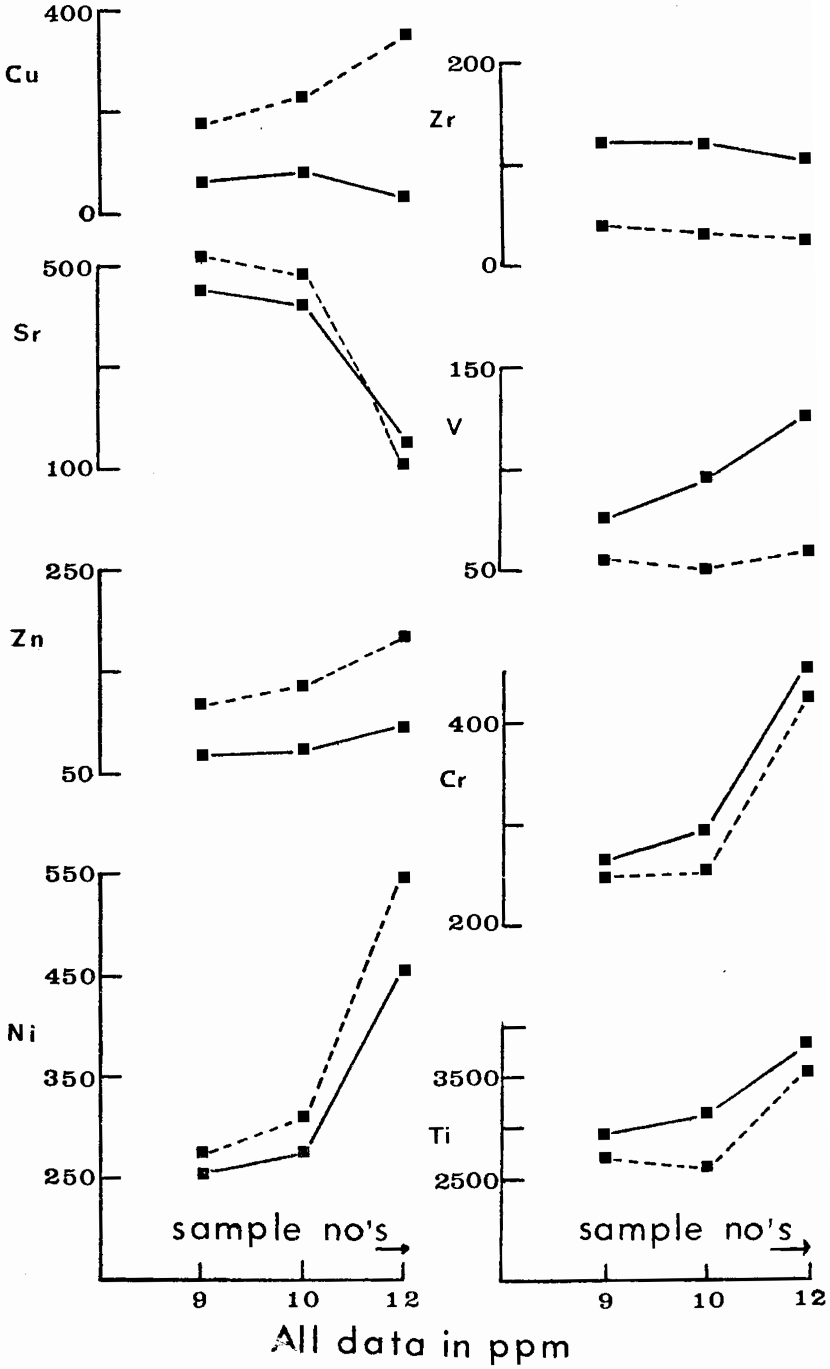

Fig. 15. Cu, Sr, Zn, Ni, Zr, V, Cr, and Ti contents for the bulk and 1 micron fraction of the three samples 9, 10 and 12. ——— bulk samples. – – – – 1 micron fraction.

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of Sr rises with increasing $CaCO_3$ content (except samples 7, 5, 21 and 19).

The high strontium content for the samples 7 and 11 (411 ppm and 510 ppm respectively) could be due to secondary infiltration into the porous material (GOLDSCHMIDT, 1954) as these samples are coarse grained and loose. The low values of strontium for the samples 12 and 13 (150 ppm and 176 ppm respectively) are not surprisingly low. Sr concentrations are as low as 120 - 250 ppm for deep sea sediments on a carbonate free base (WEDEPOHL, 1960 ; TUREKIAN, 1964), The greater part of Sr in these samples is probably adsorbed from solution onto clay minerals.

The content of Ba in the samples studied here ranges between 8 and 592 ppm. The highest content of this element is found in the samples 7 and 11 and it is concentrated, like strontium, by secondary infiltration into the porous material, while the lowest content is found in the carbonate group. If these two samples (7 and 11) are neglected, the values range between 8 and 318 ppm with an average of 163 ppm. GOLDSCHMIDT (1954) reported 154 - 462 ppm Ba in marine sediments. BATTACHARYA (1970) reported higher amounts up to 2000 ppm for sediments from Northwest India. KHAN (1964) gave an average value of 344 ppm for calcareous shales and marls.

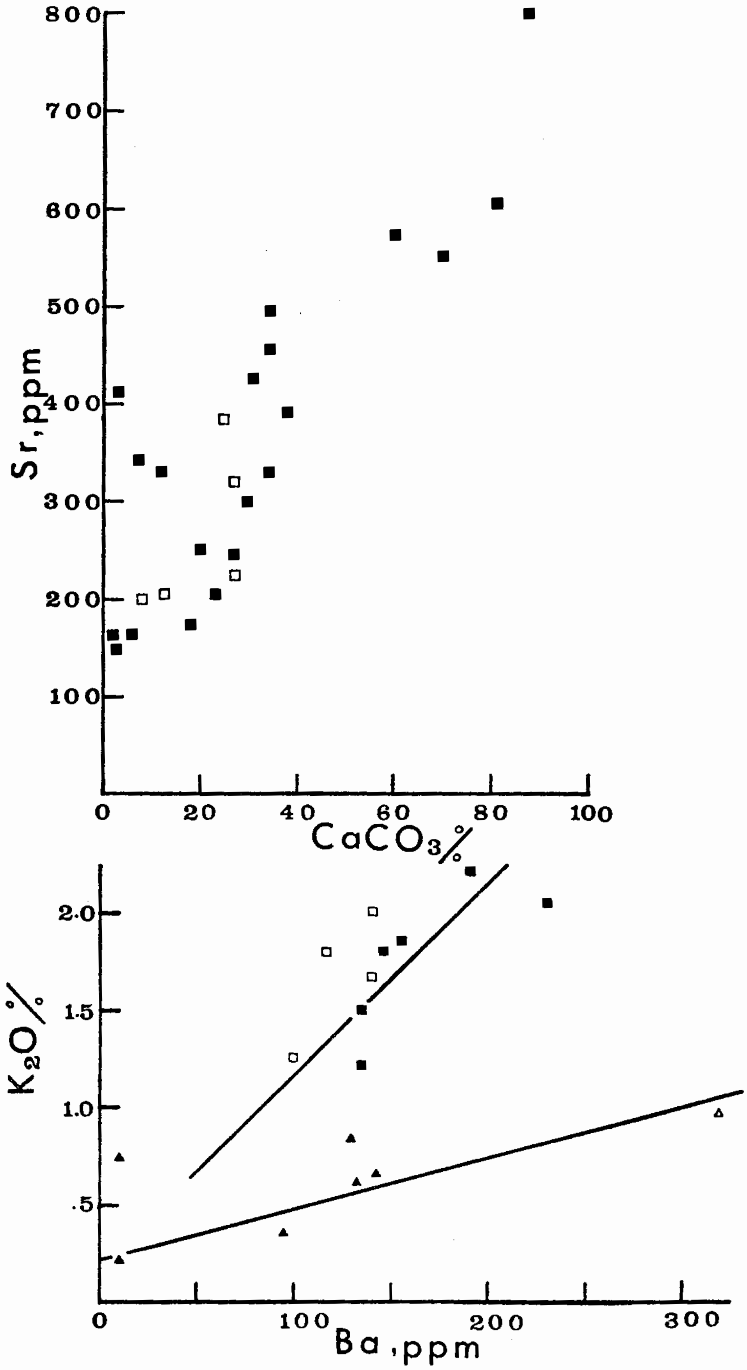
If Ba is platted against K_2O $^0/_0$ (Fig. 17) a linear relationship between the two is observed, we can therefore assume that Ba is located in the clay mineral illite. The two trends observed are due to the lower potassium content of the carbonate samples.

4. **Zinc (Zn).**

The Zn contents in the samples do not differ substantially between the three groups. They range between 50 and 104 ppm with the lower values occuring in the carbonates. These values are close to those usually given in the litterature for similar samples.

5. **Scandium (Sc) and yttrium (Y).**

The Sc contents in the samples from Aegina range from 4 ppm to 204 ppm with the higher values occuring in the carbonate group. BHATTACHARYA (1970) gave values between 5 and 10 ppm Sc for the clay fraction of sediments from Northwest India ; he reported that in his samples, which were carbonate - free, scandium occured as a substituent in clay minerals. TUREKIAN and WEDEPOHL (1961) gave 13 ppm Sc for shales and 1 ppm for carbonates. NORMAN and HASKIN (1968) reported 11.9 ppm Sc for a composite of 40 shales from North America and no more than 1 ppm for limestones.



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Unlike TUREKIAN and WEDEPOHL'S, NORMAN and HASKIN'S results, in the samples from Aegina Sc occurs in high amounts in carbonates. If we plot scandium concentrations against percentage of CaO a linear positive correlation is observed (Fig. 18).

The Y contents of the samples vary from 3 ppm to 27 ppm with the lower values found in carbonate samples. TUREKIAN and WEDEPOHL (1961) gave 30 ppm Y for carbonates and 26 ppm for shales. The highest Y content found in the analysed samples was in the siliceous-agrillaceous samples and ranges between 21 and 27 ppm.

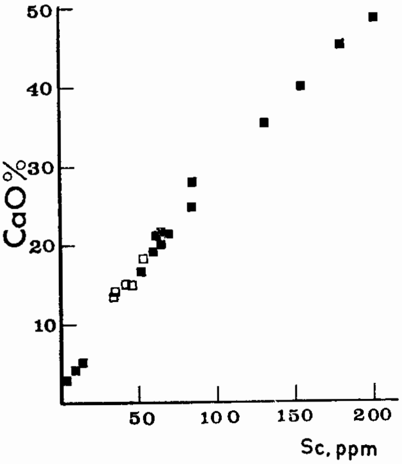

Fig. 18. CaO against scandium content.

A plot of the illite percentage and Y ppm (Fig. 19) shows a positive relationship indicating that this element is associated with illite.

6. Lanthanum (La), cerium (Ce) and neodymium (Nd).

The lanthanum (La^{3+}) content in the samples studied here varies from 2 ppm to 30 ppm. For five carbonate samples La content was below

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←

Fig. 16. Strontium against $CaCO_3$ content.
■ — present study □ — TSOLI, 1972
(Symbols in all the subsequent figures are the same as in this figure).

Fig. 17. K_2O agaist barium content.
▲ — carbonate samples.
■ □ — rest of the samples.

the lowen limit of detection. The average for all the samples is 8 ppm. The higher values found in the siliceous-argillaceous samples and the lower carbonates. RONOV et al. (1967) gave an average of 25.5 ppm for sedimentary rocks from the Russian Platform.

The Ce^{3+} (r = 10.7 Å) contents in the samples range from 21 to 60 ppm with a mean value of 44.5 ppm. RONOV et al. (1967) reported 49.5 ppm for sedimentary rocks of the Russian Platform and TUREKIAN WEDEPOHL (1961) gave 59 ppm for shales, 92 ppm for sandstones and 11.5 for carbonates.

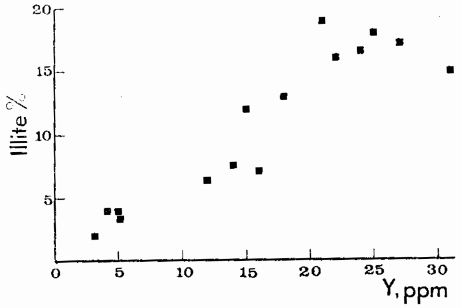


Fig. 19. Illite against yttrium content.

The Nd^{3+} (r = 1.04 Å) contents vary from 14 ppm to 30 ppm with a mean value of 19.5 ppm which is close to that reported by RONOV et al. (1967) of 32.1 ppm.

7. **Vanadium (V), chromium (Cr) and nickel (Ni).**

The concentration of vanadium in these samples varies between 8 ppm and 127 ppm; in two carbonate samples, 22 and 23, V was found below the lower limit of detection. TUREKIAN and WEDEPOHL (1961) reported 130 ppm vanadium for shales, 20 ppm for sandstones and 20 ppm for carbonates. BHATTACHARYA (1970) gave values between 80 and 200 ppm V for the clay fraction of sediments from Northwest India, and SUMMERHAYES (1972) reported 175 ppm vanadium for a representative silt sample from Moroccan sediments.

When the contents of vanadium are against percentage of illite there is an obvious relationship (Fig. 20).

The concentrations of V ppm in the 1 micron fraction of the samples 9, 10 and 12 range between 50 and 80 ppm. As can be seen, there is an impoverishement of V in the fine fraction. Vanadium belongs to the group of elements for which transport by solution is insignificant, the transport being effected monstly in suspended material.

The Cr contents in the samples range between 27 ppm and 516 ppm, the lowest concentration being found in the carbonate group. These

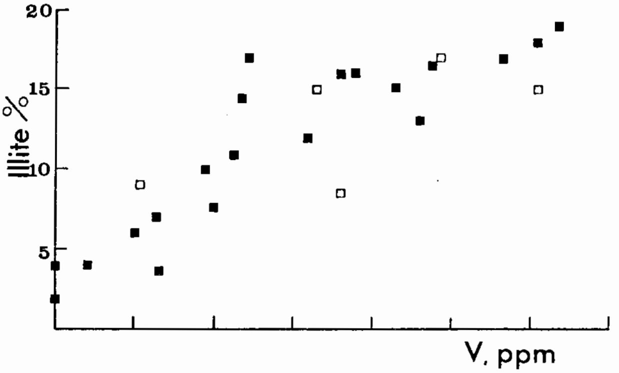


Fig. 20. Illite against vanadium content.

values are much higher than the values reported in sedimentary rocks by other investigators. TUREKIAN and WEDEPOHL (1961) gave 90 ppm Cr for shales, and 35 and 11 ppm for sandstones and carbonates respectively. KHAN (1964) reported 146 ppm for shales, and 116 ppm for marls.

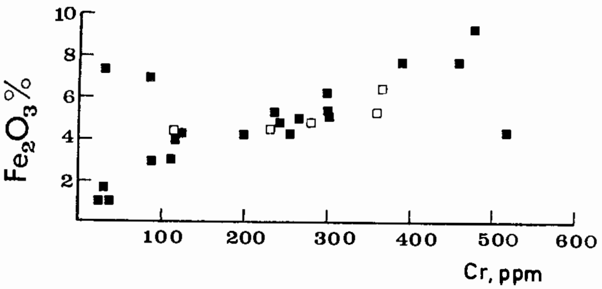


Fig. 21. Fe_2O_3 against chromium content.

During weathering under oxidative and alkaline conditions Cr may be oxidized to Cr^{6+} in which condition it is extremely mobile, whilst reducing and acid conditions probably lead to the reduction of Cr to Cr^{3+} and its retention in the products of weathering. If Cr is not released from the igneous minerals by weathering some relationship to iron might be expected. If, for the samples studied here, we plot Cr ppm against

Fe_2O_3 % (Fig. 21) a moderate correlation is observed. This suggests that most of the Cr is located in detrital Cr bearing minerals.

As in the case of vanadium, chromium is impoverished in the 1 micron fraction of the samples 9, 10 and 12 with Cr concentrations 248, 257 and 429 ppm respectively (Fig. 15).

The content on Ni in the samples from Aegina is high and ranges between 34 ppm and 516 ppm if we exclude sample 3b which contains 751 ppm. The lowest concentration of this element occurs in sample 23 which is almost entirely composed of calcite.

TUREKIAN and WEDEPOHL (1961) reported 68 ppm Ni for shales, 2 ppm for sandstones and 20 ppm for carbonates, KHAN (1964) gave 64 ppm for 25 shales, 15.5 ppm for limestones and 54 ppm for marls.

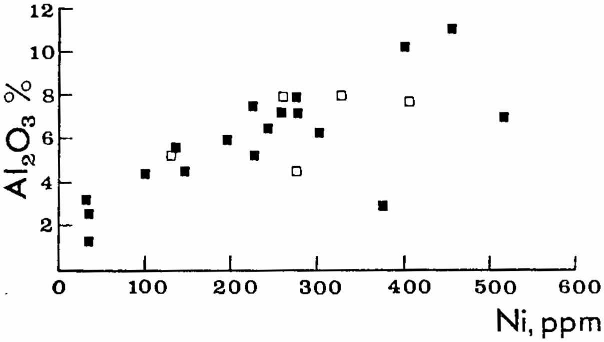


Fig. 22. Al_2O_3 against nickel content.

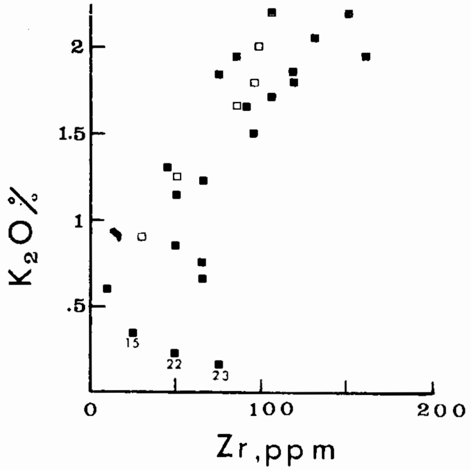
HIRST (1958) also found a control of clay minerals on Ni content in the Paria sediments. In the present study we could accept a control of clay minerals on Ni content because of the relationship between Al_2O_3 % and Ni ppm (Fig. 22). Some of the samples are anomalous in character. The very high amount of nickel on sample 3b and the low amounts in samples 7 and 11 do not follow the linear relationship. The two latter samples are quite different from the rest in their textural and mineralogical characters; as far as sample 3b concerns, it is in the beginning stage of dolomitization.

The Ni contents in the 1 micron fraction for the samples 9, 10 and 12 are 274 ppm, 311 ppm and 548 ppm respectively (Fig. 15), are higher than those for the bulk samples.

8. **Zirconium (Zr) and titanium (Ti).**

The Zr^{4+} (0.79 Å) contents of the samples from Aegina range between 12 ppm and 162 ppm. The carbonates are slightly depleted in this element but there are not great fluctuations between the different types of samples. TUREKIAN and WEDEPOHL (1961) reported 160 ppm, 220 ppm and 19 ppm Zr for shales, sandstones and carbonates respectively.

The enrichement of Zr content in the more sandy samples e. g. 7 and 11 (162 ppm and 148 ppm respectively) may be explained by the mechanical concentration of the detrital mineral zircon.



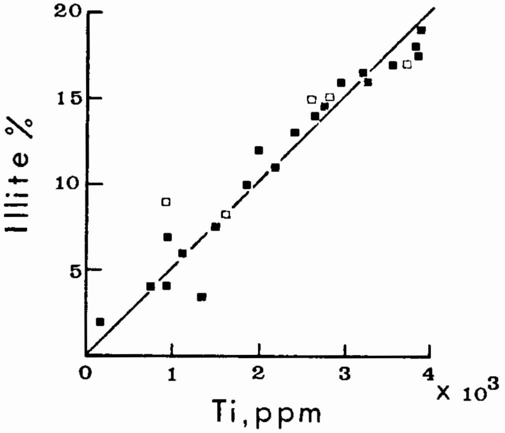


Fig. 23. K_2O against zirconium content.
Fig. 24. Illite against titanium content.

In figure 23, K_2O $^0/_0$ is plotted against Zr ppm for the samples studied here. The sympathetic relationship shows that there is a control of this element by clay minerals.

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For most of the samples titanium has been analysed as a trace element; its contents range between 156 ppm and 3,828 ppm. The lowest concentration of this element occurs in sample 23 which is almost a pure calcite, and the highest in the most sandy sample No. 7. TUREKIAN and WEDEPOHL (1961) gave values 4,600 ppm for shales, 1,500 ppm for sandstones and 400 ppm for carbonates. BHATTACHARYA (1970) reported values between 1,500 and 6,000 ppm for the clay fraction of sediments from Northwest India. SUMMERHAYES (1972) found 5,022 ppm for a representative silt sample of Moroccan sediments and 8,413 ppm for another silt sample of Saharan sediments.

In figure 24 a positive linear correlation is observed between illite percentage and Ti ppm in the samples. This supports the suggestion that Ti is structurally combined in illite.

Titanium concentrations were found impoverished in the 1 micron fraction (Fig. 17) of samples 9, 10 and 12 with contents 2,706 ppm, 2,617 ppm and 3,580 ppm respectively.

5. DISCUSSION

The clay formations from the island of Aegina show a complete spectrum of compositions from siliceous to calcareous type; three groups of samples could be distinguished :

a) Siliceous-argillaceous samples, b) intermediate group, and c) carbonate group of samples.

The significant features of the chemical composition are the dominance of calcium over magnesium, potash over soda in high silica siliceous samples, high lime in calcareous samples and the presence of iron mainly in the ferric state.

The major variations in chemical composition are generally related to mineralogy :

1. variation in silicon content is essentially a function of quartz and clay mineral content.
2. calcium and magnesium ; the main bulk of both elements is found in carbonates occuring in the sediments.
3. most of the potassium and much of the sodium is present in clay minerals.
4. the direct relationship between Al_2O_3 and Ti, SiO_2, and Fe_2O_3 and between Fe_2O_3 and SiO_2, appears to be a function of the original detrital content of the sediments.

Dilution by increasing amount of carbonates decreased the absolute amounts without changing the relative amounts of these elements.

From the present work the major element geochemistry is considered to be controlled firstly by the detrital fraction (Al, Si, Ti, Fe) and secondly by minerals such as carbonates (calcite, dolomite) which are believed to be the main means by which material was incorporated into the sediments from solution.

The distribution of most of the trace elements differs in the three groups of samples. The direct relationship of Al_2O_3, K_2O and some trace elements has been demonstrated. This suggests that a large proportion of the contents of the trace elements (Rb, V, Ni, Zr, Ti) appears to be structurally combined in detrital clay minerals, and their variation between the various samples is controlled by the proportion of the clay minerals present. The alternative of entry to structure through the inclusion of adsorbed elements by structural reconstitution is possible as the clay minerals have undergone a certain structural reconstitution in the sedimentary environment. This may be the case for nickel ; concentration of this element rises to 751 ppm for samples occuring in an environment characterised by a beginning dolomitization which is the domain between detrital and chemical sedimentation favourable for clay mineral transformations. Entry in solution is shown by elements such as Sr, Ba (?).

Comparison of the chemistry of the samples studied here with those from the east part of the island (Saint - Thomas), reveals great mutual similarities. According to their major and trace element geochemistry, samples from Saint - Thomas were found to belong to the intermediate and carbonate groups of samples.

The similarities in mineralogy, chemistry and stratigraphic position of the Aeginete clay formations occuring west and east of Marathovouno suggest that they have a common origin and have undergone a similar evolution. They are considered to be a marine environment sedimentary formation made up of products derived from the weathering of the old lavas and of the older carbonate rocks.

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