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HIGH FLUORINE CONTENTS IN THE PLIOCENE VOLCANIC ROCKS OF THE GOLCÜK AREA, ISPARTA, SW TURKEY

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ABSTRACT

The Gölcük area in central Anatolia represents a post tectonic Pliocene volcanism upon a Mesozoic paleorift in the entire Taurides margin. In this connection the tectonic structures of the region result from the main alpine orogenic phases of the Helleno-Tauric belt. The study area consists of sedimentary and volcanic rocks. As allochthonous, the Triassic through Upper Cretaceous Akdag-limestone and the Upper Cretaceous to Lower Tertiary volcano-sedimentary series constitute the basement rocks. They are transgressively overlain by marine clastic series of Eocene and conglomerate of Oligocene age. The volcanic rocks are tephriphonolite (stage i), pyroclastic series represented by friable tuff, ignimbrite, and pumice tuff (stage ii), and trachyandesite with trachyte (stage iii) as vents, dikes, and volcanic domes. They indicate a sodic alkaline character.

As F-bearing minerals, the volcanics consist of pyroxene, hornblende, biotite, fluorapatite, and extreme small fluorite crystals. Additionally, the glassy groundmass can be added to the F-carriers. The F-contents in the volcanic rocks show a close correlation with P₂O₅ and are generally controlled by fluorapatite consequently. This assumption can be established by the predominance of high REE contents. Moreover, it is a novelty that the F-contents display a remarkable depletion from basic towards the acidic rocks which might be attributed to discharging of the F. portions during fumarolic activity.

INTRODUCTION

The Gölcük area, situated in the SW part of the province capital Isparta (Fig. 1), represents a post tectonic Pliocene volcanic field upon a Mesozoic paleorift in the western Taurides (POISSON et al. 1984), the so called Isparta angle between Lycian and Hadim-Hoyran-Beysehir nappes (ÖZGÜR et al. 1990). The tectonic structures of the region results from the main alpine orogenic phases of the Helleno-Tauric belt (KISSEL et al. 1989). From Paleocene through Quaternary, an extensive volcanic activity took place in central Anatolia (INNOCENTI et al. 1975; ERCAN 1986) which is related to the Afro-Arabian plate being subducted under the Euro-Asiatic plate. The volcanic rocks of the Gölcük area belong to a Pliocene sequence.

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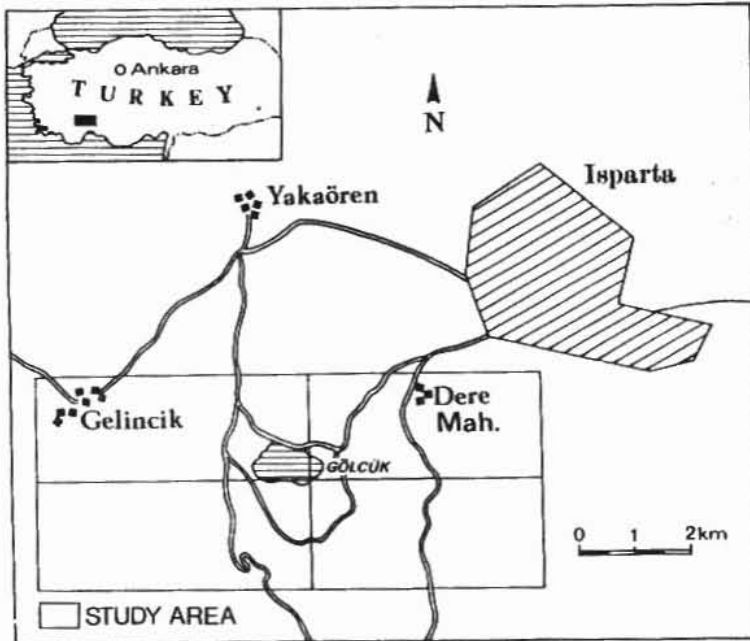


Fig. 1: Location map of the Gölcük area, Isparta, SW Turkey

Due to high fluorine contents in shallow aqueous systems as drinking water of the Gölcük area up to 6 mg/l we investigated the whole rock series, especially the volcanic rocks (ÖZGÜR et al. 1990; FEKDEGER et al. 1990, 1992). The aim of this paper is to elucidate the origin of the high fluorine contents in the volcanic rocks and the evolution of volcanic activity in the Gölcük area, because the shallow aqueous systems in the area is characterized by unusually high fluorine contents.

GEOLOGIC SETTING

In the study area, the basement rocks are the Triassic through Upper Cretaceous Akdag-limestone and the Upper Cretaceous to Lower Tertiary volcano-sedimentary series which are considered as allochthonous. Stratigraphically, they are transgressively overlain by marine clastic series of Eocene and conglomerate of Oligocene age. The volcanic rocks in the area belong to Lower Pliocene sequence from 4.07 ± 0.20 to 4.70 ± 0.50 Ma (LEFEVRE et al. 1983).

The volcanic rocks consist of lava flows and pyroclastic series. The lava flows are tephriphonolite, trachyandesite, and trachyte, as indicated by more than 60 rock analyses (PEKDEGER et al. 1992; Fig. 2; Tab. 1). The outcrops of tephriphonolite around the caldera now occupied by Gölcük lake constitute the first volcanic stage. The second stage is strongly characterized by volcanic explosions around the center of the recent Gölcük caldera. As third volcanic stage, trachyandesites and trachytes occur as different extrusions in size and shape of vents, dikes, and volcanic domes.

The second volcanic stage is represented by a pyroclastic sequence constituted by friable tuff (150 m), ignimbrite (20 m), and pumice deposit (10 m) exhibiting a composition ranging from trachyandesites to trachytes (Fig. 2). They are believed to be source of the high fluorine contents in the shallow aqueous systems in this area (PEKDEGER et al. 1992). The friable tuff is the greater part of the pyroclastic series and contains levels rich in lapillis and bombs.

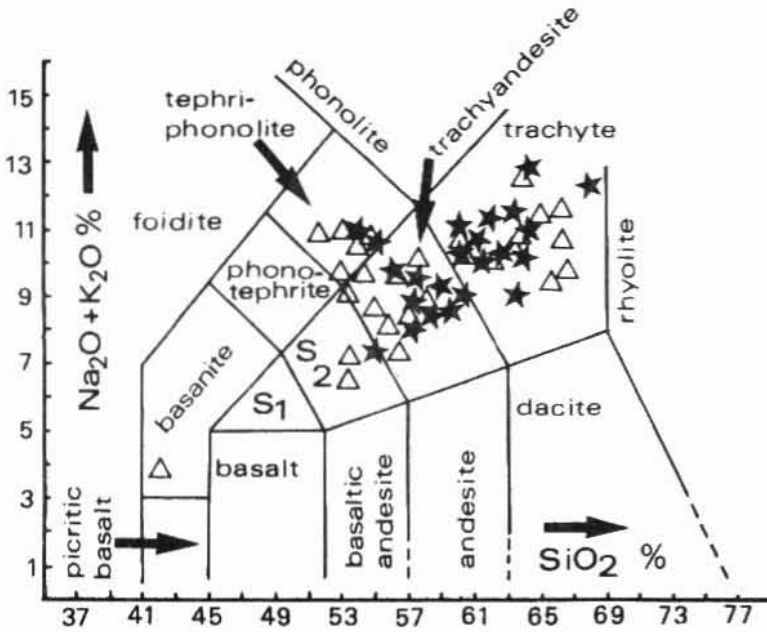


Fig. 2: Discrimination of the Gölcük lava flows (Δ) and pyroclastic series (\star) according to the classification scheme of LE MAITRE (1984). S1: trachybasalt; S2: benmoreite (Na) or shoshonite (K).

Moreover, the Akdag-limestone, the clastic materials of serpentinite and radiolarite, and relicts of tephriphonolite and xenoliths as deep-seated rocks are incorporated in friable tuff. In comparison to friable tuff, the ignimbrite distinguishes by its coarse and unsorted occurrence. The pyroxenitic xenoliths occur only in pyroclastic series sporadically and consist of pyroxene with inclusions of fluorapatite, orthoclase, olivine, anorthite, nepheline, ilmenite, and magnetite.

Generally, the volcanic rocks consist primarily of varying constituents of K (Na)-sanidine, oligoclase, pyroxene, biotite, hornblende, pyroxenitic xenoliths, glassy groundmass, and minor quantities of fluorapatite, fluorite, and sphene commonly. Moreover, the tephriphonolite contain augite and nepheline additionally. As an important F-tracer in the volcanic rocks, fluorapatite can be observed microscopically (Fig. 3), which shows geochemically a depletion of fluorine contents from the basic towards to the acidic rocks generally.

SAMPLING AND ANALYTICAL METHODS

For the rock analyses, 217 samples have been obtained from the Gölcük-lake area and its environs (PEKDEGER et al. 1992). The rock sampling has been taken place according to the principle representative sample of each rock formation. Major and some trace elements (Ba, Sr, Rb, Cr, Co, Ni, Zr, and Th) were determined by X-ray fluorescence spectrometry at the Institut für Chemie, Freie Universität Berlin, with a routine precision better than $\pm 5 \%$ for most elements (Tab. 1).

Rare earth elements (La, Ce, Sm, Eu, Tb, Yb, and Lu) were determined by instrumental neutron activation at the Hahn-Meitner Institut für Kernforschung, Berlin, with a routine precision better than $\pm 9 \%$ for most elements (DULSKI and MÖLLER 1975) using GSP-1 of U.S. Geological Survey as the reference standard. Cu, Pb, and Zn were determined by atomic absorption, and F by ion-sensitive electrode at the Institut für Geologie, Geophysik und Geoinformatik, Freie

Universität Berlin, with a precision better than $\pm 5\%$. For all analyses, BCR-1 and GSP-1 rock standards have been used (PEKDEGER et al 1992; Tab. 1).

The statistical parameter of these determined major and trace elements in the volcanic rocks of the Gölcük area are presented in Tab. 1. Moreover, we refer to ÖZGÜR et al. (1990) and PEKDEGER et al. (1992) due to REE analyses and their interpretations additionally.

	Trachyandesite							Trachyte							
	n	range	min	max	\bar{x}	δ	m	n	range	min	max	\bar{x}	δ	m	
SiO ₂ %	11	6.29	50.63	56.92	53.71	2.20	52.73	11	6.35	59.64	65.99	63.17	2.35	63.16	
Al ₂ O ₃ %	11	2.72	15.33	18.05	16.62	0.83	16.23	11	2.95	16.05	19.00	17.18	0.92	16.88	
Fe ₂ O ₃ %	11	1.35	5.09	6.44	5.93	0.48	5.95	11	3.57	1.16	4.73	2.98	1.02	2.55	
HgO %	11	2.72	2.44	5.16	3.70	0.79	3.40	11	2.05	0.34	2.39	1.27	0.70	1.06	
CaO %	11	3.90	5.43	9.33	6.97	1.26	6.69	11	2.81	1.65	4.46	2.89	1.04	2.81	
Na ₂ O %	11	3.12	2.83	5.95	3.64	0.92	3.17	11	2.13	4.39	6.52	5.29	0.59	5.34	
K ₂ O %	11	3.36	2.41	5.77	4.61	1.11	4.88	11	2.63	4.03	6.66	5.32	0.74	5.30	
TiO ₂ %	29	1.85	0.40	2.25	0.88	0.40	0.77	29	1.04	0.26	1.30	0.59	0.22	0.53	
H ₂ O %	29	0.10	0.01	0.11	0.06	0.03	0.06	29	0.09	0.01	0.10	0.04	0.03	0.04	
P ₂ O ₅ %	11	0.43	0.44	0.87	0.68	0.14	0.68	11	0.29	0.06	0.35	0.22	0.09	0.23	
F ppm	29	2960	240	3200	1415	699	1358	29	2275	150	2425	993	555	895	
V ppm	11	65	106	171	135	20	127	11	50	30	88	58	21	50	
Cr ppm	28	398	10	408	98	106	55	29	244	6	250	36	44	25	
Co ppm	8	31	9	40	19	9	17	8	48	1	49	15	17	9	
Ni ppm	29	182	4	186	46	46	30	29	232	2	234	32	43	22	
Cu ppm	29	79	1	80	36	21	35	29	63	4	67	23	15	18	
Zn ppm	29	954	42	996	120	171	87	29	98	23	121	66	24	65	
Rb ppm	11	134	79	213	130	35	126	11	106	101	207	146	32	138	
Sr ppm	11	2800	3000	5800	4427	987	4200	11	3200	1200	4400	2718	944	2600	
Zr ppm	11	186	288	454	377	53	360	11	400	220	620	334	107	289	
Ba ppm	11	1300	2300	3600	3045	468	3000	11	1600	900	2500	2018	431	2000	
Pb ppm	8	429	1	430	49	79	34	11	244	6	250	55	51	32	
Th ppm	11	61	35	96	52	16	47	11	65	29	94	50	18	41	
		Tephriphonolite							Fyroclastic series						
SiO ₂ %	5	2.69	50.86	53.55	52.30	0.96	52.16	23	13.86	52.54	66.40	57.76	3.63	57.45	
Al ₂ O ₃ %	5	1.65	15.56	17.21	16.48	0.63	16.18	23	4.30	14.80	19.10	16.52	0.93	16.23	
Fe ₂ O ₃ %	5	1.08	5.56	6.64	6.27	0.41	6.34	23	5.39	1.57	8.96	4.40	1.20	4.15	
HgO %	5	0.98	3.06	4.04	3.39	0.44	3.06	23	4.73	0.15	4.88	2.20	0.96	2.12	
CaO %	5	1.61	6.71	8.32	7.35	0.78	6.78	23	8.02	0.57	8.59	4.49	1.95	4.50	
Na ₂ O %	5	1.29	3.85	5.14	4.67	0.49	4.73	23	4.56	1.11	5.67	3.97	0.94	3.97	
K ₂ O %	5	0.61	5.37	5.98	5.65	0.26	5.41	23	6.92	3.94	10.86	5.58	1.31	5.41	
TiO ₂ %	15	1.17	0.70	1.87	0.91	0.28	0.81	67	1.27	0.05	1.32	0.59	0.20	0.37	
H ₂ O %	15	0.10	0.06	0.16	0.09	0.03	0.08	67	2.94	0.01	2.94	0.11	0.35	0.07	
P ₂ O ₅ %	5	0.47	0.58	1.05	0.76	0.18	0.67	23	0.70	0.05	0.75	0.39	0.19	0.38	
F ppm	15	562	1258	1820	1619	157	1635	66	2317	33	2650	1030	484	972	
V ppm	5	61	113	174	135	25	116	23	140	20	160	85	40	78	
Cr ppm	15	330	10	340	53	81	25	67	284	6	290	51	43	40	
Co ppm	4	16	10	26	19	8	21	18	66	1	67	24	20	13	
Ni ppm	15	56	10	66	24	15	18	67	174	4	178	37	36	28	
Cu ppm	15	78	20	98	63	21	64	67	296	5	301	46	39	40	
Zn ppm	15	70	86	156	106	20	97	67	249	16	285	96	43	83	
Rb ppm	5	22	98	120	111	11	99	23	170	94	264	164	35	163	
Sr ppm	5	1500	4700	6200	5860	654	6000	23	6400	200	6600	4048	1582	4360	
Zr ppm	5	253	382	535	462	70	405	23	524	74	598	384	97	387	
Ba ppm	5	800	2800	3600	3380	335	3400	23	4000	500	4500	2630	1000	2900	
Pb ppm	15	60	2	62	35	16	29	67	465	5	470	68	70	52	
Th ppm	5	91	6	97	55	33	48	22	79	18	97	62	16	62	

Tab. Υποκλιτή Βηθλοθήκη Οξείδωσης Τηφής Γεωλογίας Α.Π.Θ. elements in various volcanic rocks of the Gölcük area. For locations see PEKDEGER et al. (1992). n: number of samples; \bar{x} : mean; δ : standard deviation; m: median.

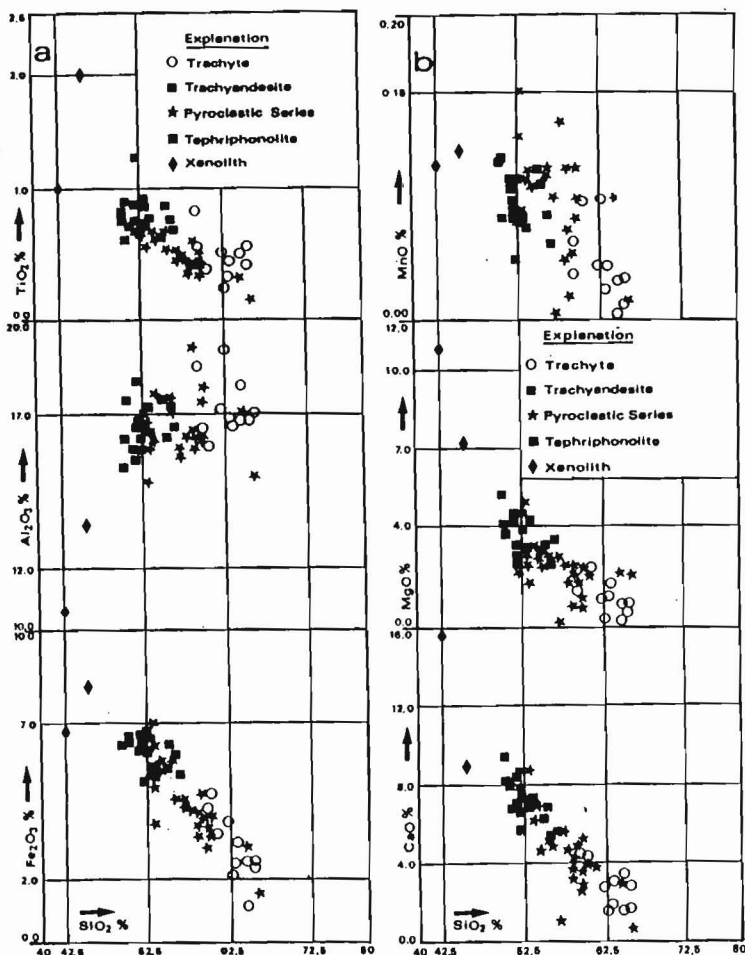


Fig. 4: Plot of SiO₂ versus TiO₂, Al₂O₃, and Fe₂O₃ (a) as well as MnO, MgO, and F (b) in the Gölcük volcanic rocks

identical with the mean value of 1000 ppm of the alkaline pyroclastics (KOKUBU 1956). The F-bearing minerals in the pyroclastic series are F-apatite, biotite, hornblende, pyroxene, fluorite, and glassy groundmass. In comparison to other volcanic rocks, an important portion of fluorine in the pyroclastic series may also be attributed to the glassy groundmass (FLÜHLER et al. 1982), because these rocks contain up to 90 % glassy groundmass.

During F-contents in trachyandesite (volcanic stage iii) distinguish by a range of 240 to 3200 ppm and a background value of 1415 ppm trachyte (volcanic stage iii) show fluorine contents in a range of 150 to 2425 ppm and a background value of 933 ppm. These high F-contents can be attributed to the various mineral phases, i.e. F-apatite, biotite, hornblende, and pyroxene.

Generally, there is a close correlation between F and P₂O₅ in the volcanic rocks which could indicate the geochemical role of fluorapatite as one of the important F-carriers (Fig. 7). Furthermore, this diagram displays a depletion of fluorine from basic toward the acidic rocks as a novelty of our investigations which is known as the fluorine depletion process. It might be interpreted by an increasing discharge of fluorine during fumarolic stages subsequent to the volcanic eruptions indicating a degassing of an open system.

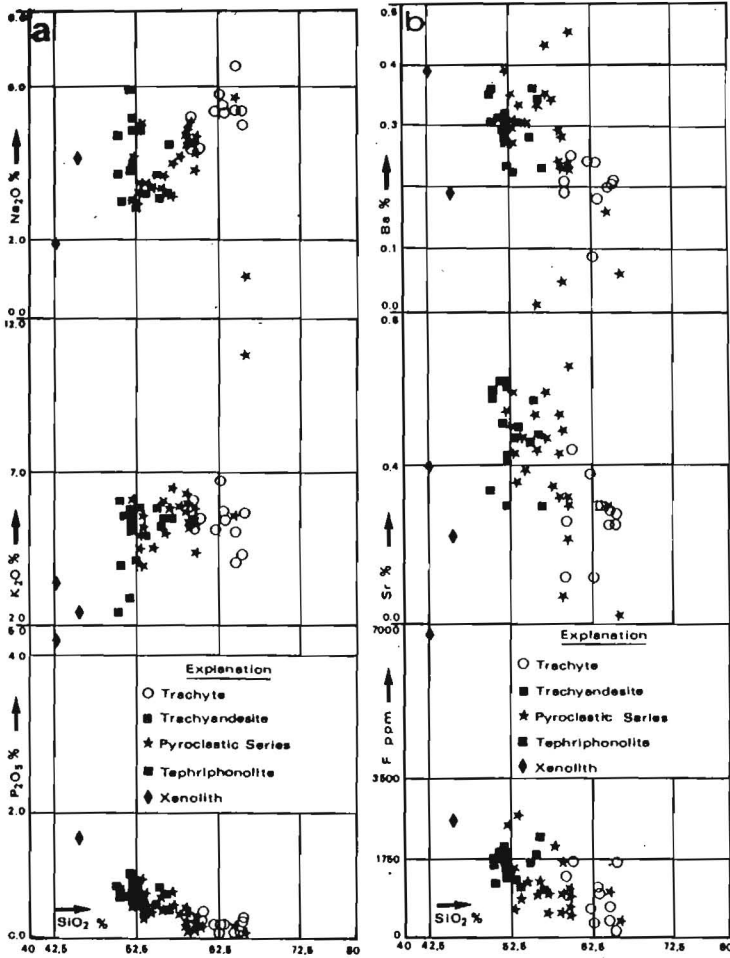


Fig. 5: Plot of SiO₂ versus Na₂O, K₂O, and P₂O₅ (a) as well as Ba, Sr, and F (b) in the Gölcük volcanic rocks

Moreover, the volcanic rocks are distinguished by extremely high REE contents with a maximum of 0.15 % of REE which can be derived from the occurrence of F-apatite (ÖZGÜR et al. 1990; PEKDEGER et al. 1992). The remarkable similarity of the REE patterns of the volcanic rocks suggests a common petrogenic origin for the whole rock spectrum of the volcanic sequence (CAPALDI et al. 1972).

PLIOCENE VOLCANISM

The volcanic activity in the Gölcük area has been divided into three stages (ÖZGÜR et al. 1990; Fig. 8). The basic tephriphonolite emplaced in the area of Gölcük lake, and were accompanied by local eruptions like a ring dike (stage i). Subsequently, the tephriphonolite lavas have been strongly affected by volcanic gases and dust explosions around the center of Gölcük intensively which marks the start of the second volcanic stage (stage ii). Products of this stage are great masses of friable tuffs, ignimbrites, and pumice tuffs dominating the recent landscape which reveals a series of strong explosion forming the recent caldera. The coarse-grained pyroclastic components, like bombs and lapillis, consist of sedimentary rocks, basic xenoliths, and tephriphonolite. They contain neither trachyandesites nor trachytes. Isolated extrusions of trachyandesites

and trachytes have taken place at various localities in the center and surrounding area of the Gölçük caldera (stage iii). They are preserved as vents, dikes, and volcanic domes proving that the trachytes are always the latest volcanic event.

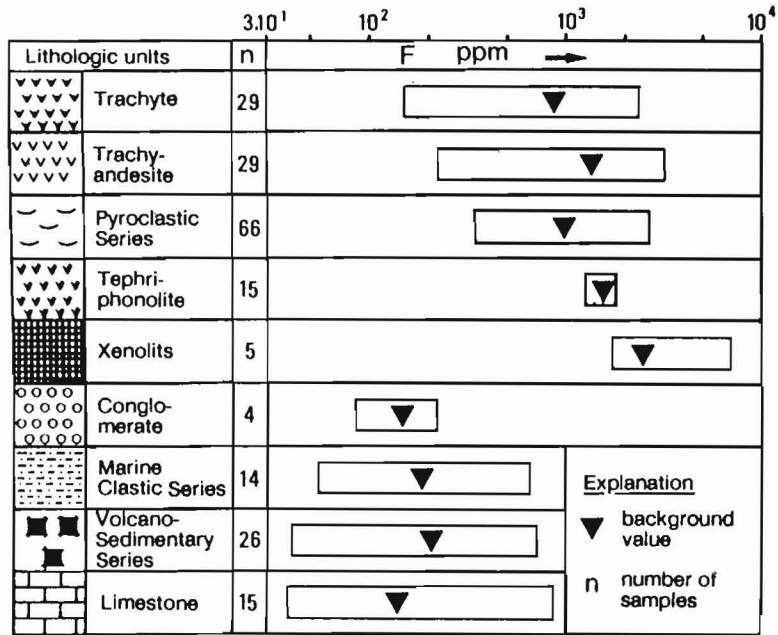


Fig. 6: Range and background values of fluorine in various volcanic rocks of the Gölçük area

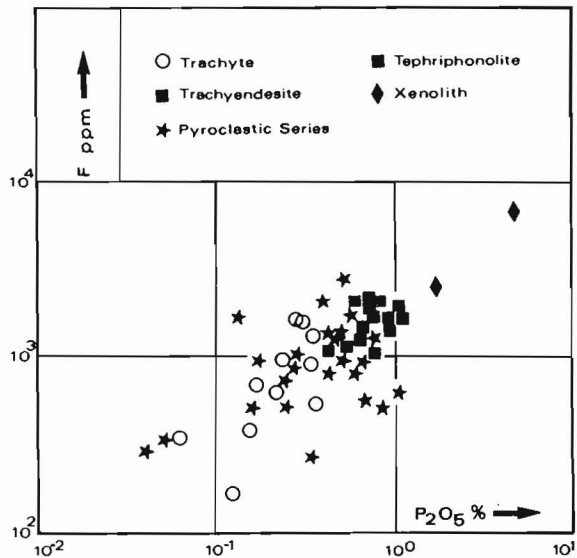


Fig. 7: Close correlation between F and P₂O₅ in various volcanic rocks of the Gölçük area

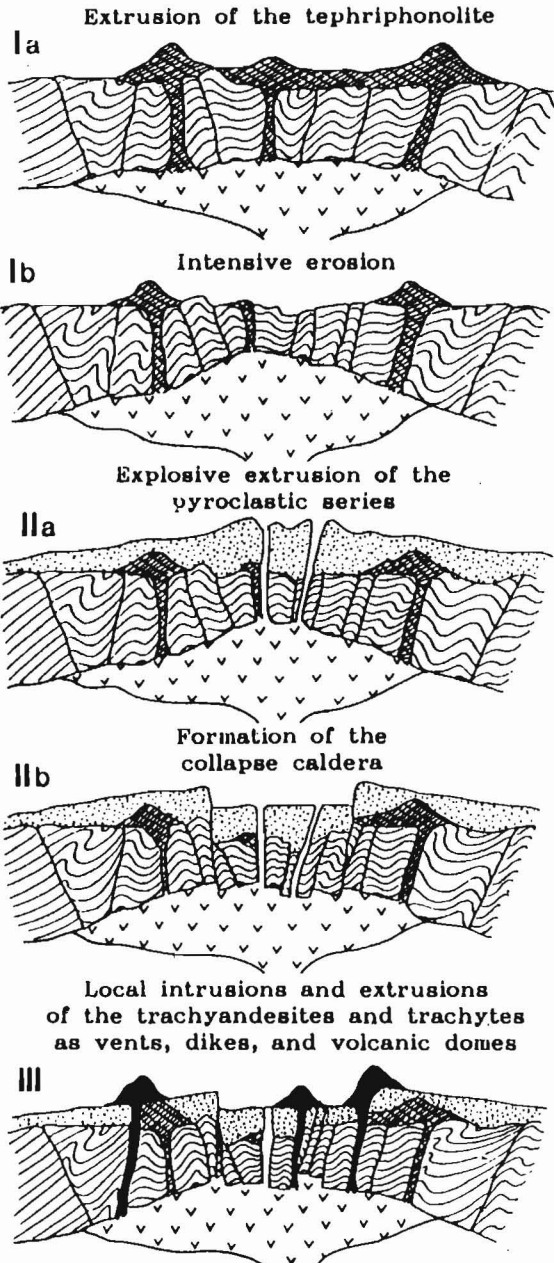


Fig. 8: Schematic record of the volcanic rocks in the Golcük area. Not to scale.

DISCUSSION AND CONCLUSIONS

The volcanic activity in central Anatolia seems to have developed in relation to the plate tectonic evolution of this region. As a result of formation of the plate tectonic event which is connected with the Afro-Arabian plate being subducted under the Euro-Asiatic plate (DEWEY et al. 1973), the volcanism began at least as early Paleocene continuing to Quaternary consequently (INNOCENTI et al. 1975, 1982; ERCAN 1982).

The volcanic activity in the Gölcük area is of Pliocene age (LEFEVRE et al. 1983) and shows a Na-alkaline character (PEKDEGER et al. 1992). The volcanic rocks in the area are one of the youngest events in central Anatolia. The unambiguously origin of the volcanic rocks and of the metamorphic overprinted xenoliths as deep-seated rocks is debatable, it will be reported by detailed investigations of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ in a separate paper. The pyroxenitic xenoliths originate probably from the fragments of the oceanic crust which have been taken place in the time of ophiolitic activity.

In the Gölcük area, the volcanics start with the basic tephriphonolite lavas (stage i), succeeded by the pyroclastic series represented by friable tuff, ignimbrite, and pumice tuff (stage ii), and finally ending with trachyandesite and trachyte (stage iii).

The volcanic rocks in the area are characterized by high fluorine contents. They can be attributed to different mineral phases as essential F-carrier, i.e. F-apatite, biotite, hornblende, fluorite, and glassy groundmass. Moreover, the mineral phase pyroxene can contain F-contents ranging from 100 to 340 ppm (KOKUBU 1956; GREEN 1982). F-apatite is also an ubiquitous mineral. F versus P_2O_5 displays a close correlation which shows remarkable relative depletion of fluorine contents from the basic towards the acidic volcanic rocks as a novelty of this investigation. It can be interpreted that an important portion of F might be discharged during fumarolic activity and through interaction of hydrothermal water with the volcanic rocks. Furthermore, the small variability of the REE patterns indicates a close petrogenic relationship of the different volcanic stages (ÖZGÜR et al. 1990). They are differentiation products of a common magma chamber.

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