28. CHEMICAL STUDIES OF AMPHIBOLES, PYROXENES, AND OTHER MINERALS FROM CARIBBEAN DEEP-SEA SEDIMENTS, LEG 15.

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INTRODUCTION

A survey of the chemical composition of amphiboles, pyroxenes, and some other minerals was undertaken using an electron microprobe on mineral grains that had been picked individually from deep-sea sediments. Table 1 gives analyses of thirty-one amphiboles from twelve sediment samples (each representing a distinct core), nineteen analyses of clinopyroxenes (from ten cores, including three separate fragments from a single large grain), four analyses of orthopyroxenes (from three cores), four analyses of oxides (from four cores), and an analysis of a biotite. Low summations resulted in the discarding of four additional analyses; these probably represented grains that were either too small or so fractured that the somewhat defocussed electron beam intercepted the plastic mounting medium. At least three distinct spots were counted on each grain; five spots for the Fe-Mg-Si analyses.

Most of the minerals represent airborne or pumice-rafted volcanic detritus. One sample (150-4-1, 89-90) represents a turbidite sand of continental provenance and other samples (154-8, 154A-18) are from volcanic sands of possibly diverse origins.

Cooccurring minerals were analyzed in several samples: amphibole-clinopyroxene in 151-10; clinopyroxene-orthopyroxene in 154A-18, 148-8, and 149-31; oxide-pyroxenes in 148-8, 148-29, and 150-4 (turbidite); and biotite-amphobole in 152-10.

All analyses were done on an Applied Research Laboratories electron microprobe during a single run, using the same standards for all the analyzed minerals. For this reason, matrix corrections were unduly large in some cases, giving rise to inaccuracies perhaps as high as ±10 relative percent.

Amphiboles

Most of the amphiboles of the present group are hornblendes (Table 1; Figure 1) with no distinctive chemical characteristics. One group of amphiboles is distinctly pargasitic and also strikingly high in Ti (These ten samples average 2.90 percent TiO_2). A third small group is more aluminous than the hornblendes, but not very high in Ti. A fourth group, a single sample, is an amphibole chemically transitional between hornblende and tremolite.

Most of the amphibole samples are relatively homogeneous; that is, count rates vary by generally less than 5 per cent from minimum to maximum. Some notable exceptions show marked (10-20 per cent) variations in Si, Fe, and Mg (analysis 20), and Al (analysis 4). There are smaller variations (less than 10 per cent) of Ti (analysis 4), Al (analyses 30, and 31), Ca (analysis 7), and Fe and Mg (analysis 31).

The heterogeneous amphibole assemblage in Cores 148-29 and 148-31 confirms that this volcanic sand is polygenetic and suggests that, in part, it might be of metamorphic derivation. The aluminous hornblendes of the turbidite of Core 150-4 are probably metamorphic, as suggested by the remaining mineral assemblage (Donnelly and Nalli, this volume).

The distinctive titaniferous pargasitic hornblendes (Cores 151-6 and 152-4) are, with one exception, confined to the northern Colombian Basin area (Sites 151 and 152) and to a specific time interval (late Paleocene and younger). They may represent a stage in the evolution of calc-alkaline or subalkaline magmas in the Jamaica-Beata Ridge area. Early Paleocene hornblendes from the same cores (151-10, 151-11, 152-10) are, by contrast, normal hornblendes with average Ti values.

Pyroxenes

The clinopyroxenes studied here (Table 2) plot in a rather small field in the pyroxene quadrilateral (Figure 2) and are otherwise slightly distinguished by their Ti and Al contents (Figure 3). The plot of Figure 2 shows remarkably little scatter, considering the span of time (Paleocene to Pleistocene) and space (Lesser Antilles to Panama) involved. The trend shown is more calcic than the Skaergaard trend, which fits the pyroxenes from the basalts and dolerites very well (Donnelly et al., "Basalts and Dolerites. . .", this volume). The present trend suggests an origin in explosive calc-alkaline volcanic magmas and the homogeneity suggests a uniformity or at least comparability of process and materials in space and time.

The pyroxenes are all reasonably homogeneous, with most of the heterogeneity (compositional zoning) reflected in the Ca values. Analyses 48, 55, 57, 68, and 69 show relatively large variations in Ca from spot to spot, and analysis 62 shows a smaller variation. Marked variations in Fe (analyses 57 and 67), Mg (analysis 67), and Al (analysis 57) are also seen. Smaller variations occur in Fe (analysis 48), Mg (analysis 57), and Al (analysis 41).

A distinctive iron enrichment is seen in two samples from Core 149-31; indeed the ferrohypersthene of Sample 149-31(CC) is one of the most iron rich orthopyroxenes known (Table 3). This iron enrichment probably reflects differentiation of late Eocene magmas in the Lesser Antilles, but further speculation about its significance is not possible.

The tie lines of Figure 2 connecting orthopyroxenes with cooccurring clinopyroxenes show a "reasonable"

TABLE 1
Amphibole Analyses

Sample	146-28-2 (56-58)	148-3-4 (131-132)	148-16-4 (103-104)	148-29(CC)							148-31(CC)				150-4-1 (89-90)		151-6-1(140-141)			
Analysis No.	26	40	20	29	30	31	32	33	34	35	16	17	18	19	9	10	12	13	14	15
SiO_2	49.8	48.0	42.7	50.4	49.5	53.9	45.3	49.2	48.2	49.2	48.8	48.1	42.8	49.2	41.9	43.5	43.6	42.7	42.0	42.7
TiO_2	1.43	1.58	2.37	1.17	1.08	0.36	1.40	1.25	1.36	1.36	1.69	1.28	1.52	1.28	1.39	1.87	2.76	2.89	2.70	3.50
Al_2O_3	6.1	7.6	10.5	6.6	6.9	3.0	11.9	7.2	8.1	6.8	6.6	8.3	13.2	6.6	11.8	12.9	11.2	12.6	12.6	11.4
FeO^a	13.2	17.0	12.7	12.6	12.6	11.4	9.6	13.7	11.9	13.4	13.8	12.6	11.2	12.5	16.8	12.8	13.8	11.7	11.6	13.4
MnO	0.63	0.23	0.21	0.40	0.67	0.55	0.12	0.40	0.25	0.52	0.31	0.29	0.14	0.33	0.53	0.18	0.26	0.15	0.15	0.22
MgO	14.3	12.2	13.4	16.2	16.1	16.9	16.6	15.3	15.7	15.1	14.7	15.3	15.1	15.7	9.9	13.4	13.5	14.3	14.2	13.1
CaO	10.9	10.2	10.3	10.1	9.8	9.6	10.9	10.4	11.2	10.2	10.8	10.9	11.2	10.4	10.5	10.4	10.5	11.3	11.2	10.5
Na_2O	1.3	1.4	2.3	1.1	1.3	0.4	2.2	1.2	1.7	1.3	1.3	1.4	2.2	1.2	1.5	2.1	2.6	2.6	2.6	2.7
K_2O	0.34	0.29	0.12	0.09	0.06	0.06	0.13	0.18	0.23	0.12	0.15	0.07	0.27	0.08	0.42	0.23	0.13	0.14	0.14	0.14
Sum	98.0	98.5	94.6	98.6	98.0	96.2	98.1	98.8	98.6	98.0	98.2	98.2	97.6	97.3	94.7	97.4	98.4	98.4	97.2	97.7
Age	Campanian	Pleistocene	Pliocene	pre-Miocene?							pre-Miocene?				Early Miocene		Late Oligocene			

TABLE 1 – *Continued*

Sample	151-10-1(43)			151-11-5 (35-36)	152-4-1(41)				152-10-1 (147)		154A-1-1 (89-91)
Analysis No.	2	3	45	21	22	23	24	25	4	7	36
SiO_2	41.8	47.8	46.8	50.2	43.5	44.0	44.1	45.7	48.6	48.5	49.0
TiO_2	3.21	1.46	1.68	1.10	2.92	3.62	2.58	2.46	1.32	1.47	0.83
Al_2O_3	13.5	8.3	9.0	7.4	13.9	10.7	9.7	8.4	7.0	7.5	7.6
FeO^a	10.7	12.4	12.1	13.2	12.4	12.0	12.8	12.7	12.7	12.2	12.7
MnO	0.12	0.42	0.33	0.32	0.15	0.27	0.40	0.42	0.39	0.38	0.45
MgO	14.4	15.4	14.9	15.4	13.3	14.2	13.2	14.3	15.0	14.8	15.3
CaO	11.4	10.2	10.2	9.7	10.5	10.9	11.3	10.9	10.6	10.9	10.0
Na_2O	2.6	1.7	1.7	1.4	2.8	2.6	2.2	2.1	1.3	1.2	1.3
K_2O	0.19	0.18	0.28	0.15	0.20	0.15	0.18	0.17	0.33	0.26	0.10
Sum	97.9	97.9	97.0	98.9	99.7	98.4	96.5	97.2	97.2	97.2	97.3
Age	Early Paleocene			Early Paleocene	Late Paleocene				Paleocene		Pleistocene

[a]Total Fe as FeO.

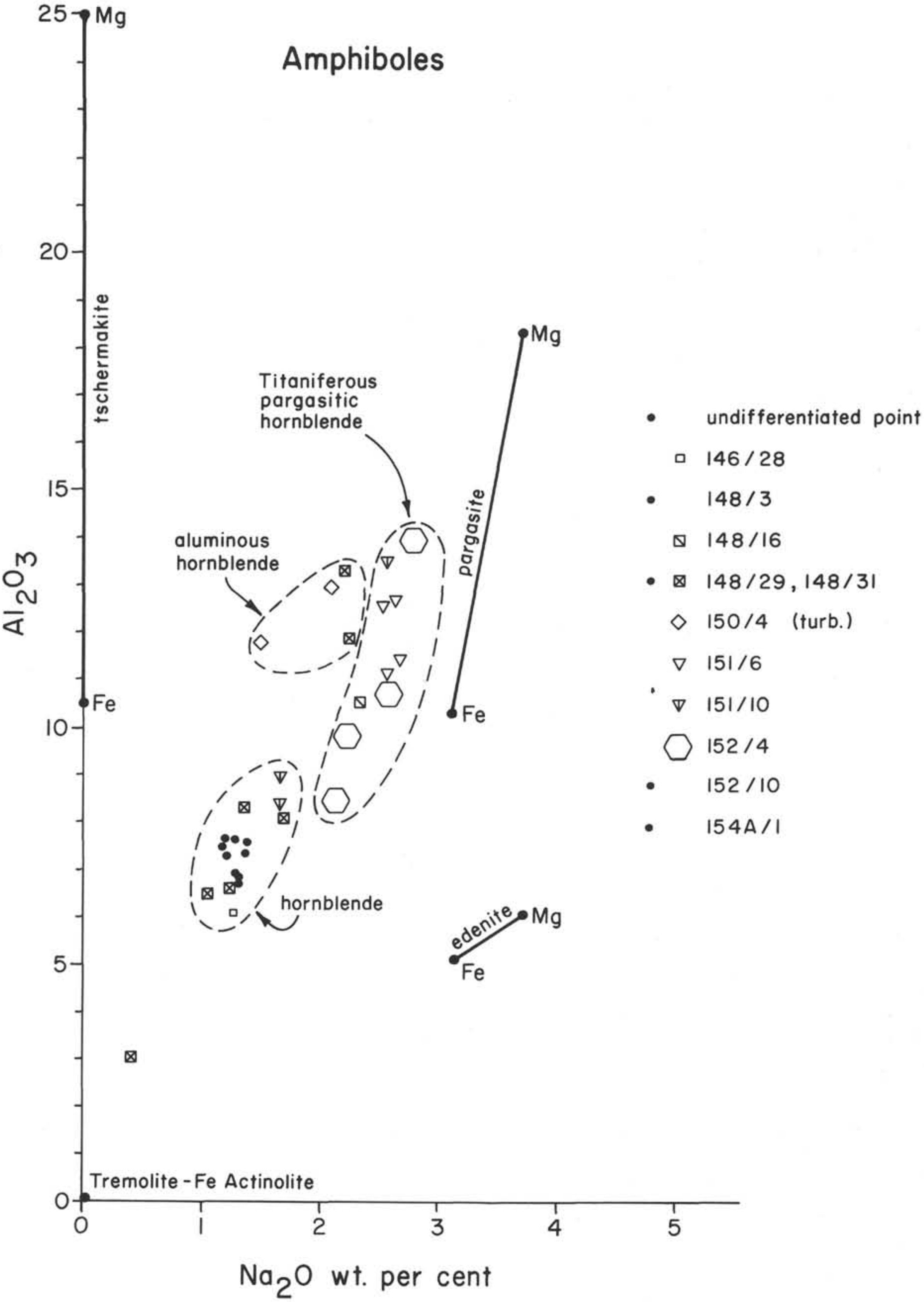

Figure 1. *Plot of Al_2O_3 versus Na_2O for amphiboles. Theoretical compositions of tschermakite, pargasite, and edenite are shown as ranges, assuming complete substitutions between Mg and Fe^{++}, and $Al_{(4)}$ and Fe^{+++}. A cluster of points within the hornblende field is too dense to allow identification of the core for each point. The titaniferous pargasitic hornblendes have a minimum TiO_2 value of 2.37 per cent and an average value of 2.90 per cent.*

TABLE 2
Clinopyroxene Analyses

Sample	148-8-3 (62-63)	149-11(CC)		149-31-2 (138-148)	149-41-2 (106-107)		150-4(CC)	150-5(CC)[b]			151-10-1 (43)	152-1-1 (25-30)
Analysis No.	55	68	69	56	57	58	67	47	48	49	44	46
SiO_2	51.4	51.2	52.4	50.6	51.4	52.4	53.0	52.3	52.5	52.7	53.0	51.1
TiO_2	0.51	0.51	0.42	0.25	0.81	0.49	0.40	0.50	0.62	0.64	0.53	0.91
Al_2O_3	2.2	4.1	1.4	0.4	4.2	1.3	1.2	1.9	1.6	1.8	3.0	3.6
FeO^a	10.9	7.9	14.0	19.1	7.2	13.1	13.1	10.6	12.3	11.7	6.8	10.0
MnO	0.42	0.00	0.00	1.14	0.17	0.54	0.47	0.37	0.47	0.44	0.17	0.27
MgO	14.1	14.6	13.0	14.5	14.8	13.1	13.1	14.7	14.6	14.1	16.0	15.0
CaO	19.5	22.0	19.0	2.5	22.2	19.9	20.0	19.7	18.8	19.4	21.7	19.5
Na_2O	0.5	0.0	0.0	0.06	0.3	0.2	0.3	0.3	0.3	0.3	0.2	0.3
K_2O	0.04	0.00	0.00	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.01
Sum	99.6	100.3	100.2	98.6	101.1	101.0	101.6	100.4	101.2	101.1	101.4	100.7
Age	Pleistocene	Late Miocene		Late Eocene	Middle Eocene		Early Miocene	Early Miocene			Early Paleocene	Early Eocene

TABLE 2 – *Continued*

Sample	154-8-2(94-95)			154A-18(CC)			
Analysis No.	59	60	61	62	64	65	66
SiO_2	51.6	51.4	51.1	53.4	53.4	52.4	53.3
TiO_2	0.52	0.63	0.39	0.53	0.49	0.53	0.42
Al_2O_3	3.0	3.4	1.7	2.5	2.3	2.8	2.0
FeO^a	6.9	8.3	8.0	9.3	8.3	10.2	8.8
MnO	0.31	0.41	0.37	0.37	0.40	0.35	0.60
MgO	15.4	15.2	14.8	15.5	15.6	15.2	15.7
CaO	21.9	21.0	21.4	20.5	20.4	20.0	20.4
Na_2O	0.4	0.3	0.4	0.4	0.4	0.4	0.3
K_2O	0.02	0.01	0.2	0.02	0.02	0.01	0.02
Sum	100.0	100.6	98.2	102.3	101.3	101.9	101.6
Age	Late Miocene			Late Miocene			

[a]Total Fe as FeO.

[b]Fragments of large single crystal.

orientation when compared to other igneous suites. Although the cooccurrence of pyroxenes in a deep-sea sediment does not indicate the cooccurrence of these two minerals in the original igneous melt (especially in the case of 154A-18, which is a volcanic sand), the slopes of these tie lines are consistent with a magmatic coexistence.

The overall chemistry of the pyroxenes has several notable features. First, many of the samples are magnesian, relative to other igneous clinopyroxenes (compare the analyses of Deer et al., 1963), suggesting that relatively little differentiation has taken place in these melts prior to eruption. Second, the values of Ti and Al are relatively low, perhaps for the same reason. However, Ti/Fe ratios of these pyroxenes are inherently lower then the average igneous clinopyroxene.

The final chemical feature of note is the relatively high value of Mn in all of these pyroxenes. When compared to the values of MnO given by Deer et al. (1963) for igneous pyroxenes, the present group is consistently about 0.2 per cent higher for a given Fe content. A possible explanation is that this igneous province is relatively Mn-rich, but the amphibole Mn values are typical for igneous amphiboles. A second explanation is that the chemical instability of pyroxenes in marine sediments, which leads through solution effects to their characteristic etched appearance, results in the replacement of the original divalent ions in the structure by Mn through ion exchange during diagenesis. The behavior of Mn in the marine sedimentary environment is still not completely understood, and the possibility of the formation of Mn-enriched silicates during diagenesis should be investigated.

Other Minerals

Analyses of other minerals are shown in Table 4. The oxides analyzed are titaniferous magnetites (Cores 148-8, 148-29) of probable volcanic origin (one analysis, 53, is heterogeneous), an ilmenite (Core 152-18) which is possibly derived as clastic detritus from the basalts of Core 152-23,

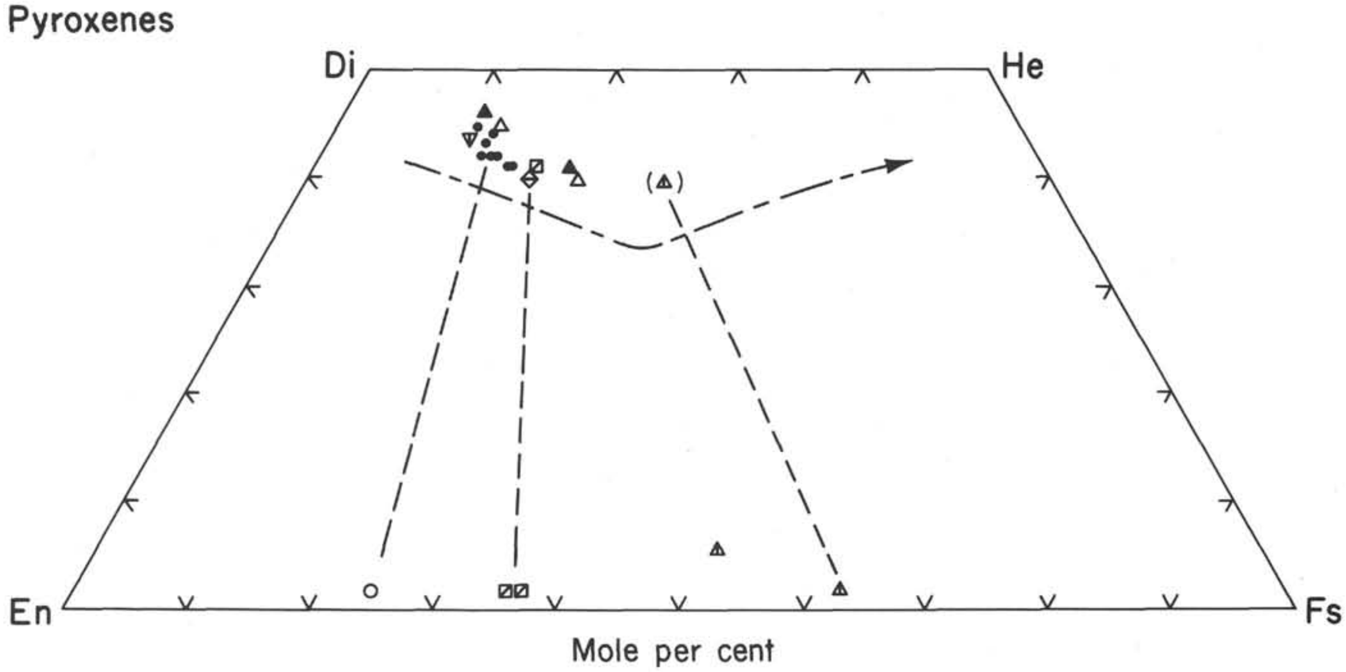

Figure 2. *Plot of pyroxenes on the pyroxene quadrilateral, using Fe, Mg, and Ca values only and plotting as mole per cent. The Skaergaard trend is shown as a long- and short-dashed line. Tie lines between cooccurring clino- and orthopyroxene assemblages are shown as short-dashed lines. A cluster of points in the clinopyroxene field is too dense to allow for identification of each point. The point in parentheses is not listed in Table 1 because of a low summation; however, the elemental ratios appear to be correct. The three values for Core 150-5 are averaged here to a single point. Legend is in Figure 3.*

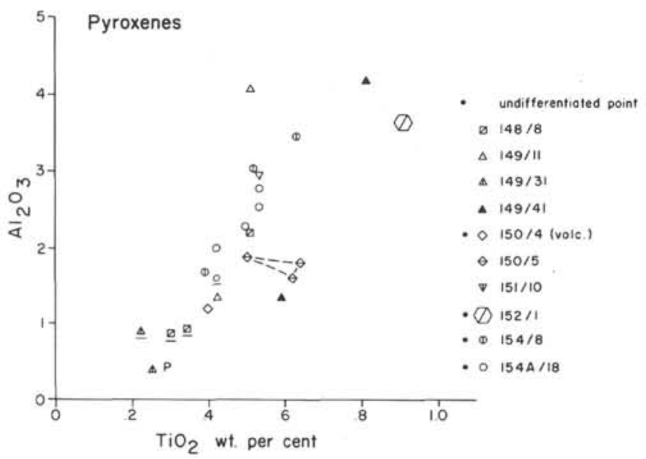

Figure 3. *Plot of Al_2O_3 versus TiO_2 for the pyroxenes. Point labelled P is a pigeonite; underlined points are orthopyroxenes. The three individual fragments of the single grain from Core 150-5 are connected by a short-dashed line.*

and an apparently homogeneous hemo-ilmenite grain from the turbidite (Core 150-4). This last is not of a typically volcanic composition and could represent high grade (granulite) metamorphism in the area of provenance.

Biotite from Core 152-10 is somewhat high in Ti and Mg, compared with other igneous biotites (Deer et al., 1963). The summation is low, probably because of grain size and shape, but the analysis is included here because of the Ti value.

SUMMARY

The amphiboles and pyroxenes analyzed are mostly typically calc-alkaline, but they reflect some variations and differentiation of melts. The most interesting variation is in Ti, which is high in the amphiboles, the sole biotite, the ilmenite grain, and the one clinopyroxene all from the northern Colombian Basin area (Sites 151-152). Both the basalt and its clinopyroxenes at Site 151 are also noticeably high in Ti (Donnelly et al., "Basalts and Dolerites . . .", this volume), suggesting that this entire area is a Tri-rich igneous province.

This brief investigation has uncovered several phenomena worthy of more extended investigation. They are the variations in degree of differentiation with time (the Fe-rich pyroxenes of Core 149-31), the regional variations in chemical composition (the high Ti at Sites 151 and 152), and the generally high Mn of the pyroxenes. We believe further work is indicated in all of these areas.

REFERENCE

Deer, W. A., Howie, R. A. and Zussman, J., 1963. Rock-Forming Minerals. Volume 2, Chain Silicates. New York (John Wiley and Sons).

TABLE 3
Orthopyroxene Analyses

Sample	148-8-3 (62-63)		149-31 (CC)	154A-18 (CC)
Analysis No.	50	51	42	63
SiO_2	52.1	52.2	49.4	52.8
TiO_2	0.30	0.34	0.22	0.42
Al_2O_3	0.87	0.92	0.90	1.6
FeO[a]	22.0	21.8	34.4	15.8
MnO	0.74	0.68	1.49	0.59
MgO	21.5	21.8	11.0	27.2
CaO	1.02	1.01	0.86	0.88
Na_2O	0.04	0.03	0.02	0.03
K_2O	0.02	0.02	0.02	0.01
Sum	98.6	98.8	98.3	99.3
Age	Pleistocene		Late Eocene	Late Miocene

[a]Total Fe as FeO.

[b]Fragments of a large single crystal.

TABLE 4
Other Minerals

Mineral	Biotite	Ti-magnetite		Hemo-ilmenite	Ilmenite
Sample	152-10-1 (147)	148-8-3 (62-63)	148-29 (CC)	150-4-1 (89-90)	
Analysis No.	6	53	28	11	1
SiO_2	34.3	0.0	0.0	0.05	0.0
TiO_2	4.61	15.1	9.5	39.9	51.9
Al_2O_3	13.1	1.9	2.7	2.2	1.0
FeO[a]	14.2	71.1	80.9	54.0	46.2
MnO	0.18	0.62	0.44	0.51	0.46
MgO	12.5	1.0	1.6	1.4	2.7
CaO	0.05	0.10	0.11	0.16	0.09
Na_2O	0.5	0.1	0.1	0.1	0.0
K_2O	6.6	0.06	0.06	0.07	0.05
Sum	86.1	90.0	95.4	98.4	102.4
Age	Early Paleocene	Pleistocene	pre-Miocene?	Early Miocene	Maestrichtian

[a]Total Fe as FeO.