STUDY OF CLINOPYROXENES FROM THE SAMOTHRAKI OPHIOLITE BASALTS AND THEIR SIGNIFICANCE IN THE INVESTIGATION OF THE GEOTECTONIC ENVIRONMENT

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ABSTRACT

Phenocrystic clinopyroxenes from the Samothraki ophiolite, found in equilibrium with their host basalts, display tholeiitic affinities. The most important, non-quadrilateral substitutional molecule in their structure is $CaTiAl_2O_6$, as it is indicated by the rather linear relationship of Ti vs. AlIV. They show an AlVI deficiency or very low AlVI/AlIV ratios and rather high Ti/Alt ratios which are compatible with low-pressure fractionation. The minimum temperature of their formation is estimated at about 1000-1300°C.

They also show a depletion in Na content with high TiO_2/MnO ratios, as well as, a SiO_2-decrease with TiO_2-increase, implying that these clinopyroxenes are related to those from basalts erupted in spreading centres. However, some crystals with relative low TiO_2, show an influence by a subduction component. These features are consistent with the origin of their host basalts in a marginal basin regime.

ΠΕΡΙΛΗΨΗ

Φαινοκρύσταλλοι κλινοπυρόξενων από το οφιολιθικό σύμπλεγμα της Σαμοθράκης, οι οποίοι βρίσκονται σε ισορροπία με τους βασάλτες που τους φιλοξενούν, δείχνουν θολεϊτικές τάσεις. Το πιο σημαντικό, μη τετραεδρικό, μόριο υποκατάστασης είναι το $CaTiAl_2O_6$, όπως υποδεικνύεται από την αρκετά καλή γραμμική συσχέτιση του Ti ως προς το AlIV. Οι κλινοπυρόξενοι δείχνουν μια έλλειψη σε AlVI ή πολύ χαμηλούς λόγους AlVI/AlIV και αρκετά υψηλούς λόγους Ti/Alt, γεγονός που υποδεικνύει κρυστάλλωση χαμηλής πίεσης. Η ελάχιστη θερμοκρασία σχηματισμού τους υπολογίζεται σε περίπου 1000-1300°C.

Οι κλινοπυρόξενοι από τους βασάλτες της Σαμοθράκης δείχνουν επίσης πτώχευση σε Na που σε συνδυασμό με τους αρκετά υψηλούς λόγους TiO_2/MnO καθώς και το γεγονός της αύξησης του TiO_2 με μείωση του SiO_2, υποδηλώνει ότι σχετίζονται με αντίστοιχα ορυκτά από βασάλτες που δημιουργήθηκαν σε κέντρα διάνοιξης. Όμως μερικοί κρύσταλλοι με χαμηλές τιμές TiO_2, δείχνουν επιρροή και από ένα συστατικό καταβύθισης. Τα χαρακτηριστικά αυτά υποδεικνύουν ότι οι βασάλτες που τους περιέχουν πρέπει να δημιουργήθηκαν σε ένα καθεστώς περιθωριακής λεκάνης.

KEY WORDS: mineral chemistry, substitutional couple, MORB, IAT, ophiolite, marginal basin, Samothraki, North Aegean

1. INTRODUCTION

It is well known that the petrological characteristics and geochemical affinities of volcanic rocks may give important information about their geotectonic provenance. Several geochemical diagrams using immobile elements have been devised to identify the original magmatic affinities of rocks even if they are

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highly altered.

It has also been implied that the geochemistry of various minerals can provide further information about geotectonic processes. Pyroxenes are broadly used, since their chemistry may greatly contribute to such investigations. Their composition is related to several petrogenetic factors such as pressure, temperature, oxygen fugacity and order of mineral crystallisation (e.g. Leterrier et al. 1982, Beccaluva et al. 1989 and references).

This study deals with clinopyroxenes hosted in basalts from an ophiolite assemblage in Samothraki Island (N. Aegean). This ophiolite consists, from bottom to top, of gabbros, hornblende-diorites, massive dolerites and basalts, which are penetrated by doleritic dykes (Fig. 1). For a detailed geological description of the Samothraki island and the geological relationships between the ophiolite and its surrounding formations, see Tsikouras (1992) and Tsikouras & Hatzipanagiotou (1995).
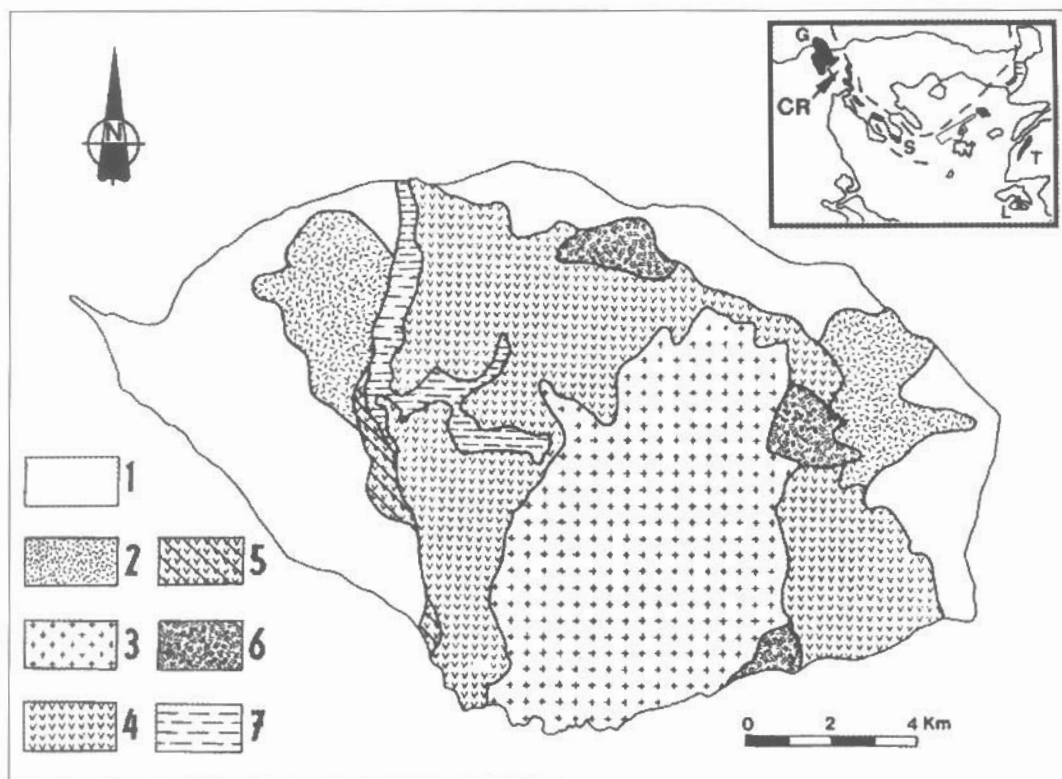

Fig. 1: Simplified geological map of Samothraki island (after Davis 1963, Heimann et al. 1972 and Tsikouras & Hatzipanagiotou 1995): 1. Neogene-Quaternary deposits, 2. Cenozoic volcanic rocks, 3. Granite, 4. Basalt-massive dolerite, 5. Diorite, 6. Gabbro, 7. Basement Unit. Inset shows the main locations of the ophiolites in the north Aegean: G: Guevgueli, S: Sithonia, E: Evros, L: Lesvos, T: Turkey. CR: Circum-Rhodope zone.

2. DESCRIPTION OF THE HOST BASALTS

The basalts occupy the top of the ophiolitic pile and are located mainly in the north-western and lesser in the south-eastern parts of the island. They are hardly distinguishable, under macroscopic observation, from the massive dolerites, thus they are not distinguished in the geological map (see Fig. 1). These basalts display intermediate, glomeroporphyritic, hyalopilitic, porphyritic and microlitic textures. Their assemblage includes plagioclase, clinopyroxene, magnetite, ilmenite and accessory zircon. They have suffered a low-grade, oceanic metamorphic episode with development of smectite, quartz, albite, epidote,

chlorite, pumpellyite, actinolite, calcite, hematite and titanite. These minerals occur both in the groundmass and within joints or amygdules.

In this study we have analysed only phenocrystic clinopyroxenes. According to Gamble & Taylor (1980) and Leterrier et al. (1982) phenocrystic compositions are more closely related to the host rock bulk chemistry than these of microlites, since the elemental partitioning is largely dependent on cooling-rate.

3. ANALYTICAL METHODS

Microprobe analyses were carried out at the Department of Earth Sciences, University of Leeds, England, with a CAMECA CAMEBAX SX 50 microanalyser, equipped with an Energy Dispersive System (EDS) and controlled by a Link system. Operating conditions were 15 kV accelerating voltage and 3.3 nA sample current.

Reference whole-rock chemical analyses are given by Tsikouras (1992) and Tsikouras & Hatzipanagiotou (1998).

4. CHEMISTRY OF THE CLINOPYROXENES

The analysed crystals are optically unzoned and rather homogeneous showing no significant chemical variations from core to rim. Representative microprobe analyses are given in Table 1. According to the I.M.A. classification (Morimoto et al. 1988) they are augites (Fig. 2).
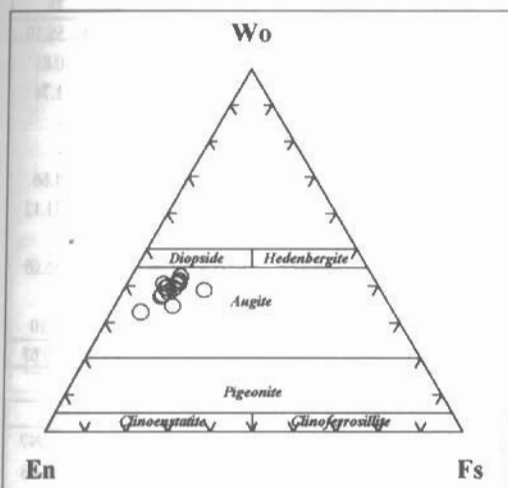
The Fe^{3+} range in these analyses is rather wide while among the "Other" elements (apart from those of the pyroxene quadrilateral ones, cf. Papike & Cameron 1976, Papike 1980) only Al and Ti reveal a slight enrichment. TiO_2 moreover is partitioned in variable degrees, displaying a wide range from 0.50 up to 1.85 % in the analysed clinopyroxenes.

Fig. 2: Plot of the analysed clinopyroxenes in the Wo-En-Fs quadrilateral. Fields after Morimoto et al. (1988).

5. DISCUSSION

The composition of magmatic clinopyroxenes is strongly controlled by the composition and the cooling history of the magma. Clinopyroxenes related to tholeiitic series are richer in Si and poorer in Al and Ti relative to those encountered in alkaline rocks (Le Bas 1962, Verhoogen 1962). The entry of Ti is also favoured by a high crystallisation temperature (Verhoogen 1962) while the cooling rate has a great influence in Ca, Fe, Mg and lesser in Al and Ti contents in clinopyroxenes (Lofgren et al. 1974, Donaldson et al. 1975). Al and Ti contents are also susceptible to oxygen fugacity and order of mineral crystallisation (Barberi et al. 1971).

Under such a complexity it is difficult to decipher which parameter played the most important role in the chemical composition of the investigated clinopyroxenes. However, it has been established that their host basalts have a tholeiitic-MORB affinity, influenced by a subduction component (Tsikouras 1992, Tsikouras & Hatzipanagiotou 1998). Plagioclase has been crystallised before clinopyroxene; this results in the removal of CaAlAlSiO₆ component leaving the residual melt and hence the clinopyroxene composition

towards a lower Al content. The somewhat high Ti and Al contents are consistent with a high temperature crystallisation (Kushiro 1960, Verhoogen 1962).

The Kd ((FeO/MgO)cpx/(FeO/MgO)lava) values are rather cohesive ranging from 0.18-0.24, suggesting equilibrium crystallisation of the clinopyroxene phenocrysts with their host basalts (Liotard et al. 1988). With respect to charge-balance maintenance in the pyroxene structure, the most important elemental substitutional couple is Ti^{VI}-Al^{IV} (Fig. 3). This relationship indicates that $CaTiAl_2O_6$ is the most important non-quadrilateral, substitutional molecule in the clinopyroxenes. The essential Al^{VI} and Na deficiencies precludes the involvement of calcium-Tschermak's and jadeite components.

The Al^{VI} deficiency or the low Al^{VI}/Al^{IV} ratios (with few exceptions) and the rather high Ti/Al^i ratios are compatible with a low pressure crystallisation for the analysed clinopyroxenes (Fig. 4). Information about the minimum temperature of the formation of the clinopyroxenes and hence their host lavas is given in Figure 5, where they suggest temperatures ranging at about 1000-1300°C. The contours at that diagram refer to low-pressures; the complete temperature-range cannot be estimated due to the absence of orthopyroxene (Lindsley 1983).

Table 1: Representative clinopyroxene analyses from the Samothraki basalts

Sample	3	4	9	10	11	16	17	20	23	24	25	26	27	28
SiO_2	50.51	50.87	50.97	51.42	51.03	49.74	53.98	53.46	52.15	53.88	53.10	52.08	52.24	55.19
TiO_2	1.24	1.23	1.11	1.02	0.96	1.85	0.58	0.89	0.50	0.54	0.75	1.01	0.68	0.81
Al_2O_3	2.63	2.77	2.57	1.36	2.54	2.43	0.30	0.29	1.88	1.20	2.43	3.02	2.38	1.74
Cr_2O_3	0.12	0.20	0.15	0.14	0.09	-	-	-	0.21	-	-	-	0.11	-
Fe_2O_3	1.49	3.16	1.11	1.86	1.46	0.16	-	-	1.79	-	-	-	0.47	-
FeO	6.36	4.75	6.30	6.23	6.63	12.18	8.65	6.99	4.39	6.49	6.50	6.49	6.29	4.66
MgO	16.63	16.79	16.64	17.58	16.18	14.77	18.40	18.37	18.31	18.03	18.51	17.52	18.76	21.12
MnO	0.44	0.29	0.38	-	-	-	0.37	0.22	0.30	0.32	0.22	0.35	0.30	-
CaO	20.47	20.02	20.29	19.91	20.99	19.00	17.40	19.72	20.42	19.48	18.26	19.36	18.22	16.05
Na_2O	-	0.65	-	0.74	-	-	-	-	-	-	-	-	-	-
K_2O	0.16	0.14	0.23	0.22	0.18	0.23	0.30	-	0.20	-	0.18	0.09	-	0.10
Total	100.05	100.87	99.75	100.48	100.06	100.36	99.98	99.94	100.15	99.94	99.95	99.92	99.45	99.67

| structural formulae on the basis of 6 oxygens														
Si	1.864	1.854	1.884	1.874	1.885	1.860	1.985	1.962	1.903	1.975	1.939	1.910	1.917	1.997
Al^{IV}	0.114	0.119	0.112	0.058	0.110	0.107	0.013	0.013	0.081	0.025	0.061	0.090	0.083	0.003
Fe^{3+}	0.021	0.027	0.004	0.051	0.005	0.004	-	-	0.016	-	-	-	-	-
	1.999	2.000	2.000	1.983	2.000	1.971	1.998	1.975	2.000	2.000	2.000	2.000	2.000	2.000
Al^{VI}	-	-	-	-	-	-	-	-	-	0.026	0.044	0.040	0.020	0.071
Ti	0.034	0.034	0.031	0.028	0.027	0.052	0.016	0.025	0.014	0.015	0.021	0.028	0.019	0.022
Cr	0.003	0.006	0.004	0.004	0.003	-	-	-	0.006	-	-	-	0.003	-
Fe^{3+}	0.020	0.060	0.027	-	0.036	-	-	-	0.033	-	-	-	0.013	-
Fe^{2+}	0.196	0.145	0.195	0.190	0.205	0.381	0.266	0.214	0.134	0.199	0.199	0.199	0.193	0.141
Mg	0.915	0.913	0.917	0.955	0.891	0.823	1.009	1.004	0.996	0.985	1.008	0.957	1.026	1.139
Mn	0.014	0.009	0.012	-	-	-	0.012	0.007	0.009	0.010	0.007	0.011	0.009	-
Ca	0.809	0.782	0.804	0.777	0.831	0.761	0.686	0.775	0.798	0.765	0.714	0.761	0.716	0.622
Na	-	0.046	-	0.052	-	-	-	-	-	-	-	-	-	-
K	0.008	0.007	0.011	0.010	0.008	0.011	0.014	-	0.009	-	0.008	0.004	-	0.005
	1.999	2.002	2.001	2.016	2.001	2.028	2.003	2.025	1.999	2.000	2.001	2.000	1.999	2.000
Wo	40.97	40.42	41.04	39.40	42.23	38.64	34.77	38.73	40.18	39.05	37.07	39.45	36.59	32.71
En	46.31	47.16	46.83	48.40	45.30	41.80	51.15	50.21	50.13	50.29	52.28	49.67	52.42	59.88
Fs	12.72	12.42	12.13	12.20	12.47	19.56	14.08	11.06	9.69	10.66	10.65	10.88	10.99	7.41
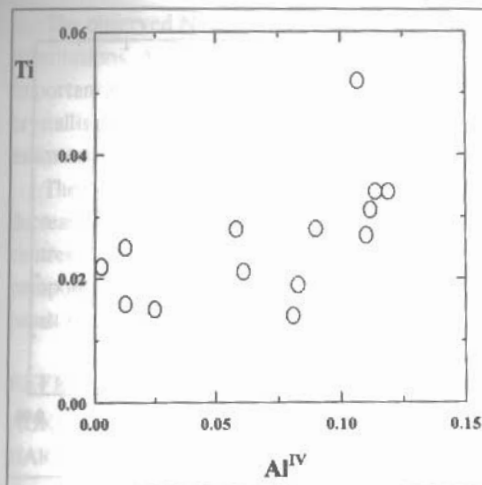
Fig. 3: Plot of the analysed clinopyroxenes in a TiVI vs. AlIV diagram.
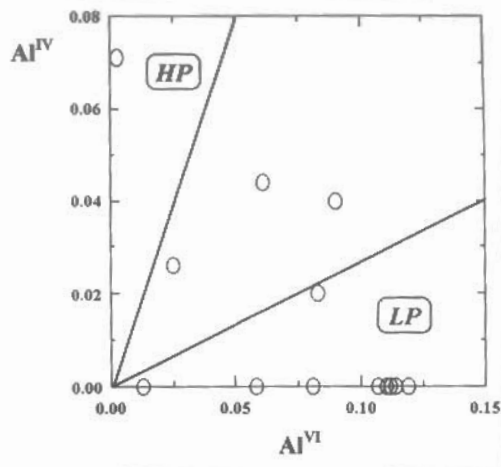
Fig. 4: Pressure estimation of the Samothraki clinopyroxenes in the AlVI vs. AlIV diagram (Aoki & Shiba, 1973), HP=High pressure field, LP=Low pressure field.
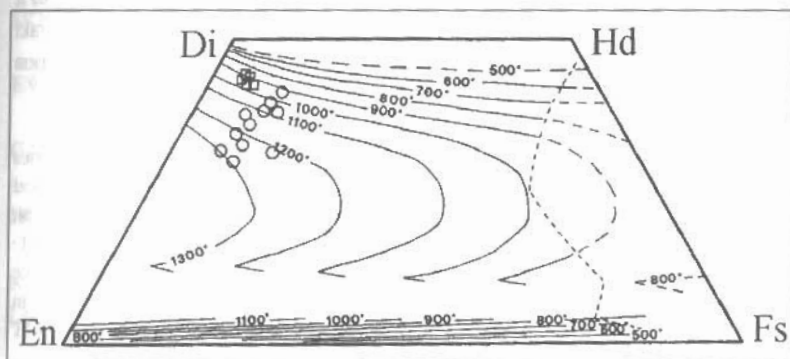

Fig. 5: Temperature estimation of the Samothraki clinopyroxenes in the Di-Hd-En-Fs quadrilateral (Lindsley, 1983).

The depletion of Na content in the clinopyroxenes structure coupled with the high TiO_2/MnO ratio suggest an ocean floor environment for the origin of these crystals and subsequently for their host lavas (see Nisbet & Pearce 1977). Moreover, with increasing TiO_2 there is a SiO_2-decrease (Table 1) implying that the analysed clinopyroxenes are best related to those from basalts erupted in a mid-ocean ridge environment. However, the affinities of those crystals having the lower TiO_2 contents are influenced by an island-arc component (see Beccaluva et al. 1989). This is also evident from the DTiCpx/rock partition coefficients ranging from 0.52 to 1.85, which are comparable with relevant values from both MORB (0.75; Bender et al. 1978) and IAT (0.3-0.6; Ewart et al. 1973).

The tectonomagmatic discrimination diagrams of Leterrier et al. (1982) reveal that the clinopyroxenes are related to tholeiitic formations from non-orogenic (i.e. tholeiites from spreading zones) environments (Fig. 6). A tholeiitic affinity is portrayed on chemical variation diagrams (Fig. 7) where the corresponding patterns moreover approximate to those of clinopyroxenes from MORB. However, some pronounced deficiencies in Ti and Cr are better correlated with clinopyroxenes from IAT.
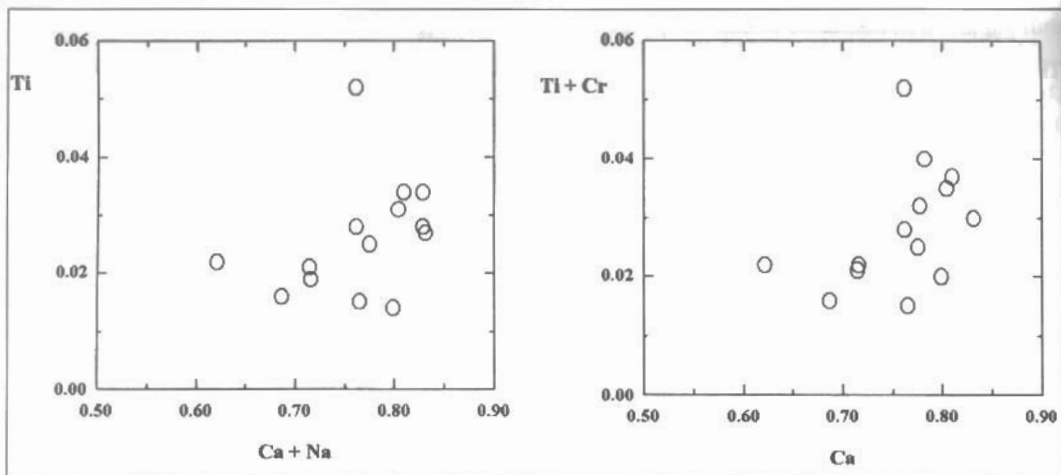
Fig. 6: Plot of the analysed clinopyroxenes from Samothraki in tectonomagmatic discrimination diagrams (Leterrier et al. 1983).

6. CONCLUSIONS

Clinopyroxene phenocrysts hosted in basalts from the Samothraki ophiolite (N. Aegean) are in equilibrium with the lava. Literature gives multiple interpretation for the elemental partitioning in the clinopyroxenes structure, thus it is not easy to suggest which is the most important factor in the chemical composition of the Samothraki clinopyroxenes. However, their host tholeiitic basalts display a MORB signature with the contribution of a subduction component.
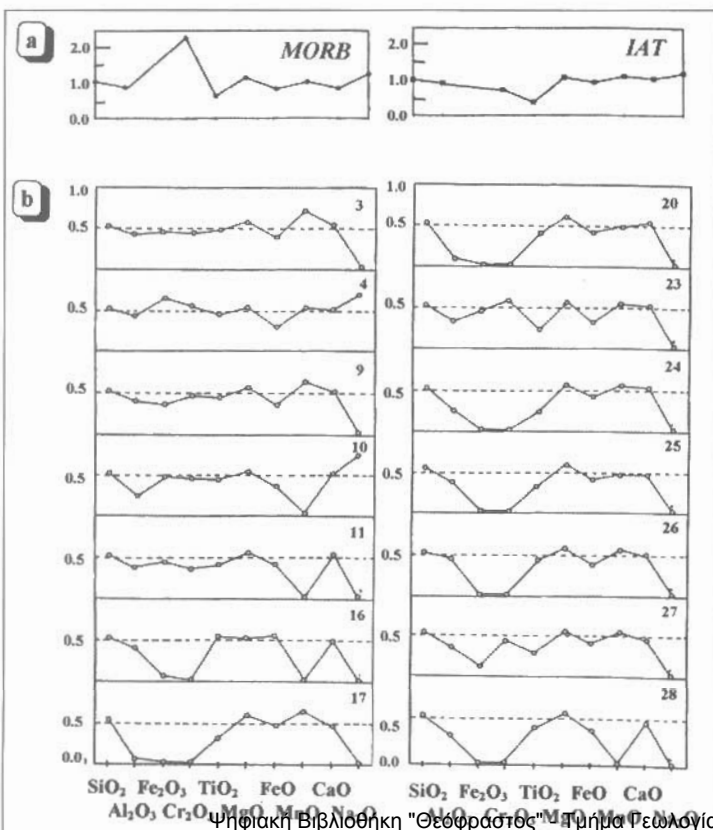

Fig. 7: a) MORB: clinopyroxenes spectrum reference (mean chemical composition in Leterrier et al. 1982) from MORB host, IAT: clinopyroxenes spectrum reference (mean chemical composition in Leterrier et al. 1982) from IAT host.
b) Chemical variation diagrams of the Samothraki clinopyroxenes versus mean clinopyroxene (Schweitzer et al. 1979).

The observed Na and AlVI deficiencies preclude the involvement of jadeite and calcium Tschermak's substitutions. A rather linear relationship between TiVI and AlIV indicate that the CaTiAl2O6 is the most important non-quadrilateral molecule in their structure. The very low AlVI values suggest a low pressure crystallisation for the analysed clinopyroxenes while the minimum temperature of their formation is estimated at about 1000-1300°C.

The Na depletion coupled with rather high TiO2/MnO ratios and the observed Ti-increase with Si-decrease suggest that these clinopyroxenes are correlated with those from basalts erupted in spreading centres. Nevertheless, some crystals with lower Ti contents involve the contribution of a subduction component. These features are compatible with the origin of the clinopyroxenes and hence their host basalt in a marginal basin environment.

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