CHAPTER 5

CHEMISTRY

SAMPLING CONSIDERATIONS

Seventy samples considered to be representative of the extrusive and intrusive rocks comprising the Nandewar Volcano were selected for chemical analysis. Analyses and C.I.P.W. norms are listed in Table 5.1 and analytical techniques are outlined in Appendix 1.

Great care was taken to obtain the freshest material available, but unfortunately many of the mafic and intermediate rocks display some evidence of deuteric alteration, particularly of the groundmass. One manifestation of this is an increase in Fe_2O_3/FeO ratios which may significantly affect the calculated normative femic constituents and important petrologic parameters such as M values. Classification schemes for mafic volcanic rocks based on normative criteria may therefore be subject to considerable uncertainty, particularly when the rocks are transitional between tholeiitic and alkaline.

To minimise these difficulties, a procedure similar to that adopted by Irving and Green (1976) in their treatment of analytical data on the Newer Volcanics of Victoria , has been used. This involves the recalculation of analytical Fe_2O_3 and FeO values to give Fe_2O_3/FeO ratios of 0.2 for the hawaiites and trachyandesites, prior to calculation of the norm. This value for the Fe_2O_3/FeO ratio is very close to the minimum based on the analytical data and it is probably a reasonable estimate of the pre-eruptive oxidation state of these magmas. Similarly, the norms of the tristanites and mafic trachytes have been calculated on the basis of a Fe_2O_3/FeO ratio of 0.5, and for the comendites and rhyolites a ratio of $Fe_2O_3/FeO = 1.0$ has been adopted. These values are also close to the minimum for these rocks.

The use of a fixed Fe_2O_3/FeO ratio is particularly important for several alkali rhyolites. Although these appear to be comparatively fresh petrographically, most of the Fe^{2+} in Fe-bearing phases has been oxidized to Fe^{3+}, presumably during a late-stage degassing event.

Non-hydrated obsidians provide the closest approach to original

TABLE 5.1

Analyses and norms of Nandewar rocks

	Hawaiites and Trachyandesites																Monzonite	
Rock Number	49000	49001	49002	49002G	49003	49004	49005	49008	49007	49009	49010[1]	49010G	49011	49012	49013	49018	49070	49070Sch.
SiO_2	46.99	46.63	47.88	45.87	47.57	47.37	47.06	47.46	50.31	47.98	49.63	49.30	50.55	50.99	50.67	52.98	56.80	64.48
TiO_2	2.65	2.21	2.85	4.15	2.23	2.92	2.79	2.65	2.25	2.64	2.28	3.03	2.63	2.30	2.48	1.81	1.75	0.56
Al_2O_3	14.55	13.84	15.39	14.10	14.34	16.30	14.88	15.32	16.40	15.41	19.02	15.92	14.90	15.92	15.89	16.26	15.86	16.99
Fe_2O_3	1.77	2.45	2.39	3.25	2.58	4.84	3.17	2.44	3.77	2.66	3.27	4.23	5.69	4.04	5.03	4.85	3.81	1.77
FeO	8.90	8.62	8.19	9.46	9.38	6.03	8.58	9.21	6.43	8.73	5.82	7.64	6.00	6.56	5.72	4.40	4.98	1.65
MnO	0.13	0.15	0.13	0.17	0.15	0.13	0.15	0.16	0.14	0.15	0.12	0.18	0.19	0.14	0.15	0.18	0.15	0.05
MgO	8.18	9.66	7.47	6.68	8.09	5.95	5.76	4.93	4.59	5.20	2.64	2.59	3.41	3.27	3.28	2.21	1.92	0.78
CaO	8.97	8.37	8.53	8.42	8.42	8.40	7.51	7.43	7.50	7.51	8.19	7.31	6.55	6.54	6.57	5.02	4.54	1.38
Na_2O	2.80	3.12	3.26	3.22	3.84	3.28	3.54	4.20	4.22	4.26	4.38	4.19	4.60	4.47	4.60	4.20	5.20	6.26
K_2O	1.43	1.05	1.52	1.60	0.99	1.54	2.13	2.20	1.79	2.15	1.64	2.23	2.30	2.49	2.47	3.53	3.06	4.98
P_2O_5	0.47	0.60	0.56	0.61	0.70	0.76	1.60	1.45	0.92	1.47	0.89	1.27	1.40	1.24	1.21	0.92	0.62	0.15
H_2O^+	2.03	2.60	0.97	1.30	0.95	1.58	1.84	1.30	0.72	0.58	0.70	0.58	0.69	0.94	1.19	2.82	0.87	0.25
H_2O^-	0.83	0.68	0.76	0.63	0.57	0.80	0.87	0.59	0.84	0.76	0.85	0.64	0.67	1.06	0.64	0.85	0.64	0.33
Total	99.70	99.98	99.90	99.46	99.81	99.90	99.88	99.34	99.88	99.50	99.43	99.11	99.58	99.96	99.90	100.03	100.20	99.63
ΣFe as FeO	10.49	10.82	10.34	12.38	11.70	10.39	11.43	11.41	9.82	11.12	8.76	11.45	11.12	10.20	10.25	8.76	8.41	3.24
$100Mg/Mg+Fe^{2+}$	62.1	65.2	60.3	53.2	59.3	54.6	51.4	47.6	49.6	49.6	38.8	32.2	39.2	40.3	40.2	34.7	37.1	45.7
Na_2O/K_2O	1.96	2.97	2.15	2.01	3.88	2.13	1.66	1.91	2.36	1.98	2.67	1.88	2.00	1.80	1.86	1.19	1.70	1.26
								C.I.P.W. *Norms**										
Q																	3.07	5.48
or	8.45	6.20	8.98	9.46	5.85	9.10	12.59	13.00	10.58	12.70	9.69	13.18	13.59	14.71	14.60	20.86	18.08	29.43
ab	23.69	26.40	27.58	25.53	28.83	27.75	29.95	30.18	35.71	31.02	36.31	35.45	38.92	37.82	38.76	35.54	44.00	52.97
an	22.91	20.66	22.87	19.29	18.97	25.21	18.42	16.45	20.52	16.58	27.39	18.05	13.22	16.02	15.41	15.09	10.90	3.55
ne				0.93	1.98			2.90		2.72	0.40				0.09			
di	15.01	13.72	12.81	15.10	14.87	9.40	6.90	9.05	8.81	9.13	6.20	8.37	8.47	6.95	7.74	3.21	6.30	1.87
hy	2.92	0.48	0.82			3.89	2.45		3.00			3.29	3.05	3.60		13.52	7.28	1.78
ol	15.16	20.93	15.78	14.78	18.99	12.02	14.93	14.63	10.68	14.77	9.15	7.82	9.62	8.88	11.11	0.09		
mt	2.58	2.66	2.54	3.04	2.88	2.55	2.81	2.80	2.41	2.73	2.15	2.81	2.73	2.51	2.52	2.15	4.20	2.57
il	5.03	4.20	5.41	7.88	4.24	5.55	5.30	5.03	4.27	5.01	4.33	5.75	5.00	4.37	4.71	3.44	3.32	1.06
ap	1.09	1.39	1.30	1.41	1.62	1.76	3.71	3.36	2.13	3.41	2.06	2.94	3.24	2.87	2.80	2.13	1.44	0.35
Rest	2.86	3.28	1.73	1.93	1.52	2.38	2.71	1.89	1.56	1.34	1.55	1.22	1.36	2.00	1.83	3.67	1.51	0.58
100*an*/*ab*+*an*	49.2	43.9	45.3	43.0	39.7	47.6	38.1	35.3	36.5	34.8	43.0	33.7	25.3	29.8	28.5	29.8	19.9	6.3
Fractionation Index[2]	32.1	32.6	36.6	35.9	36.7	36.9	42.5	46.1	46.3	46.4	46.4	48.6	52.5	52.5	53.4	56.4	65.2	87.9

* - norms for hawaiites and trachyandesites based on $Fe_2O_3/FeO = 0.2$

1 - sample contains approximately 20 percent plagioclase phenocrysts

2 - D.I. + ac + ns; G - groundmass separate; Sch. - schlieren

TABLE 5.1 (continued)

Analyses and norms of Nandewar rocks

	Tristanites								Mafic				Trachytes						
Rock Number	49075	49076	49077	49078	49079	49080	49074	49081	49082	49097	49083	49084	49085	49086	49087	49088	49090	49089	49091
SiO_2	55.82	55.79	55.90	55.37	56.58	56.83	57.46	59.56	60.03	59.79	59.89	61.51	62.85	62.87	62.65	63.05	63.86	64.60	63.95
TiO_2	1.51	1.69	1.71	1.77	1.65	1.32	1.00	1.04	1.07	1.03	0.93	0.75	0.63	0.63	0.48	0.64	0.45	0.51	0.95
Al_2O_3	16.92	15.87	15.83	16.01	16.71	16.95	17.46	16.65	16.43	16.61	16.44	16.98	16.45	16.44	16.84	16.24	15.84	16.42	18.46
Fe_2O_3	3.84	4.02	4.25	6.72	5.15	3.98	3.49	2.90	3.67	4.15	3.81	2.21	2.14	2.44	5.90	2.41	5.13	1.96	1.82
FeO	4.70	5.25	4.60	3.07	3.65	4.00	2.85	3.60	2.79	2.85	2.81	3.17	3.07	2.73	0.15	2.59	0.60	3.09	0.35
MnO	0.15	0.17	0.15	0.14	0.12	0.15	0.09	0.12	0.12	0.11	0.12	0.15	0.13	0.11	0.16	0.12	0.13	0.13	0.02
MgO	1.75	1.81	1.83	1.54	1.68	1.48	1.30	1.53	0.97	0.93	0.66	0.28	0.60	0.37	0.16	0.33	0.07	0.41	0.04
CaO	4.57	4.44	4.52	4.00	4.11	4.23	3.14	3.24	3.28	2.54	2.38	1.71	1.64	1.68	1.10	1.66	0.49	1.26	0.98
Na_2O	5.47	5.38	5.33	5.32	5.25	5.62	5.16	5.60	5.88	5.95	5.39	5.38	6.31	6.37	6.25	6.47	5.82	6.25	6.18
K_2O	3.07	3.21	3.17	3.20	3.53	3.25	4.75	4.08	4.42	4.62	5.46	5.56	5.23	5.14	5.57	5.17	5.60	5.38	6.12
P_2O_5	0.65	0.69	0.72	0.73	0.55	0.55	0.60	0.32	0.35	0.28	0.39	0.28	0.10	0.12	0.13	0.13	0.07	0.06	0.05
H_2O^+	0.49	0.30	0.61	1.13	0.36	0.59	1.23	0.37	0.40	0.40	0.80	0.52	0.10	0.32	0.53	0.37	0.82	0.04	0.08
H_2O^-	0.89	0.93	1.05	0.87	0.76	1.14	1.08	0.86	0.48	0.47	0.99	0.61	0.57	0.43	0.17	0.68	0.91	0.25	0.23
Total	99.83	99.55	99.67	99.87	100.10	100.09	99.61	99.77	99.89	99.73	100.07	99.34	99.82	99.65	100.09	99.86	99.79	100.36	99.23
ΣFe as FeO	8.16	8.87	8.42	9.12	8.28	7.58	5.99	6.21	6.09	6.58	6.24	5.16	5.00	4.93	5.46	4.76	5.22	4.85	1.99
$100Mg/Mg+Fe^{2+}$	35.7	34.5	36.0	30.4	34.4	33.5	35.9	38.9	29.2	26.7	21.5	12.3	23.7	16.3	7.0	15.2	3.4	17.9	4.9
Na_2O/K_2O	1.78	1.68	1.68	1.66	1.49	1.73	1.09	1.37	1.33	1.29	0.99	0.97	1.21	1.24	1.22	1.25	1.04	1.16	1.01
									C.I.P.W. Norms*										
Q	0.32	0.81	1.47	1.53	1.34	0.75	0.56	2.20	1.27	0.46	1.49	3.98	1.52	1.91	1.22	1.80	5.83	3.70	2.38
or	18.14	18.97	18.73	18.91	20.86	19.21	28.07	24.11	26.12	27.30	32.27	32.86	30.91	30.37	32.92	30.55	33.09	31.79	36.17
ab	46.28	45.52	45.10	45.01	44.42	47.55	43.66	47.38	49.75	50.35	45.61	45.52	53.39	53.90	52.88	54.75	49.25	52.88	52.29
an	12.55	9.67	9.91	10.35	11.60	11.43	10.45	8.24	5.38	4.97	4.54	5.76	1.12	1.08	1.45		0.56	0.86	4.59
di	4.90	6.57	6.51	3.97	4.35	5.00	1.00	4.78	7.26	4.93	4.04	0.78	5.44	5.59	2.78	6.40	1.25	4.32	
hy	7.69	7.45	7.03	8.12	7.64	6.71	7.13	6.03	3.18	4.78	4.39	4.40	2.81	2.03	3.80	1.34	4.13	2.95	0.52
mt	4.08	4.43	4.21	4.56	4.14	3.79	3.00	3.10	3.05	3.29	3.12	2.58	2.50	2.46	2.73	2.38	2.61	2.43	0.99
il	2.87	3.21	3.25	3.36	3.13	2.51	1.90	1.98	2.03	1.96	1.77	1.42	1.20	1.20	0.91	1.22	0.85	0.97	1.80
ap	1.51	1.60	1.67	1.69	1.27	1.27	1.39	0.74	0.81	0.65	0.90	0.65	0.23	0.28	0.30	0.30	0.16	0.14	0.12
Rest	1.38	1.23	1.66	2.00	1.12	1.73	2.31	1.23	0.88	0.87	1.79	1.13	0.67	0.75	0.70	1.05	1.73	0.29	0.31
100*an/ab+an*	21.3	17.5	18.0	18.7	20.7	19.4	19.3	14.8	9.8	9.0	9.1	11.2	2.0	2.0	2.7	0.0	1.1	1.6	8.0
Fractionation Index1	64.8	65.3	65.3	65.5	66.6	67.5	72.3	73.7	77.1	78.1	79.4	82.4	85.8	86.2	87.0	87.1	88.2	88.4	90.8
Agpaitic Index2	0.73	0.78	0.77	0.76	0.75	0.75	0.78	0.82	0.88	0.89	0.90	0.88	0.98	0.98	0.97	1.00	0.99	0.98	0.91

* - norms for tristanites and mafic trachytes based on $Fe_2O_3/FeO = 0.5$

1 - D.I. + ac + ns

2 - Molecular $(Na_2O+K_2O)/Al_2O_3$

TABLE 5.1 (continued)

Analyses and norms of Nandewar rocks

	Peralkaline Trachytes												Comendites					
Rock Number	49102	49098	49098G	49103	49099	49100	49104	49107	49101	49105	49106	49108	49162[†]	49160	49161	49163	49164	49165
SiO_2	64.30	63.95	62.73	64.78	65.48	65.79	64.80	64.73	67.05	67.06	65.77	67.57	67.66	66.96	68.85	72.82	70.37	73.63
TiO_2	0.51	0.42	0.54	0.46	0.81	0.34	0.44	0.46	0.38	0.37	0.39	0.34	0.33	0.35	0.36	0.14	0.11	0.28
Al_2O_3	15.90	15.38	15.18	16.36	14.92	15.00	15.75	16.05	14.56	15.31	16.25	15.50	13.79	14.04	14.37	12.95	15.73	13.79
Fe_2O_3	1.57	2.98	3.02	1.82	2.86	2.93	4.90	3.68	3.64	3.08	2.86	2.36	5.12	3.23	2.49	2.35	1.30	0.65
FeO	3.48	2.85	3.82	2.97	2.77	2.48	0.73	1.17	1.58	1.05	1.23	0.85	0.12	1.97	2.04	0.85	0.22	0.12
MnO	0.13	0.14	0.20	0.14	0.12	0.10	0.08	0.09	0.09	0.08	0.09	0.05	0.15	0.11	0.11	0.03	0.02	n.d.
MgO	0.21	0.16	0.16	0.41	0.26	0.08	0.08	0.12	0.03	0.26	0.30	0.05	0.07	0.10	0.02	0.03	0.27	0.01
CaO	1.36	1.22	1.60	1.31	0.72	0.57	0.36	0.57	0.31	0.30	0.30	0.21	0.84	0.94	0.48	0.19	0.21	0.12
Na_2O	6.37	6.78	6.60	6.46	6.46	6.37	6.43	6.49	6.51	6.61	6.90	6.38	5.18	5.78	5.87	5.32	6.46	4.96
K_2O	5.24	5.36	5.16	5.52	5.24	5.13	5.47	5.49	5.04	5.34	5.56	5.75	5.14	5.18	5.27	4.37	4.81	5.35
P_2O_5	0.08	0.06	0.06	0.06	n.d.	0.03	0.06	0.05	0.04	0.02	0.03	0.04	0.03	0.03	0.03	0.02	n.d.	0.03
H_2O^+	0.40	0.21	0.21	0.05	0.09	0.54	0.50	0.45	0.19	0.20	0.01	0.26	0.56	0.05	0.13	0.27	0.23	0.16
H_2O^-	0.19	0.28	0.28	0.12	0.40	0.42	0.73	0.90	0.47	0.30	0.23	0.32	0.44	0.61	0.29	0.47	0.44	0.22
Total	99.74	99.79	99.56	100.46	100.13	99.78	100.33	100.25	99.89	99.98	99.92	99.68	99.43	99.35	100.31	99.81	100.17	99.25
ΣFe as FeO	4.89	5.53	6.54	4.61	5.34	5.12	5.14	4.48	4.86	3.82	3.80	2.97	4.73	4.88	4.28	2.96	1.39	0.70
Na_2O/K_2O	1.22	1.27	1.28	1.17	1.23	1.24	1.18	1.18	1.29	1.24	1.24	1.11	1.01	1.12	1.11	1.22	1.34	0.93
C.I.P.W. Norms*																		
Q	3.78	2.04	0.79	2.46	6.10	6.91	4.46	3.86	9.83	7.98	3.48	9.15	16.11	12.09	13.82	24.65	13.57	24.35
or	30.97	31.67	30.49	32.62	30.97	30.32	32.32	32.44	29.78	31.56	32.86	33.98	30.37	30.61	31.14	25.82	28.42	31.62
ab	52.61	49.27	49.35	53.42	47.57	48.59	50.56	51.99	46.83	49.02	52.63	47.71	42.31	43.38	44.57	42.28	54.13	41.14
di	5.46	5.00	6.68	5.28	3.13	2.34	1.23	2.20	1.14	1.19	1.13	0.69	3.51	3.95	1.94	0.72	0.86	0.24
hy	2.19	4.34	4.40	2.62	4.66	4.95	4.98	3.68	5.16	4.41	4.50	3.05	0.83	1.65	2.07	1.70	0.93	
ac	1.14	5.52	5.72	1.10	5.33	4.67	3.39	2.58	4.84	3.81	3.79	2.97	1.34	4.87	4.49	2.41	0.47	0.73
ns		0.43			0.24				0.64	0.60	0.34	0.68						
mt	1.88		0.40	1.75		0.22	0.87	0.95					2.76	1.09	0.85	0.94	0.77	0.15
il	0.97	0.80	1.03	0.87	1.54	0.65	0.84	0.87	0.72	0.70	0.74	0.65	0.63	0.66	0.68	0.27	0.21	0.53
ap	0.19	0.14	0.14	0.14		0.07	0.14	0.12	0.09	0.05	0.07	0.09	0.07	0.07	0.07	0.05		0.07
Rest	0.59	0.49	0.49	0.17	0.49	0.96	1.23	1.35	0.66	0.50	0.24	0.58	1.00	0.66	0.42	0.74	0.67	0.43
Fractionation Index[1]	88.5	88.9	86.4	89.6	90.2	90.5	90.7	90.9	91.9	93.0	93.1	94.5	90.1	91.0	94.0	95.2	96.6	97.8
Agpaitic Index[2]	1.02	1.10	1.08	1.01	1.09	1.07	1.05	1.04	1.11	1.09	1.07	1.08	1.02	1.08	1.07	1.04	1.01	1.01
Σfemics[3]	11.8	16.2	18.4	11.8	14.9	12.9	11.5	10.4	12.6	10.8	10.6	8.1	9.1	12.3	10.1	6.1	3.2	1.8

* - norms for peralkaline trachytes and comendites based on Fe_2O_3/FeO = 0.5 and 1.0 respectively

n.d.- not detected

[1] - D.I. + ac + ns

[2] - Molecular $(Na_2O+K_2O)/Al_2O_3$

[3] - Sum of normative femic constituents, as defined by Washington (1917)

† - denotes member of the older alkali rhyolite group

TABLE 5.1 (continued)

Analyses and norms of Nandewar rocks

	Alkali Rhyolites												
Rock Number	49119†	49120†	49122†	49121†	49123	49124	49127	49125	49131	49126	49128	49129	49130
SiO_2	67.46	66.38	68.37	65.76	68.76	69.54	70.66	71.25	72.18	69.79	69.65	72.98	74.55
TiO_2	0.34	0.44	0.34	0.40	0.32	0.22	0.40	0.36	0.26	0.37	0.20	0.28	0.27
Al_2O_3	14.68	15.53	13.70	15.52	14.97	16.30	14.62	15.39	15.84	16.57	15.95	14.17	13.82
Fe_2O_3	5.01	4.96	5.31	5.09	4.24	1.83	1.17	1.32	0.61	1.08	1.61	1.14	0.87
FeO	0.07	0.14	0.08	0.10	0.10	0.40	0.30	0.13	0.09	0.17	0.32	0.33	0.20
MnO	0.07	0.08	0.11	0.11	0.10	0.03	0.12	n.d.	n.d.	0.02	0.01	0.02	0.01
MgO	0.10	0.02	0.13	0.07	0.17	0.10	0.28	0.19	0.18	0.17	0.04	0.05	0.01
CaO	0.39	0.26	0.16	0.38	0.13	0.39	0.37	0.26	0.18	0.34	0.25	0.12	0.12
Na_2O	4.90	5.28	4.75	5.77	5.09	5.67	5.52	5.16	5.02	5.82	6.19	4.98	4.82
K_2O	5.00	5.43	5.26	5.41	5.38	5.29	5.08	5.60	5.57	5.89	5.36	5.17	5.10
P_2O_5	0.04	0.06	0.03	0.05	0.02	n.d.	0.04	0.01	n.d.	n.d.	0.03	0.03	0.02
H_2O^+	1.01	0.62	0.85	0.68	0.88	0.59	0.49	0.24	0.12	0.12	0.16	0.35	0.16
H_2O^-	0.67	0.41	0.51	0.36	0.29	0.28	0.69	0.31	0.29	0.13	0.21	0.44	0.24
Total	99.74	99.61	99.60	99.70	100.45	100.64	99.74	100.22	100.34	100.47	99.98	100.06	100.19
ΣFe as FeO	4.58	4.60	4.86	4.68	3.92	2.05	1.35	1.32	0.64	1.08	1.77	1.36	0.98
Na_2O/K_2O	0.98	0.97	0.90	1.07	0.95	1.07	1.09	0.92	0.90	0.99	1.16	0.96	0.95
						C.I.P.W. Norms*							
Q	18.10	13.68	19.22	10.09	17.35	15.00	18.22	18.96	21.01	12.42	12.61	23.87	26.75
C	0.59	0.64			0.59	0.54		0.39	1.23			0.24	0.20
or	29.55	32.09	31.08	31.97	31.79	31.26	30.02	33.09	32.92	34.81	31.67	30.55	30.14
ab	41.46	44.68	40.19	48.82	43.07	47.98	46.71	43.66	42.48	49.25	52.20	42.14	40.78
an	1.67	0.90	0.53	0.47	0.51	1.93	0.11	1.22	0.89	1.69		0.40	0.46
di			0.06	0.95			1.18				0.92		
hy	2.13	1.80	2.39	1.58	2.05	0.98	0.38	0.54	0.45	0.42	0.25	0.38	0.09
mt	3.32	3.34	3.52	3.39	2.84	1.48	0.98	0.96	0.28	0.73	1.20	0.98	0.71
hm									0.13	0.04			
il	0.65	0.84	0.65	0.76	0.61	0.42	0.76	0.68	0.49	0.70	0.38	0.53	0.51
ap	0.09	0.14	0.07	0.12	0.05		0.09	0.02			0.07	0.07	0.05
Rest	1.68	1.03	1.36	1.04	1.17	0.87	1.18	0.55	0.41	0.25	0.53[1]	0.79	0.40
Fractionation Index[2]	89.1	90.4	90.5	90.9	92.2	94.2	95.0	95.7	96.4	96.5	96.6	96.6	97.7
Agpaitic Index[3]	0.92	0.94	0.99	0.99	0.95	0.92	1.00	0.95	0.90	0.96	1.00	0.97	0.97

* - norms for alkali rhyolites calculated with $Fe_2O_3/FeO = 1.0$

† - denotes members of the older alkali rhyolite group

n.d. - not detected

[1] - includes 0.16 ac

[2] - D.I. + ac + ns

[3] - Molecular $(Na_2O+K_2O)/Al_2O_3$

magmatic liquid compositions, but unfortunately such rocks are not represented amongst the Nandewar volcanic products. Consequently aphyric or only slightly porphyritic lavas with less than 10 volume percent phenocrysts were selected for analysis. Some idea of the compositional differences between peralkaline silicic crystalline and glassy rocks from the same flow can be gleaned from analysis of internal crystalline portions, and marginal chilled facies of flows. The major changes resulting from crystallization include the loss of Na, F and Cl (Carmichael, 1962; Noble, 1965,1967; Ewart *et al.*, 1968; Baker and Henage 1977), as well as variable oxidation of Fe (Noble, 1967; Rosholt and Noble 1969). Loss of Na and halogens is the most severe modification, with reported differences between glassy and crystalline varieties being as high as 20 percent of the Na_2O, 50 percent of the F and 80 percent of the Cl (Noble *et al.*, 1967). Borodin and Pavlenko (1974) suggested that Zr, Hf, Nb, Ta, Th, U and the REE may also be lost to various degrees as soluble or volatile fluoride complexes. However, Baker and Henage (1977) found from a comparison of crystalline and glassy comendites that although important losses of Cs, Fe and the REE may occur, the levels of Al, Si, Zr, Hf, Nb, Ta, Th, U, Rb and the proportions of the REE are not significantly affected by crystallization of the peralkaline silicic magma.

GENERAL CHEMICAL CHARACTERISTICS OF THE SERIES

Silica Saturation

After correction of Fe_2O_3/FeO ratios for post-eruptive oxidation effects, which tends to reduce the amount of *hy*, the norms of the Nandewar mafic rocks are characterized by up to 3 percent *ne* on the one hand and up to 5 percent *hy* on the other. When plotted on the basis of *di+ne+ol+hy* = 100 (Fig. 5.1a), these straddle the critical plane of silica undersaturation in the 'basalt tetrahedron' (Yoder and Tilley, 1962), thereby illustrating their transitional character.

Normative *qz* first appears in the tristanites and gradually increases, reaching a maximum of 26.8 wt. percent *qz* in the alkali rhyolites. Feldspathoid-bearing or *ne*-normative salic rocks are not represented in the Nandewar series. This is consistent with the observation of Coombs (1963) that oversaturated peralkaline volcanics are typically

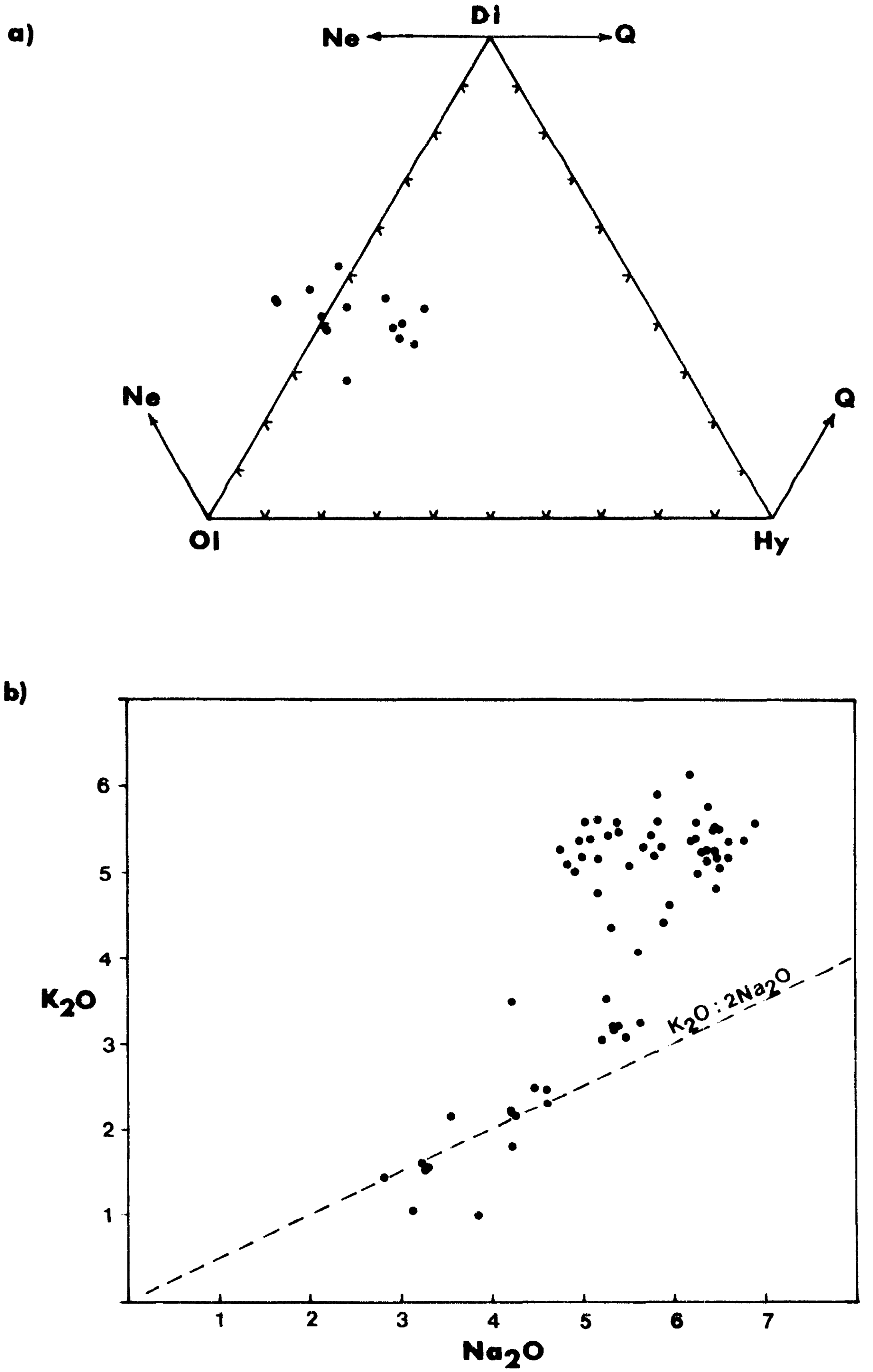

Fig. 5.1 (a) Normative diopside-hypersthene-olivine-nepheline diagram (Yoder and Tilley, 1962) depicting the transitional nature of the Nandewar hawaiites and trachyandesites.

(b) Plot of Na_2O vs K_2O (weight percent).

associated with transitional basaltic types, whereas phonolitic types are associated with more strongly undersaturated basalts (generally basanitic).

Alkali-Alumina Relations

The mildly potassic character of the Nandewar rocks is apparent in a plot of Na_2O versus K_2O (Fig. 5.1b), from which it is clear that the majority of the rocks have Na_2O/K_2O ratios less than 2.0. Coombs and Wilkinson (1969), following Macdonald and Katsura (1964), used this figure to distinguish between sodic and moderately potassic volcanic series in the basalt - 'andesite' range.

The molecular ratio $(Na_2O + K_2O)/Al_2O_3$ increases gradually throughout the series reaching a maximum of 1.11 in the peralkaline trachytes and decreasing to values slightly greater than unity in the comendites. This trend of increasing, followed by decreasing peralkalinity, with increasing acidity of the host is well displayed in a plot of Agpaitic Index (molecular $(Na_2O + K_2O)/Al_2O_3$) against SiO_2 content (Fig. 5.2a). The alkali rhyolites which exhibit a wide range of Agpaitic Indices (0.9 to 1.0) are not included in this diagram.

A plot of Al_2O_3 versus $Na_2O + K_2O$ (Fig. 5.2b) indicates that the transition from the non-peralkaline mafic trachytes to the peralkaline trachytes appears to have involved mainly an increase in alkalies (principally Na_2O), with a slight decrease in Al_2O_3 contents. On the other hand, the transition from the peralkaline trachytes to the comendites seems to have involved depletion of Al_2O_3, Na_2O and, to a lesser extent, K_2O. The alkali contents of the alkali rhyolites overlap those of the comendities and the alkali rhyolites appear to be comparatively enriched in Al_2O_3 at a given total alkali content. This is reflected by the appearance of 0.2 to 1.2 percent *c* in the norms of several alkali rhyolites. The appearance of normative *c* is not regarded as due to alteration or to analytical error, but rather reflects an excess of Al in the alkali feldspars which together with quartz and a little iron oxide are the sole constituents of these rocks.

Classification

The rocks have been classified using the normative and chemical criteria proposed by Coombs and Wilkinson (1969) for the mafic and

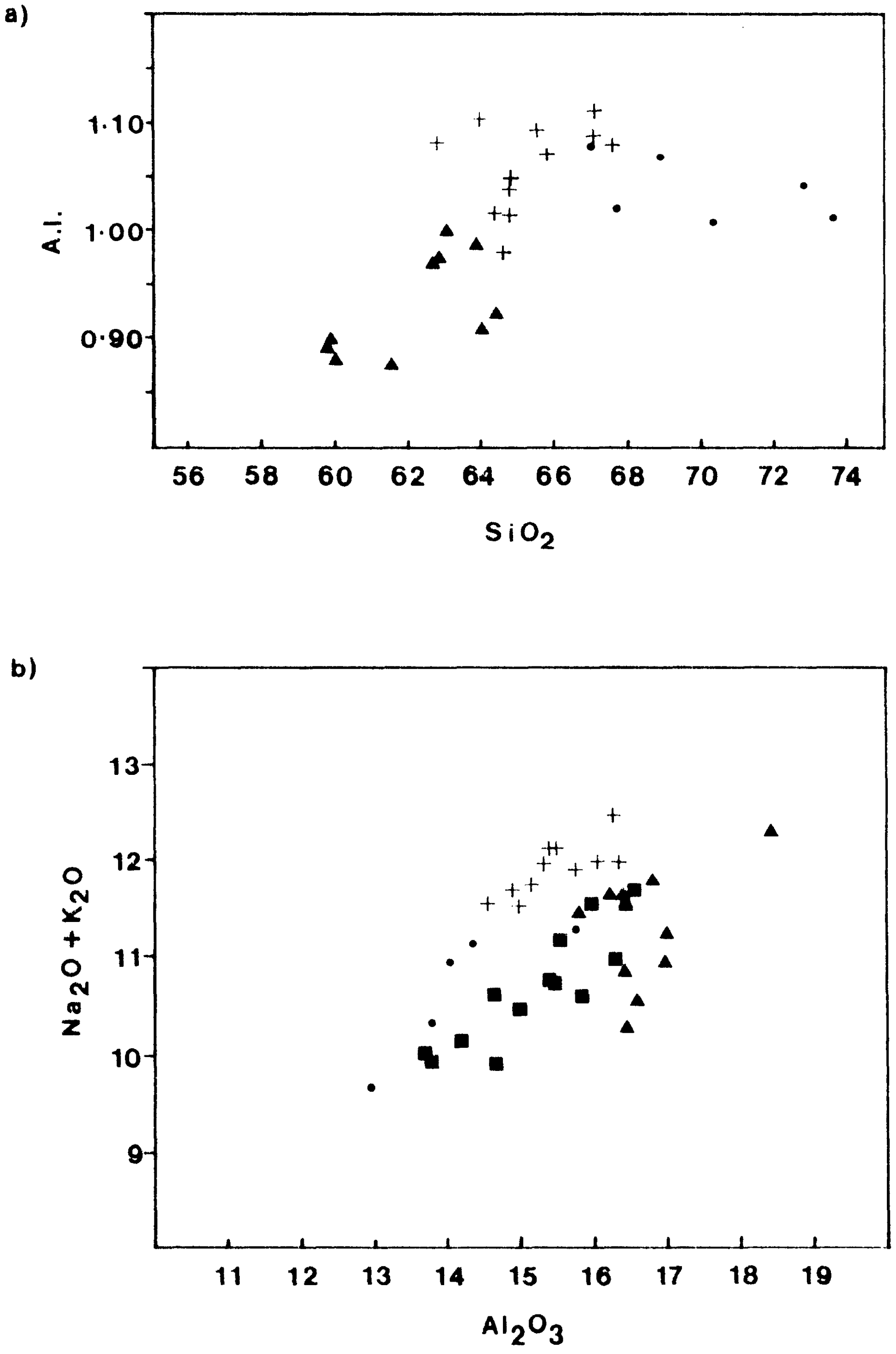

Fig. 5.2: Variation of (a) Agpaitic Index as a function of SiO_2 (wt. percent), and (b) Na_2O + K_2O as a function of Al_2O_3 (wt. percent) for the mafic trachytes (triangles), peralkaline trachytes (crosses), alkali rhyolites (squares) and comendites (circles).

intermediate rock types and by MacDonald and Bailey (1973) for the peralkaline variants. A plot of normative *qz* versus total normative femics (*Σdi+wo+hy+ol+ac+mt+il+hm+ap*, as defined by Washington (1917); Fig. 5.3a) indicates the comenditic affinities of the Nandewar peralkaline rocks, reflecting their higher Al_2O_3 and lower total Fe compared with well-documented pantelleritic types such as those from Pantelleria (Villari, 1974) and Boina, Ethiopa (Barberi *et al.*, 1975).

The somewhat arbitary divisions between the mafic and intermediate types are shown in the plot of Differentiation Index (D.I.) against normative plagioclase composition 100*an/ab+an* (Fig. 5.3b). Perhaps the two important features of this diagram are firstly, the absence of rocks with 100 *an/ab+an* greater than 50 (i.e. strictly basaltic[1] with normative labradorite), and secondly, the paucity of specimens in the D.I. range 56 to 65, despite detailed sampling of the volcanic sequence.

Major Element Variation

Chemical variation within volcanic suites has been traditionally observed and evaluated diagrammatically by Harker diagrams where oxide components are plotted against SiO_2 contents (wt. percent). Although these diagrams have proved useful for portraying chemical trends within a given volcanic series, in general they do not provide sufficient evidence, in isolation, to decide whether one or more specific differentiation controls have been operative.

Chayes (1964) drew attention to the limitations of these diagrams caused by the 'constant sum effect' (i.e. the fact that the major oxide components sum to nearly 100 percent). He demonstrated that any process which greatly expands the variance of silica relative to other oxides also leads to a strong negative correlation between silica and at least 3 of the other oxides. Consequently, a number of magmatic differentiation processes, including fractional crystallization, magma mixing, and vapour transport are capable of producing a range of rock compositions with strong correlations on Harker diagrams.

In spite of these shortcomings, the Harker-*type* variation diagram is an effective method of graphically portraying the trends of chemical variation within a group of rocks and the major and minor element data have been plotted (Figs 5.4 and 5.5) using the Fractionation Index as

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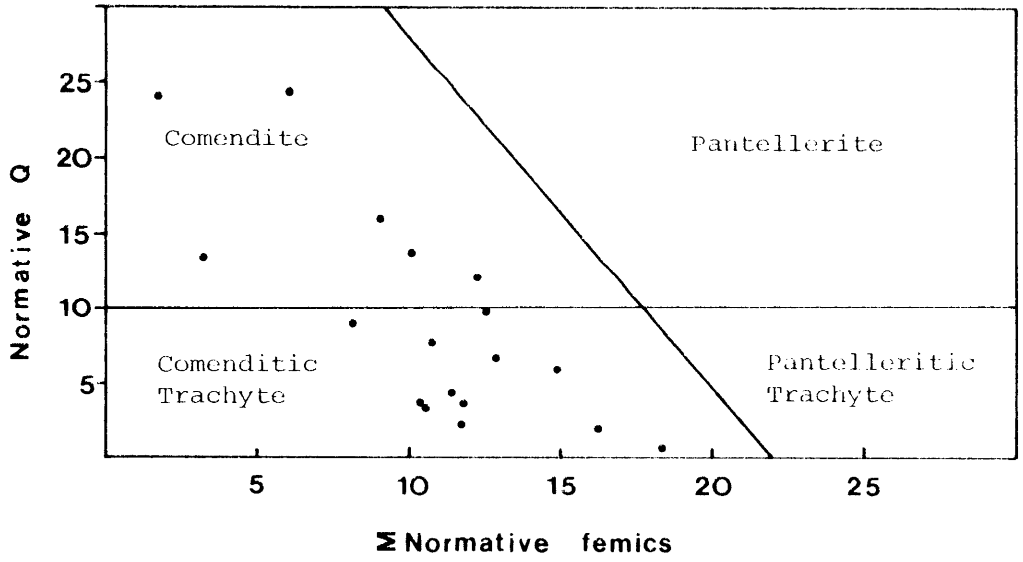
[1] Nandewar mafic volcanics designated as 'basalt' by Abbott (1969) contain normative andesine.

a)



b)

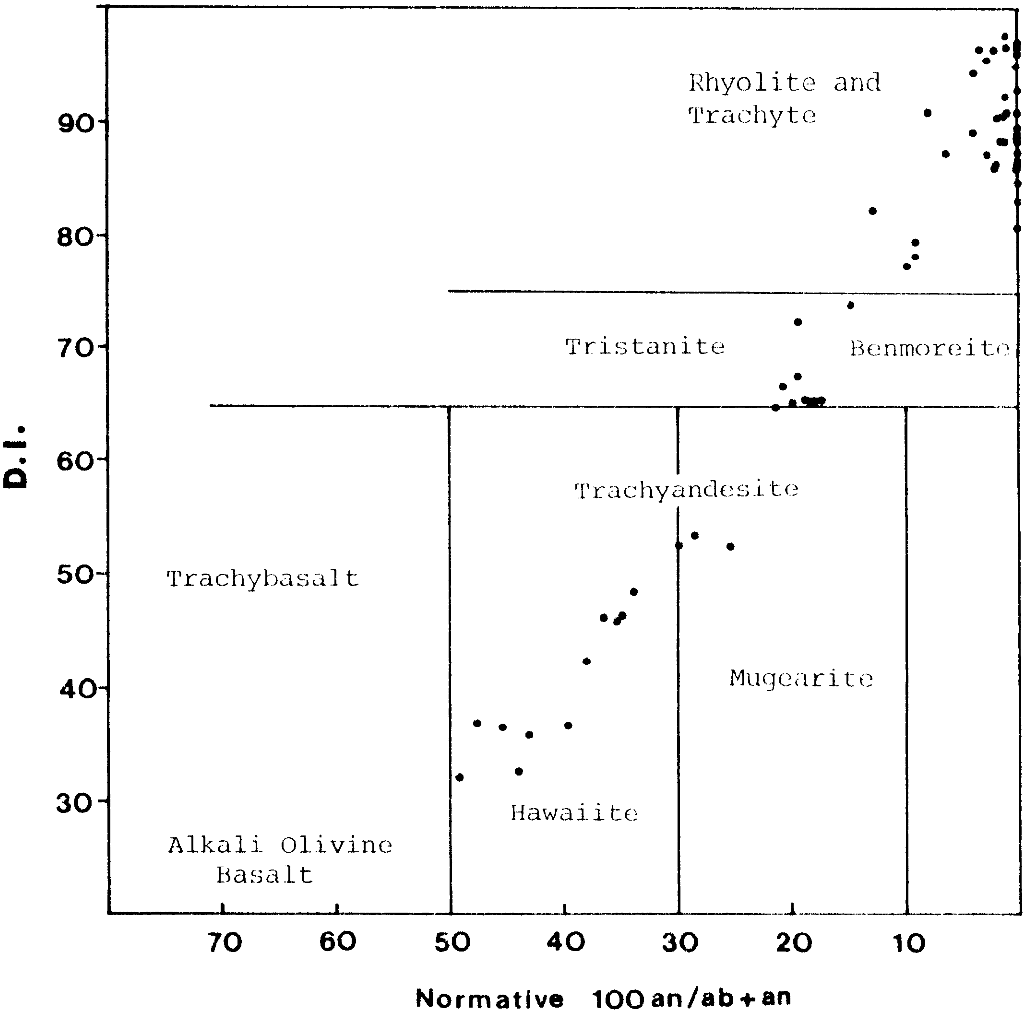


Fig. 5.3: (a) Classification scheme for peralkaline silicic rocks after Macdonald and Bailey (1973) showing their arbitrary boundary line between the pantelleritic and comenditic fields.

(b) Classification scheme for basic and intermediate rock types after Coombs and Wilkinson (1969).

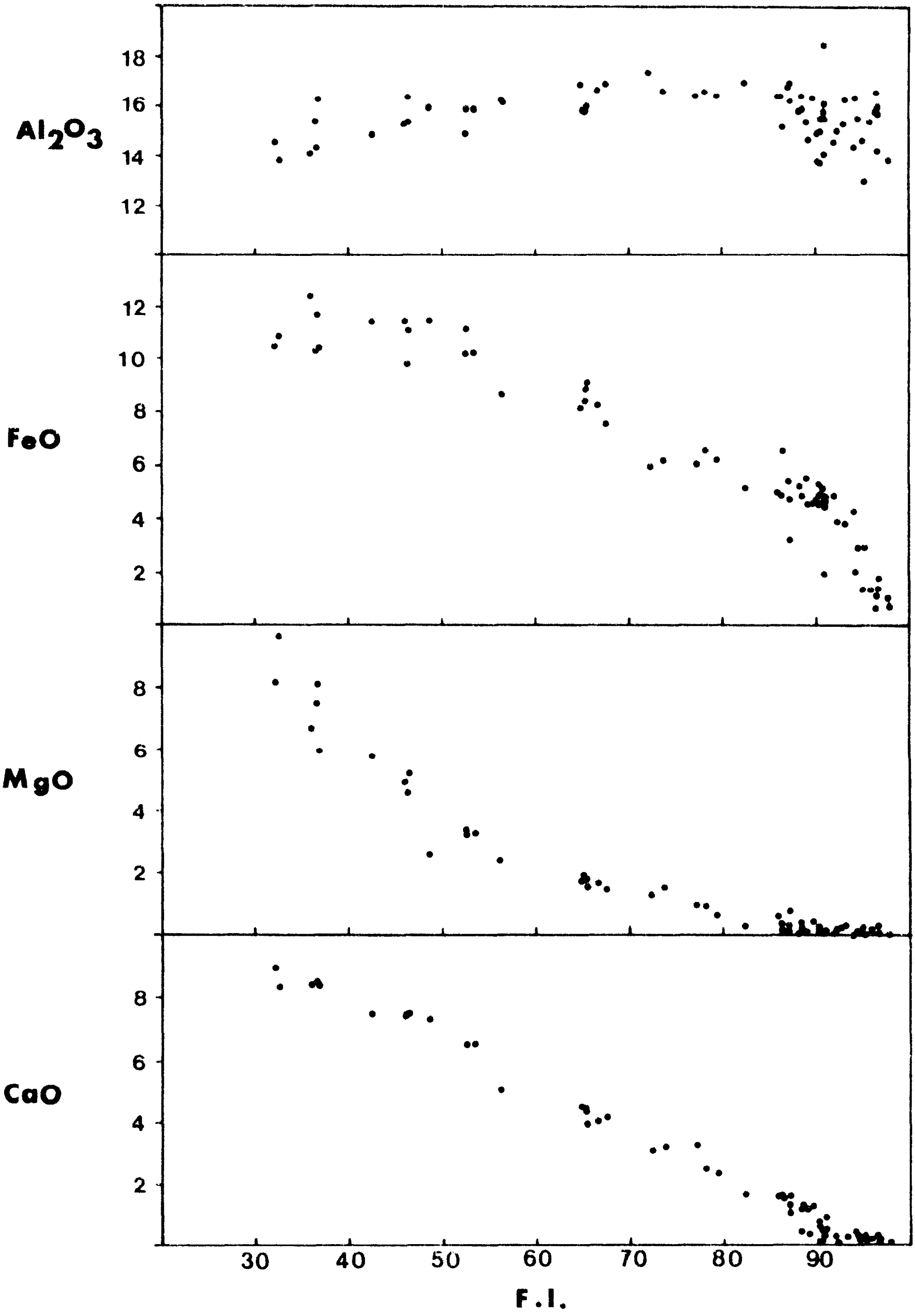


Fig. 5.4: Variation of major elements (weight percent) as functions of Fractionation Index (F.I.) in the Nandewar series. FeO refers to total Fe calculated as FeO.

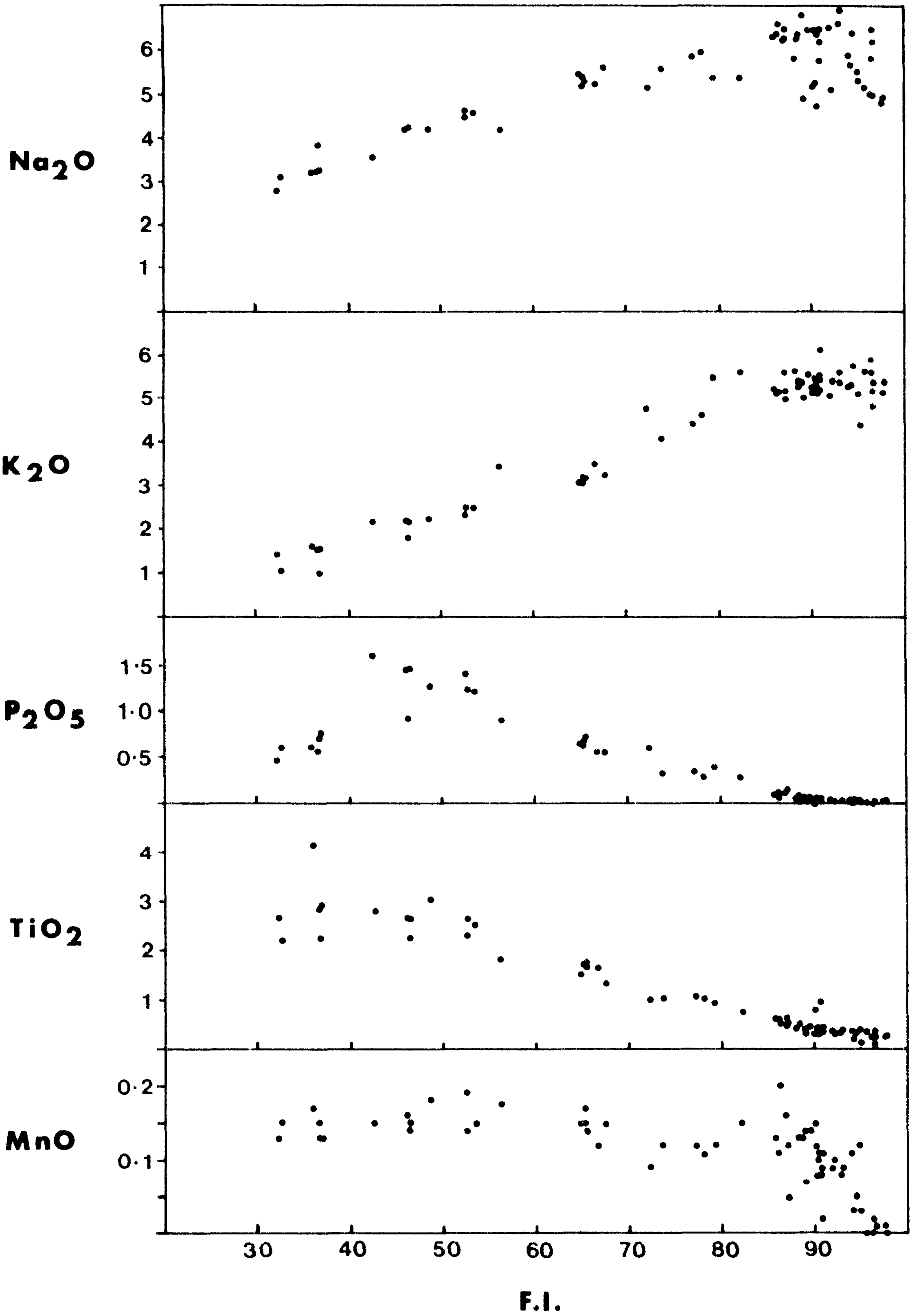


Fig. 5.5: Variation of major and minor elements (weight percent) as functions of Fractionation Index (F.I.) in the Nandewar series.

the abscissa, in place of SiO_2. The Fractionation Index (F.I.), proposed by Macdonald (1969), combines the Thornton-Tuttle Differentiation Index and normative acmite and sodium disilicate (i.e. D.I. + *ac* + *ns*). The latter take account of Na in peralkaline rocks which normally only appears as *ab* and/or *ne* in non-peralkaline types. The stages at which the various phenocryst species appear and disappear throughout the series are also shown diagrammatically (Fig. 5.6) to ascertain whether or not changes in potential crystal extracts can be correlated with any changes in major element chemistry.

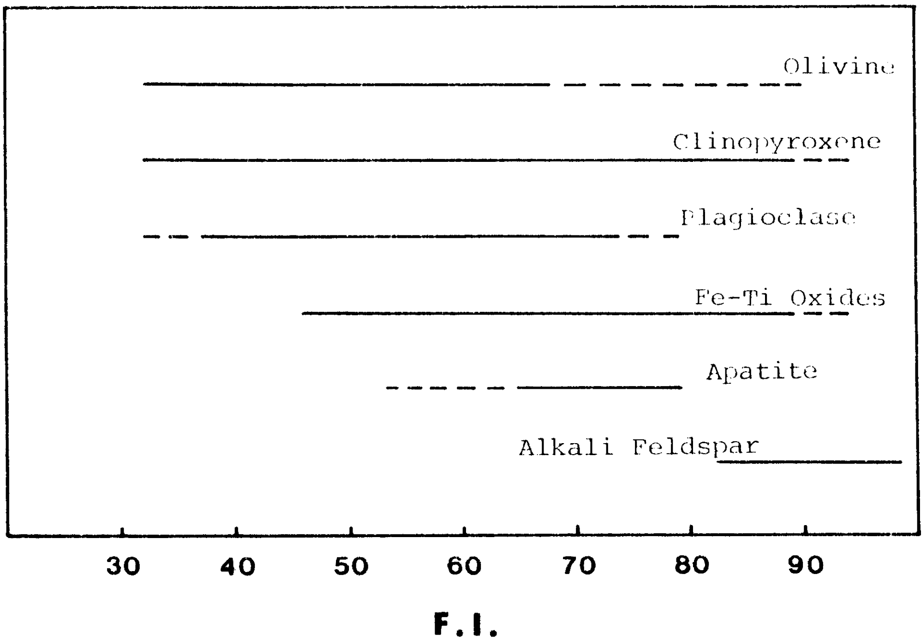


Fig. 5.6: Persistence of phenocrysts in the Nandewar lavas as functions of Fractionation Index of the hosts.

The SiO_2 content increases gradually throughout the series except for a marked gap between 53.0 and 55.4 percent SiO_2 which corresponds roughly with the so-called 'Daly Gap' delineated by Chayes (1963). Chayes found there is a distinct paucity in the number of analyses of alkaline volcanic rocks from the oceanic islands spanning the

SiO_2 range 53 to 57 percent.

Al_2O_3 increases gradually in the transition from the hawaiites to the mafic trachytes and then decreases in the peralkaline trachytes and comendites. However, the Al_2O_3 content of the comendites and alkali rhyolites is variable, and rocks of similar F.I. exhibit a range of 13.0 to 15.7 weight percent Al_2O_3. These variations in Al_2O_3 content are accompanied by similar variations in Na_2O and K_2O, and reflect differences in the modal abundances of alkali feldspar and quartz. The occurrence of plagioclase as an important and usually dominant phenocryst phase in the hawaiites, trachyandesites and tristanites, suggests that it may have been critical in controlling derivative liquid compositions if plagioclase fractionation had been operative. Taken at face value, the removal of significant amounts of plagioclase appears inconsistent with increasing Al_2O_3 content in potential derivative liquids. However, this trend could be in part accommodated by the simultaneous removal of phases with very low Al_2O_3 contents such as olivine and Ca-rich pyroxene.

Total Fe as FeO varies little in the hawaiites and trachyandesites, whereas MgO decreases quite dramatically from 9.7 to 2.6 weight percent MgO over the F.I. range 32 to 53. Over this interval Mg-depletion can be correlated with decreasing modal olivine, even though olivine persists as a phenocryst phase. Similarly, the stage at which total Fe as FeO begins decreasing (F.I. ~50) roughly coincides with the appearance of Fe-Ti oxides as phenocrysts in relatively more mafic hosts. Total Fe and MgO both undergo continued depletion throughout the series to very low levels ($\Sigma FeO = 0.64$ wt. percent, $MgO = 0.01$ wt. percent) in the alkali rhyolites (cf. Table 5.1). It should be noted that total Fe as FeO decreases from 3 to 4 weight percent in several comendites to less than 1 percent in the more evolved alkali rhyolites at a stage in the crystallization history of the respective hosts when alkali feldspar is the only phenocryst type.

Na_2O and K_2O increase throughout the series until the peralkaline trachyte stage is reached (F.I. ~88) after which there is considerable variation, particularly in the Na_2O contents of the comendites and alkali rhyolites. Although some of the variability of the Na_2O contents of these high F.I. rocks is a result of variable modal feldspar contents, loss of some Na during extrusion and crystallization of the vesicular alkali rhyolites is also indicated, particularly where these rocks have Na_2O/K_2O ratios less than unity.

At first glance the variation of P_2O_5 with F.I. could best be described as an initial increase, followed in the more evolved rocks by a gradual depletion. Alternatively this plot (Fig. 5.5) could be viewed as the result of *two* intersecting trends. The hawaiites exhibit a trend of increasing P_2O_5 with increasing F.I. which intersects a trend of decreasing P_2O_5 content extending from the trachyandesites (F.I. = 42.5) through the tristanites to the more evolved rocks. The stage at which depletion of P_2O_5 becomes apparent (F.I. = 42 to 50) does not coincide with the first appearance of apatite as a phenocryst phase (F.I. ~53). Furthermore, continued depletion of P_2O_5 from the more evolved mafic trachytes (F.I. ~87, P_2O_5 = 0.13 wt. percent) to the alkali rhyolites and comendites (P_2O_5 < 0.01 wt. percent) cannot be correlated with the occurrence of apatite as a phenocryst phase in these trachytes.

The trend of TiO_2 with F.I. bears some similarity to that of P_2O_5. There is a slight increase in TiO_2 up to the stage at which the Fe-Ti oxides appear as phenocrysts (F.I. ~45 to 50), after which it becomes gradually depleted. In contrast to the behaviour of P_2O_5 in the rhyolitic rocks, the TiO_2 content of these rocks does not continue to decrease as a result of the absence of phenocrystal Fe-Ti oxides.

The Mn contents of the Nandewar volcanics remain essentially constant up to the peralkaline trachyte stage (F.I. ~88 to 90), after which Mn is then rapidly depleted, particularly in the alkali rhyolites. Sparse microphenocrysts of titanomagnetite and ferrohedenbergite are the only Mn-bearing phases in these rocks which might have been fractionated to account for Mn depletion.

Trace Element Variation

The variation of a number of trace elements (Table 5.2) and several important trace element ratios with Fractionation Index, is displayed in Figs 5.7 to 5.12.

Transition Elements

Cr and Ni are depleted at a very early stage in the series. The transition from the least evolved (F.I. ~32) to the most evolved (F.I. ~56)

TABLE 5.2

Trace Elements (μg/g)

	Hawaiites and Trachyandesites																Monzonite	
Rock Number	49000	49001	49002	49002G	49003	49004	49005	49008	49007	49009	49010[1]	49010G	49011	49012	49013	49018	49070	49070Sch
Li	8	5	6	6	7	9	6	6	6	6	7	6	7	11	10	7	13	8
Sc	-	20	-	18	-	-	-	15	-	-	-	37	-	12	-	-	-	-
V	205	183	207	315	185	195	150	148	113	140	117	129	118	120	125	70	44	4
Cr	176	277	141	228	231	84	85	106	73	95	10	9	n.d.	1	n.d.	2	2	7
Ni	120	169	105	112	126	63	59	68	38	63	34	46	2	n.d.	n.d.	n.d.	4	n.d.
Cu	50	48	43	48	48	34	33	30	28	30	19	30	17	18	18	10	14	8
Zn	95	105	100	145	110	100	130	130	108	125	95	145	135	130	127	175	135	55
Rb	26	19	28	32	18	28	41	40	29	36	30	46	45	49	48	63	64	117
Sr	659	618	766	668	697	781	814	831	774	875	916	654	616	755	756	653	483	246
Y	20	23	23	24	30	28	36	39	30	40	27	27	43	37	42	31	49	33
Zr	178	155	196	215	146	198	259	278	172	273	180	246	281	293	298	394	270	561
Nb	44	46	48	51	38	49	61	60	48	63	44	54	70	72	74	62	67	40
Cs	-	n.d.	-	-	-	-	-	0.85	-	-	-	-	-	n.d.	-	-	-	-
Ba	297	267	331	394	226	333	602	676	1909	759	428	625	578	591	596	1050	1656	946
La	33	29	36	46	32	37	59	58	34	59	33	47	62	55	58	61	61	43
Ce	63	62	62	86	58	57	106	110	70	106	69	83	97	117	102	111	107	77
Nd	32	31	33	40	30	37	63	60	42	64	32	42	56	60	54	70	59	34
Sm	-	6.5	-	9.0	-	-	-	12.3	-	-	-	11.0	-	11.8	-	-	-	-
Eu	-	2.0	-	3.0	-	-	-	3.7	-	-	-	4.1	-	3.3	-	-	-	-
Tb	-	0.72	-	1.0	-	-	-	1.1	-	-	-	1.3	-	1.3	-	-	-	-
Dy	-	-	-	6.4	-	-	-	8.7	-	-	-	8.0	-	-	-	-	-	-
Yb	-	1.5	-	2.3	-	-	-	2.5	-	-	-	2.6	-	2.6	-	-	-	-
Lu	-	0.31	-	0.33	-	-	-	0.36	-	-	-	0.38	-	0.36	-	-	-	-
Hf	-	3.2	-	-	-	-	-	6.6	-	-	-	-	-	5.7	-	-	-	-
Ta	-	2.6	-	-	-	-	-	4.4	-	-	-	-	-	3.9	-	-	-	-
Pb	4	5	5	7	5	5	6	9	9	9	7	9	13	6	18	10	14	13
Th	2	2.8	2	3.1	n.d.	n.d.	n.d.	4.7	n.d.	n.d.	n.d.	2	5	5.5	3	8	4	11
U	-	1.3	-	-	-	-	-	1.3	-	-	-	-	-	1.0	-	-	-	-
K/Rb	457	459	451	415	457	457	431	457	512	496	454	403	424	422	427	465	397	353
Ba/Rb	11.4	14.1	11.8	12.3	12.6	11.9	14.7	16.9	65.8	21.1	14.3	13.6	12.8	12.1	12.4	16.7	25.9	8.1
Th/U	-	2.2	-	-	-	-	-	3.7	-	-	-	-	-	5.3	-	-	-	-
La/Yb	-	19.7	-	20.0	-	-	-	23.0	-	-	-	-	-	21.6	-	-	-	-
Sm/Eu	-	3.2	-	3.0	-	-	-	3.3	-	-	-	-	-	3.6	-	-	-	-

1 - sample contains approximately 20 percent plagioclase phenocrysts

G - groundmass separate, Sch. - Schlieren

\- not determined, n.d. - not detected

TABLE 5.2 (continued)

Trace Elements (µg/g)

	Tristanites										Mafic Trachytes								
Rock Number	49075	49076	49077	49078	49079	49080	49074	49081	49082	49097	49083	49084	49085	49086	49087	49088	49090	49089	49091
Li	9	8	7	11	11	8	8	12	11	11	7	6	13	15	7	14	16	16	7
Sc	-	13	-	-	-	-	10	-	-	-	14	12	-	-	-	9	-	-	-
V	35	31	37	34	20	26	17	18	31	25	10	16	3	9	5	8	2	3	9
Cr	2	2	n.d.	n.d.	n.d.	4	6	8	6	3	n.d.	3	n.d.	n.d.	n.d.	2	3	n.d.	4
Ni	n.d.	n.d.	n.d.	2	10	2	11	12	5	12	n.d.	n.d.	9	4	8	8	2	5	n.d.
Cu	11	11	11	11	10	10	7	12	11	10	9	10	7	8	11	8	5	8	4
Zn	125	135	135	135	145	125	115	125	130	125	130	125	145	145	175	160	125	145	145
Rb	57	64	60	59	75	61	54	94	82	91	66	81	89	94	105	93	105	113	78
Sr	583	516	525	534	607	569	399	487	274	266	102	189	41	39	29	42	8	24	89
Y	42	44	31	57	33	41	22	29	48	40	38	36	54	78	41	91	35	28	29
Zr	338	355	358	364	419	349	308	518	501	565	395	367	626	565	927	585	511	723	482
Nb	81	85	87	85	69	79	38	75	112	95	71	63	80	96	99	95	114	91	81
Cs	-	0.40	-	-	-	-	1.06	-	-	-	n.d.	0.92	-	-	-	n.d.	-	-	-
Ba	863	865	864	899	987	913	879	884	494	541	802	953	2119	2151	144	2213	96	1153	667
La	61	59	64	87	49	54	49	50	75	70	56	49	64	116	102	94	48	39	47
Ce	97	118	104	110	103	91	99	104	115	126	105	93	119	172	189	162	78	101	76
Nd	47	58	56	77	65	47	50	57	55	73	49	30	67	86	91	68	32	51	36
Sm	-	12.8	-	-	-	-	9.7	-	-	-	8.5	5.9	-	-	-	7.6	-	-	-
Eu	-	3.8	-	-	-	-	3.5	-	-	-	3.3	2.7	-	-	-	3.8	-	-	-
Tb	-	1.2	-	-	-	-	0.82	-	-	-	1.1	0.96	-	-	-	2.0	-	-	-
Yb	-	3.1	-	-	-	-	2.0	-	-	-	3.0	2.7	-	-	-	7.6	-	-	-
Lu	-	0.48	-	-	-	-	0.33	-	-	-	0.43	0.41	-	-	-	1.3	-	-	-
Hf	-	6.7	-	-	-	-	4.9	-	-	-	6.3	6.3	-	-	-	12.6	-	-	-
Ta	-	4.8	-	-	-	-	2.7	-	-	-	4.1	3.9	-	-	-	6.5	-	-	-
Pb	9	12	10	9	11	7	7	11	10	10	9	11	15	14	14	13	13	13	10
Th	5	7.2	6	6	6	4	4.3	9	8	10	6.9	7.8	9	9	15	10.6	8	11	8
U	-	2.3	-	-	-	-	1.5	-	-	-	2.1	2.3	-	-	-	2.5	-	-	-
K/Rb	447	416	439	450	390	442	730	360	448	422	687	570	488	454	440	462	443	395	651
Ba/Rb	15.1	13.5	14.4	15.2	13.2	15.0	16.3	9.4	6.0	6.0	12.2	11.8	23.8	22.9	1.4	23.8	0.9	10.2	8.6
Th/U	-	3.1	-	-	-	-	2.9	-	-	-	3.3	3.4	-	-	-	4.3	-	-	-
La/Yb	-	19.0	-	-	-	-	24.0	-	-	-	18.5	18.5	-	-	-	12.4	-	-	-
Sm/Eu	-	3.4	-	-	-	-	2.8	-	-	-	2.6	2.2	-	-	-	2.0	-	-	-

- not determined

n.d. - not detected

TABLE 5.2 (continued)

Trace Elements (μg/g)

	Peralkaline Trachytes												Comendites					
Rock Number	49102	49098	49098G	49103	49099	49100	49104	49107	49101	49105	49106	49108	49162[†]	49160	49161	49163	49164	49165
Li	18	18	20	19	23	25	18	17	26	23	17	31	4	19	25	53	20	6
Sc	-	-	-	-	-	-	-	-	-	-	-	-	2.9	-	3.0	0.37	0.23	-
V	4	2	n.d.	3	n.d.	4	11	2	n.d.	n.d.	n.d.	n.d.	3	2	n.d.	n.d.	4	3
Cr	n.d.	2	2	n.d.	n.d.	2	3	3	2	n.d.	n.d.	n.d.	n.d.	3	3	2	n.d.	2
Ni	3	6	6	6	6	8	2	2	n.d.	6	6	11	7	6	n.d.	12	15	7
Cu	5	7	15	9	9	8	4	3	8	8	7	7	4	8	7	7	8	2
Zn	130	150	200	150	190	170	135	125	130	210	192	145	160	148	133	260	145	22
Rb	113	113	110	124	132	140	133	117	156	132	131	178	143	135	141	294	255	194
Sr	23	1	6	9	5	n.d.	3	8	n.d.	n.d.	5	4	6	6	1	2	5	n.d.
Y	62	64	62	44	29	90	36	46	35	45	43	99	76	64	25	130	207	86
Zr	639	628	719	838	864	805	704	734	833	932	884	1419	696	623	693	1245	844	647
Nb	110	127	119	105	133	163	126	127	179	146	133	266	135	124	132	282	289	148
Cs	-	-	-	-	-	-	-	-	-	-	-	-	0.87	-	0.41	1.42	0.73	-
Ba	1165	n.d.	10	496	14	n.d.	81	321	n.d.	n.d.	17	20	44	8	n.d.	4	10	12
La	105	91	76	70	37	160	79	58	105	87	61	143	96	73	28	48	754	79
Ce	156	143	136	137	95	145	124	112	172	148	120	232	147	132	144	103	707	144
Nd	76	43	60	73	55	121	55	46	76	80	63	109	74	65	23	59	371	68
Sm	-	-	13.0	-	-	-	-	-	-	-	-	-	17.8	-	5.2	14.5	78.0	-
Eu	-	-	1.1	-	-	-	-	-	-	-	-	-	0.78	-	0.43	0.18	0.97	-
Tb	-	-	1.5	-	-	-	-	-	-	-	-	-	0.97	-	0.31	3.7	6.2	-
Dy	-	-	11.0	-	-	-	-	-	-	-	-	-	-	-	-	-	23.0	-
Yb	-	-	5.6	-	-	-	-	-	-	-	-	-	6.0	-	3.1	9.7	11.0	-
Lu	-	-	0.77	-	-	-	-	-	-	-	-	-	0.82	-	0.52	1.56	1.12	-
Hf	-	-	-	-	-	-	-	-	-	-	-	-	11.9	-	14.2	29.1	21.0	-
Ta	-	-	-	-	-	-	-	-	-	-	-	-	7.3	-	7.4	18.8	19.0	-
Pb	15	12	15	18	15	16	15	18	19	11	15	20	21	17	23	17	28	29
Th	12	11	12	13	13	18	11	12	18	16	16	22	17.3	14	16.6	34.7	32.0	19
U	-	-	-	-	-	-	-	-	-	-	-	-	3.5	-	4.1	5.9	18.0	-
K/Rb	385	394	389	370	330	304	341	390	268	336	352	268	298	319	310	123	157	229
Ba/Rb	10.3	0.03	0.09	4.0	0.11	0.02	0.61	2.7	0.00	0.02	0.13	0.11	0.31	0.06	0.01	0.02	0.04	0.06
Th/U	-	-	-	-	-	-	-	-	-	-	-	-	5.0	-	4.0	5.8	1.8	-
La/Yb	-	-	13.6	-	-	-	-	-	-	-	-	-	16.0	-	9.0	5.0	68.6	-
Sm/Eu	-	-	11.8	-	-	-	-	-	-	-	-	-	22.8	-	12.1	80.6	80.4	-

- not determined

n.d. - not detected

[†] - denotes member of the older alkali group

TABLE 5.2 (continued)

Trace Elements (μg/g)

	Alkali Rhyolites												
Rock Number	49119†	49120†	49122†	49121†	49123	49124	49127	49125	49131	49126	49128	49129	49130
Li	6	8	5	13	7	27	8	6	4	14	17	18	11
Sc	-	-	-	4.6	-	-	-	-	-	-	-	-	1.2
V	3	3	n.d.	3	2	2	3	2	2	2	2	2	n.d.
Cr	2	n.d.	2	2	n.d.	n.d.	2	n.d.	n.d.	n.d.	2	n.d.	2
Ni	11	6	6	4	6	5	5	4	5	4	9	8	5
Cu	9	6	8	7	8	7	2	3	3	9	6	4	2
Zn	110	170	170	135	145	225	40	93	33	80	140	75	62
Rb	121	142	151	130	144	118	121	129	135	148	195	187	190
Sr	42	8	10	8	3	3	4	6	5	38	3	n.d.	n.d.
Y	42	70	70	63	49	56	72	48	51	42	87	95	73
Zr	631	819	680	785	736	1285	702	672	716	815	1019	833	870
Nb	102	157	138	132	103	137	159	101	106	112	166	151	163
Cs	-	-	-	0.60	-	-	-	-	-	-	-	-	2.06
Ba	567	185	165	298	28	9	66	43	32	258	11	7	4
La	51	91	66	92	48	87	108	80	73	54	95	142	41
Ce	118	151	121	154	111	121	180	171	140	117	158	214	72
Nd	56	68	60	72	59	88	85	97	78	58	87	109	27
Sm	-	-	-	14.5	-	-	-	-	-	-	-	-	4.4
Eu	-	-	-	1.2	-	-	-	-	-	-	-	-	0.30
Tb	-	-	-	0.82	-	-	-	-	-	-	-	-	0.65
Yb	-	-	-	5.5	-	-	-	-	-	-	-	-	6.4
Lu	-	-	-	0.82	-	-	-	-	-	-	-	-	0.93
Hf	-	-	-	11.9	-	-	-	-	-	-	-	-	16.5
Ta	-	-	-	7.1	-	-	-	-	-	-	-	-	9.5
Pb	18	17	23	17	16	20	14	15	12	16	15	21	29
Th	13	16	15	16.1	15	20	15	13	14	16	22	21	19.4
U	-	-	-	4.3	-	-	-	-	-	-	-	-	7.5
K/Rb	343	317	289	346	310	372	349	360	343	330	228	230	223
Ba/Rb	4.7	1.3	1.1	2.3	0.19	0.08	0.55	0.33	0.24	1.7	0.06	0.04	0.02
Th/U	-	-	-	3.8	-	-	-	-	-	-	-	-	2.6
La/Yb	-	-	-	16.7	-	-	-	-	-	-	-	-	6.5
Sm/Eu	-	-	-	12.1	-	-	-	-	-	-	-	-	14.3

- not determined

n.d. - not detected

† - denotes members of the older alkali rhyolite group

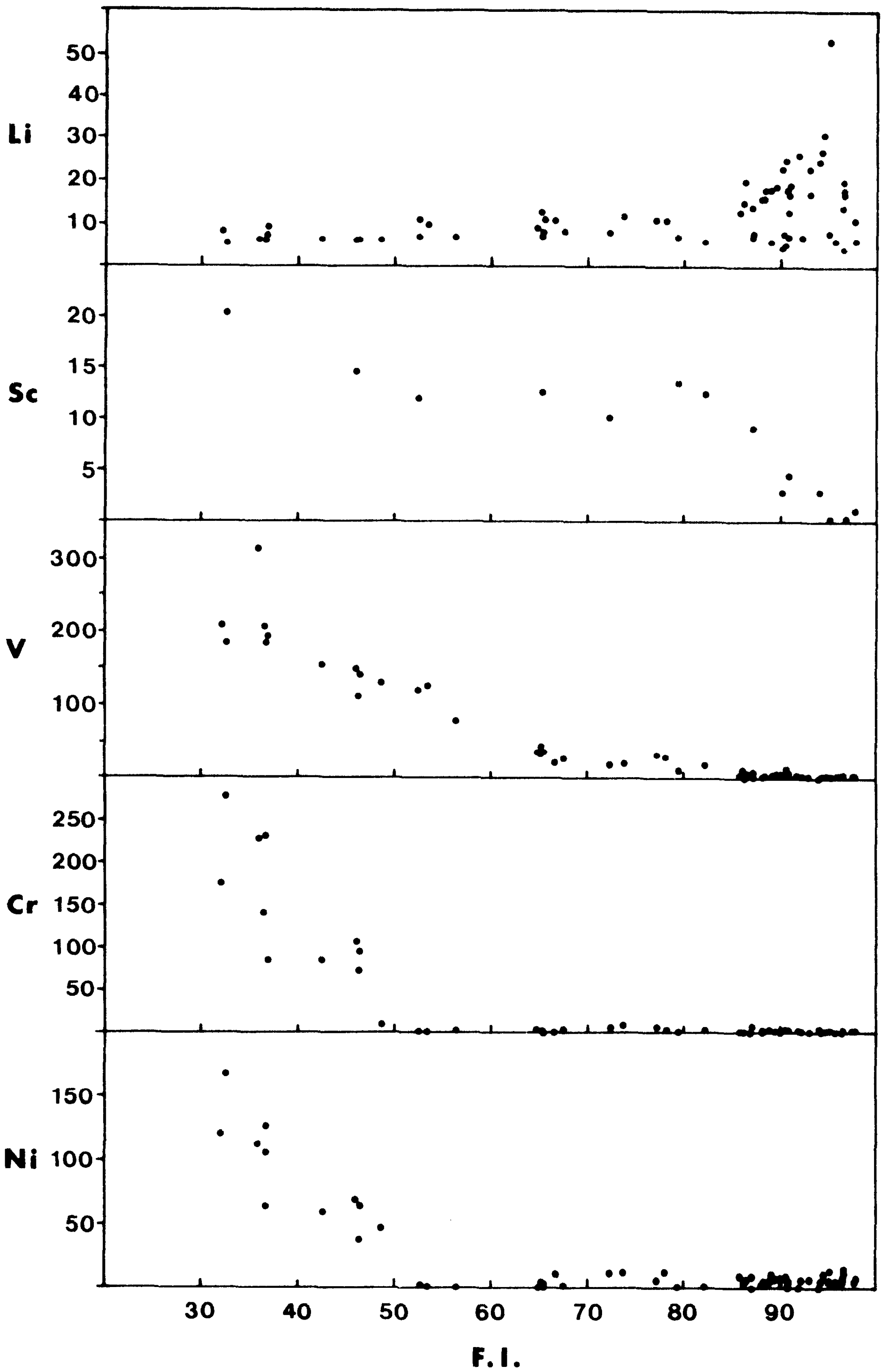


Fig. 5.7: Variation of trace elements (μg/g) as functions of Fractionation Index (F.I.) in the Nandewar series.

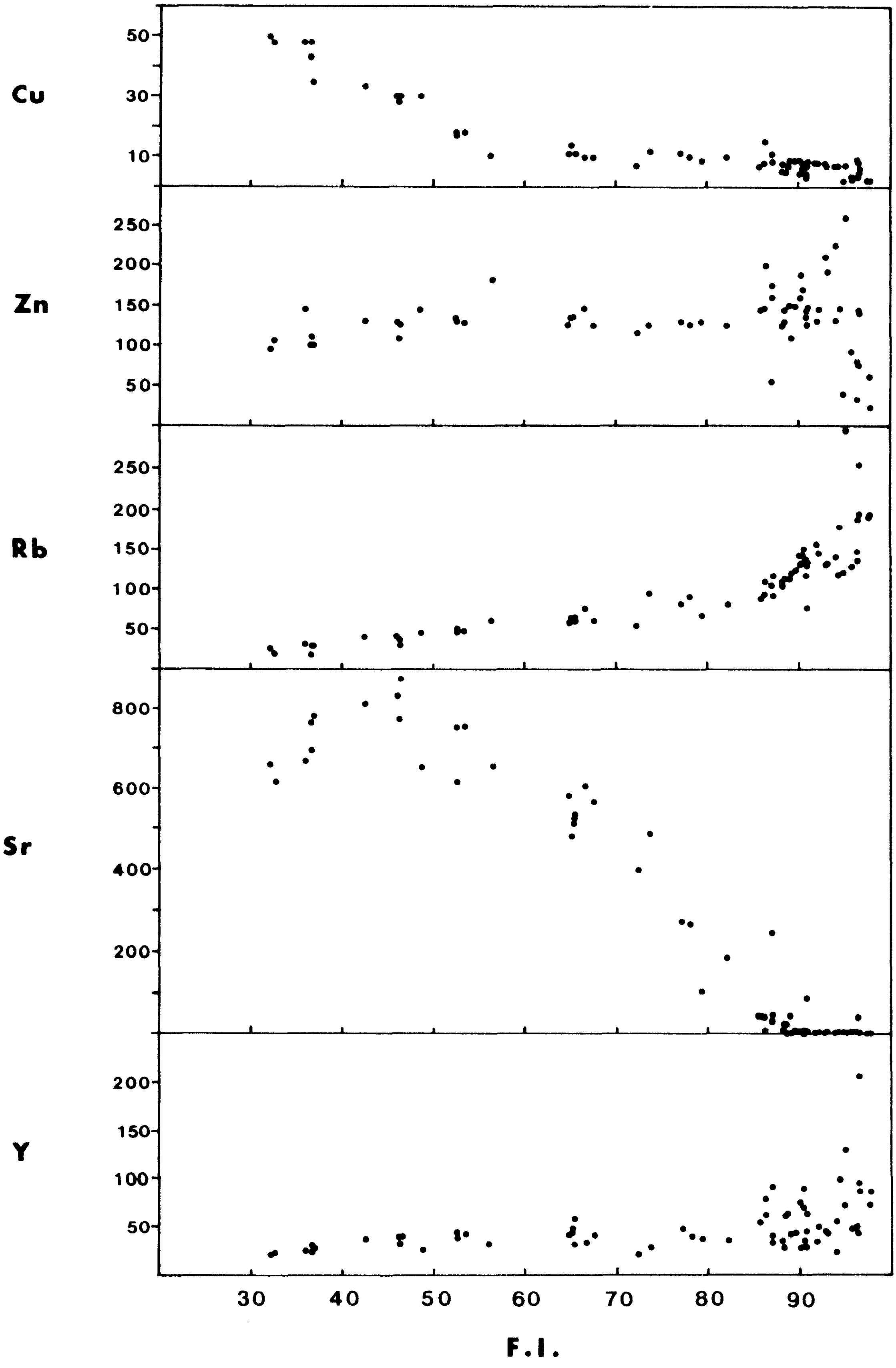


Fig. 5.8: Variation of trace elements (μg/g) as functions of Fractionation Index (F.I.) in the Nandewar series.

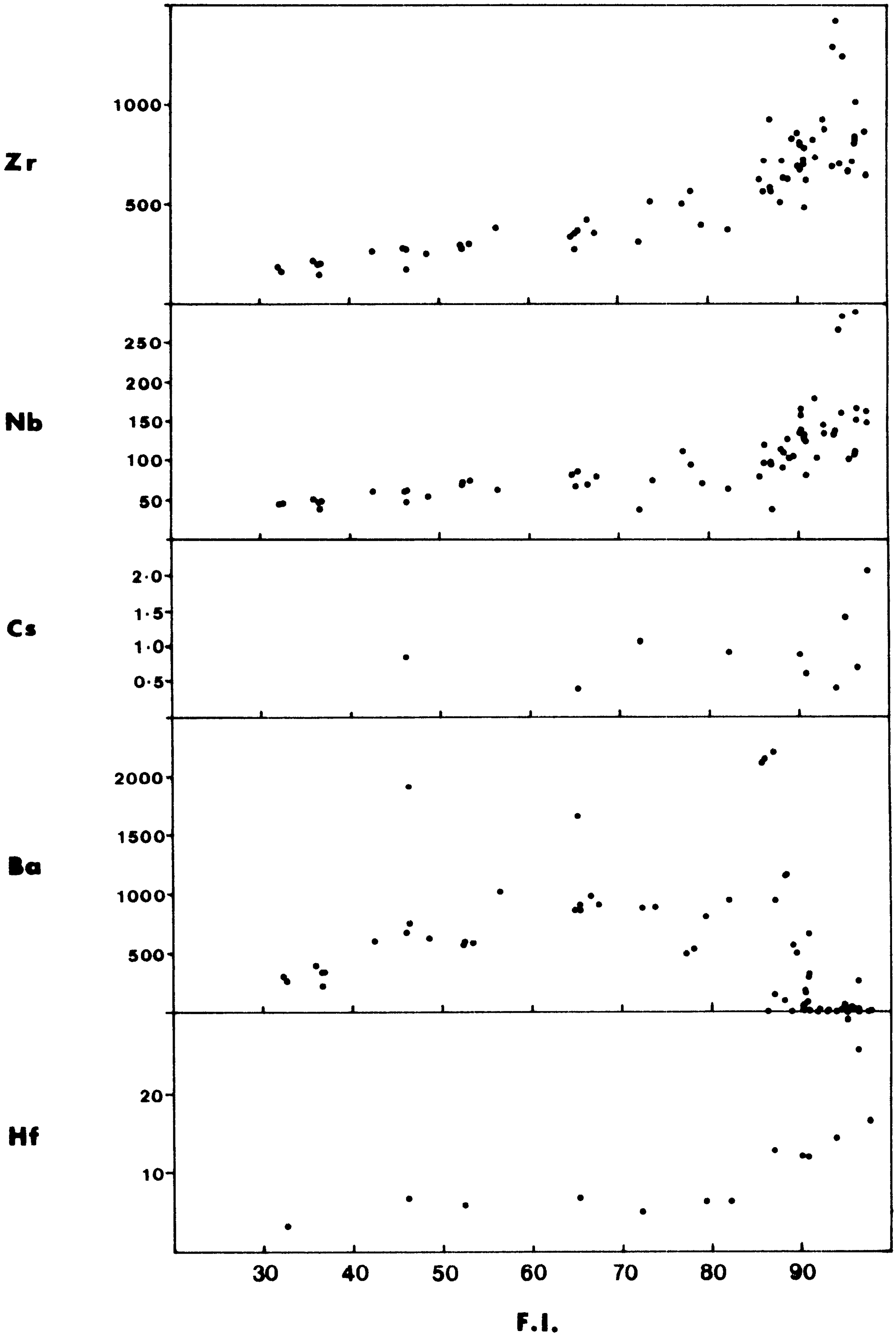


Fig. 5.9: Variation of trace elements (μg/g) as functions of Fractionation Index (F.I.) in the Nandewar series.

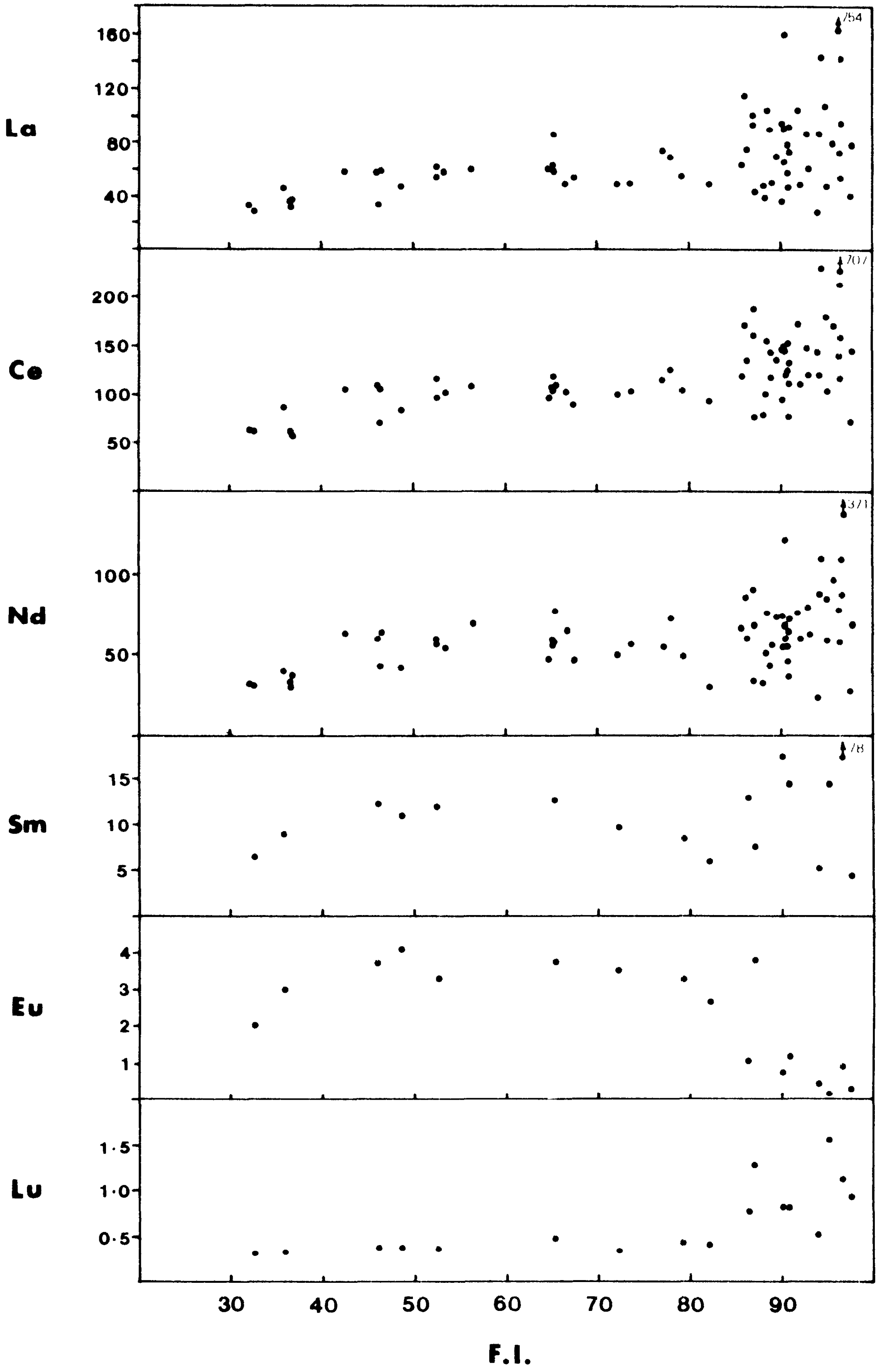


Fig. 5.10: Variation of trace elements (μg/g) as functions of Fractionation Index (F.I.) in the Nandewar series.

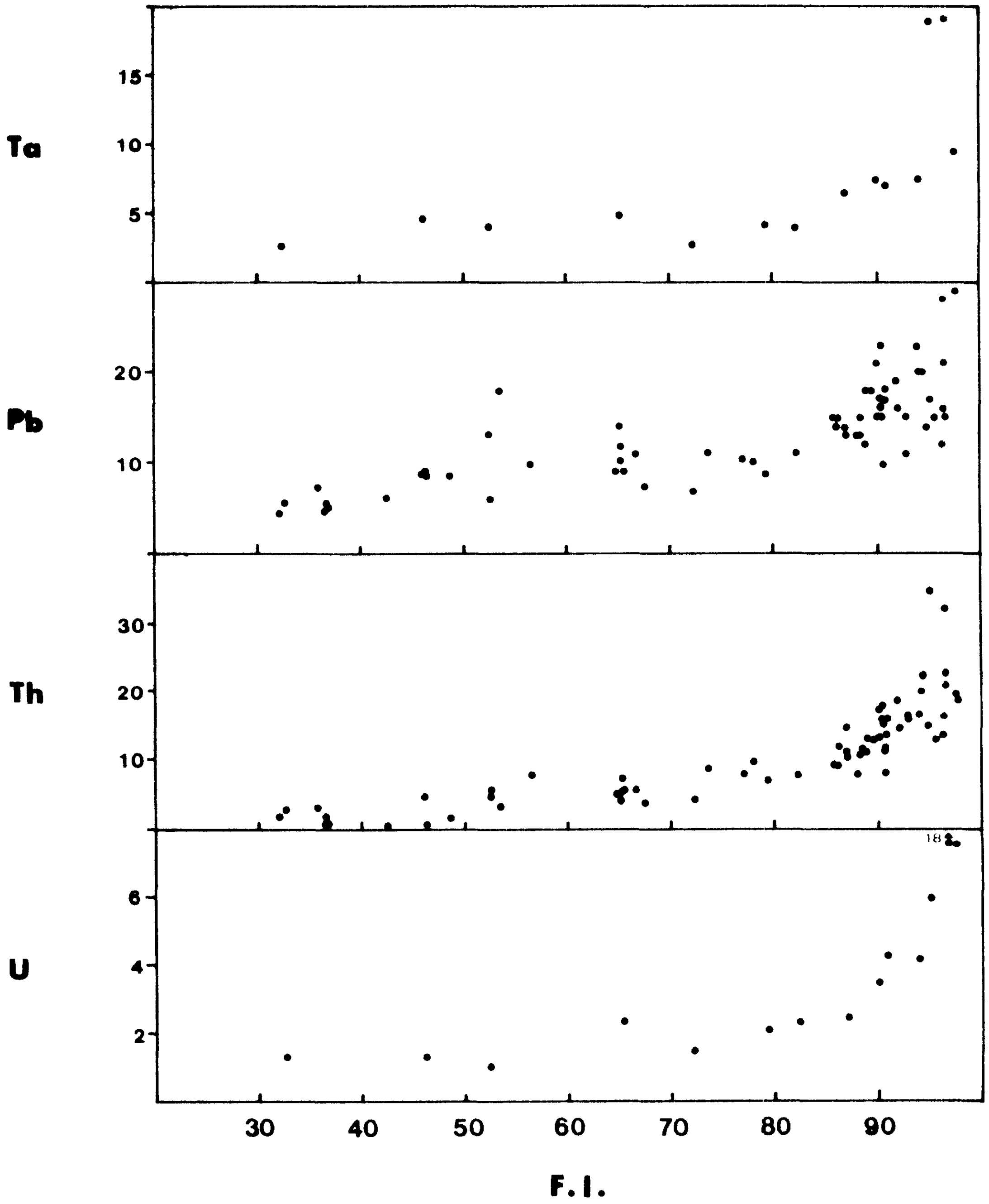


Fig. 5.11: Variation of trace elements (μg/g) as functions of Fractionation Index (F.I.) in the Nandewar series.

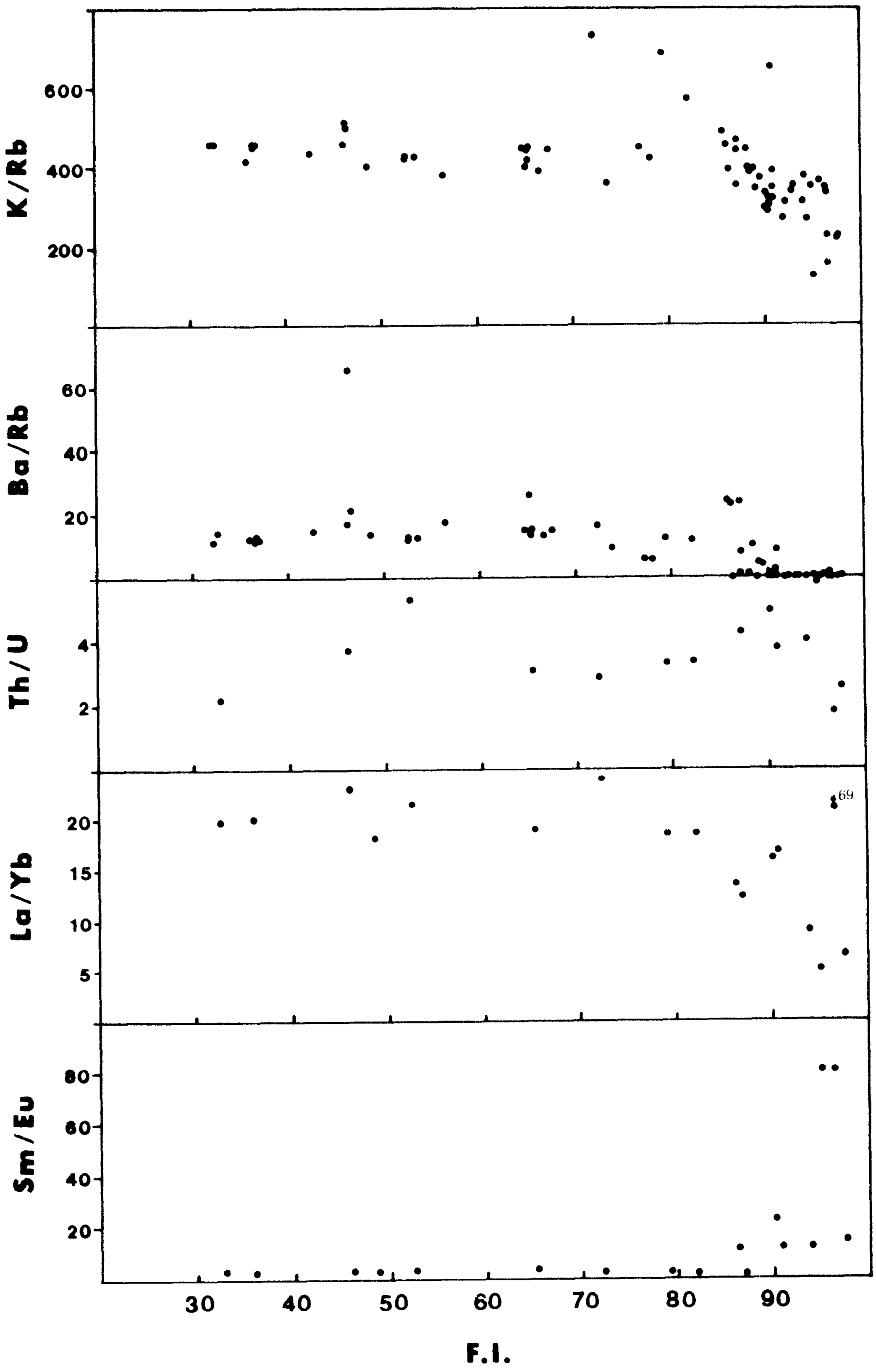


Fig. 5.12: Variation of several trace element ratios as functions of Fractionation Index (F.I.) in the Nandewar series.

hawaiites and trachyandesites is coupled with a decrease in Cr and Ni contents from greater than 250 μg/g and 150 μg/g respectively to less than 5 μg/g for both elements. Depletion of V follows a similar trend, although it occurs more gradually.

The concentration of Ni^{2+}, Cr^{3+} and V^{3+} into early crystallized phases is due to the high crystal field stabilization energies received by these transition metal ions in octahedral coordination in ferromagnesian silicate and oxide minerals relative to the melt (Burns and Fyfe, 1967; Seward, 1971; Dale and Henderson 1972). Accordingly, the early depletion of Ni and Cr is consistent with the occurrence of olivine (Ni) and Ca-rich pyroxene (Cr, Ni) as common phenocryst species, particularly in the more mafic trachyandesites and hawaiites.

The early depletion of Ni is followed by an unexpected increase in the Ni contents of several comendites. These higher Ni values (up to 15 μg/g) are not considered to be the result of contamination or analytical inaccuracy (<u>see</u> Appendix 1 for a comparison of values obtained on concurrently analyzed international standards with recommended values). A comparable trend of late-stage enrichment of Ni has also been noted in comendites and rhyolites from the Paresis volcanic complex (Siedner, 1965), the Comboyne province (Knutson, 1975), the Tweed Shield volcano N.S.W. (Duggan, 1974) and it is also a feature of the Skaergaard intrusion (Wager and Mitchell 1951), where Ni levels already depleted to < 1 μg/g in the intermediate stages of differentiation increased to 8 μg/g in the late-stage granophyres.

Sc exhibits mild depletion in the trachyandesites (F.I. = 32 to 45) after which it remains relatively constant up to F.I. ~80, and then is strongly depleted in the peralkaline trachytes and rhyolites. Concentration of Sc in early-formed Ca-rich pyroxenes of the Skaergaard intrusion was noted by Wager and Mitchell (1951), and partition coefficients ($D_{Sc}^{Cpx/liq}$ = 2.4 to 3.2) based on Ca-rich pyroxene phenocryst/groundmass data from a variety of basaltic rocks (Dale and Henderson 1972) indicate a similar distribution pattern in mafic volcanic rocks. Partition coefficients for Sc derived from Ca-rich pyroxene/groundmass compositions in the Nandewar trachyandesites (<u>see</u> Table 7.4) are comparable to those of Dale and Henderson (1972) and provide constraints on the quantity of Ca-rich pyroxene which may have been fractionated over a substantial compositional range (F.I. = 45 to 80).

A study of synthetic pyroxenes (Frondel, 1970) established that Sc^{3+} enters the 6-coordinated M1 site, and, in natural pyroxenes shares this site with Fe^{3+}, Cr^{3+}, V^{3+} and Al^{3+} as well as Mg^{2+} and Fe^{2+}. Frondel argued that Sc^{3+} dominantly replaces Fe^{3+} in octahedral sites of silicates. Although Sc shows fundamental similarities in its outer electron structure to the lanthanide elements, it apparently exhibits no coherence with these elements or with Fe^{2+} and Mg^{2+} (Norman and Haskin, 1968).

Cu decreases quite rapidly in the hawaiites and trachyandesites (F.I. = 32 to 53) and very slowly in the more evolved rocks. Cu is probably present as the monovalent ion under magmatic conditions where magnetite is stable (Wedepohl, 1974) and because of its zero octahedral site preference energy (Seward, 1971) is not strongly partitioned into any particular lattice sites. Titanomagnetite is the only phenocryst phase in the trachyandesites which has a solid-liquid partition coefficient ($D_{Cu}^{Sol/liq}$) greater than unity (see Table 7.4). Because sulphides of Cu were not detected either optically or by probing, the observed depletion in Cu can only be explained (in terms of a fractionation model) by removal of titanomagnetite at appropriate stages.

The behaviour of Zn is variable, exhibiting a slight increase up to the peralkaline trachytes (F.I. ~88) after which there is considerable scattering to higher and lower values. The highest concentrations of Zn are found in the intrusive comendites, whereas the vesicular alkali rhyolites are comparatively depleted. Zn^{2+} (like Cu^{+}) has zero octahedral site preference energy and is therefore more likely to reside in tetrahedral and octahedral sites in the melt than Cr and Ni (Burns, 1973). Partition coefficients for Zn between olivine/groundmass and titanomagnetite/groundmass in the Nandewar trachyandesites are both greater than unity (see Table 7.4) and indicate a tendency for its preferential incorporation in these phases. The increasing concentration of Zn throughout most of the series provides yet another useful constraint on the proportions and amounts of olivine and titanomagnetite which could have been fractionated to produce more evolved members of the series.

Alkali and Alkaline Earth Elements

Li increases gradually throughout the series up to the peralkaline trachytes (F.I. ~88), after which it exhibits trends of enrichment and depletion. Li is typically enriched in the intrusive comendites and depleted in the vesicular alkali rhyolites. Limited substitution of Li for Mg in octahedral sites of silicates may occur because of their similar ionic radii (Taylor, 1965).

A systematic increase of Rb concentrations with increasing F.I., as is evident for the Nandewar series (Fig. 5.8), is generally considered to reflect the strong tendency of Rb to concentrate in residual liquids during fractional crystallization. Although it is similar in size and chemical character to K, the slightly larger ionic radius of Rb evidently restricts its entry into K lattice positions (Taylor, 1965) in sanidine and anorthoclase.

The very low concentrations of Cs in the Nandewar rocks makes evaluation of variation trends difficult. Cs concentrations appear to remain relatively constant over the compositional range trachyandesite to mafic trachyte, followed by trends both of enrichment and depletion. However, these trends are not restricted to particular rock types in contrast to the behaviour of Li and Zn. Unfortunately, the variability of the data and the tendency for much of the Cs to be lost during crystallization of peralkaline silicic magmas (Baker and Henage 1977), prevent rigorous evaluation of its behaviour during fractionation processes. However, the very large size of Cs^+ (25 percent greater than K^+) should prevent its substitution in early-formed K-rich minerals, resulting in its concentration in residual liquids (Taylor, 1965).

Sr exhibits a trend of enrichment (F.I. = 32 to 45) reaching a maximum (> 800 μg/g) in the trachyandesites, and then decreases gradually to very low levels (<5 μg/g) in the peralkaline trachytes and rhyolites. Strong partitioning of Sr into plagioclase phenocrysts relative to groundmass compositions ($D_{Sr}^{Plag/gdmss}$ = 2.3 to 3.7, Table 7.4) is typical for the trachyandesites, and the inflection in the curve of Sr versus F.I. (at F.I. = 45, Fig. 5.8) broadly coincides with the occurrence of plagioclase as the dominant phenocryst type.

With a few notable exceptions Ba increases steadily from the trachyandesites to the mafic trachytes (F.I. = 32 to 88), and then decreases very sharply in the peralkaline trachytes and rhyolites. The rapid depletion of Ba and consequently of the Ba/Rb ratio (Fig. 5.12) occurs at approximately the same stage at which alkali feldspar appears as a phenocryst phase. Ba is strongly partitioned into anorthoclase phenocrysts in the mafic trachytes ($D_{Ba}^{Kfsp/liq} > 5$, Table 7.4) which is consistent with the accepted behaviour of Ba involving substitution for K^+ in early-formed K-rich phases (Taylor, 1965).

Although Pb is not an alkali or alkaline earth element, its behaviour is very similar to that of Rb and Cs and hence will be discussed here. The concentration of Pb in the Nandewar rocks increases with increasing F.I. reaching a maximum (29 µg/g Pb) in several intrusive comendites. Pb^{2+} is generally considered to substitute for K^+ in alkali feldspars due to their similarity of ionic radius. However, if fractionation of anorthoclase was important in the development of the comendites $D_{Pb}^{Anor/liq}$ must have been less than unity.

'Residual' Elements

Elements that are generally assigned to this group include the group 4b and 5b transition elements Y, Zr, Nb, Hf and Ta, as well as the actinides U and Th. Their 'residual' behaviour, or the tendency to concentrate in residual liquids, results from their high ionic charges and a tendency to form complexes in the liquid rather than enter crystal lattices (Ringwood, 1955).

These elements all increase in concentration with increasing F.I. (Figs 5.8,5.9 and 5.11) although there is considerable variation in the abundance of Y, Zr, and to a lesser extent Nb and Th, in the peralkaline trachytes, comendites and alkali rhyolites. In common with the behaviour of Li and Zn the comendites are typically enriched in the 'residual' elements relative to the alkali rhyolites of comparable F.I.

The Th/U ratio varies markedly with F.I. (Fig. 5.12) exhibiting maximum values (5.3 to 5.8, cf. Table 5.2) in trachyandesite 49012 and comendite 49163, respectively. Another comendite (49164) of similar F.I. has the lowest value of Th/U (1.8) principally resulting from a considerably higher U concentration (18 µg/g compared to 6 µg/g), while the Th levels are comparable.

Although increasing Th/U ratios in the more evolved members of rock series has been claimed for several provinces (Rogers and Adams, 1969), such a simple relationship is not apparent for the Nandewar volcanics.

Rare Earth Elements

Because of their tendency to behave as a coherent group, the rare earth elements (La to Lu) are a useful aid in interpretation of petrogenetic processes. There are, however, subtle differences in the behaviour of the light rare earth elements (LREE, La to Sm) and the heavy rare earth elements (HREE, Gd to Lu) resulting from a slight decrease in ionic radius with increasing atomic number and which is referred to as the 'lanthanide contraction'. Compared with other REE Eu often displays anomalous behaviour during differentiation because of its tendency to exist principally in the divalent state under relatively reducing magmatic conditions (Weill and Drake, 1973; Sun *et al.*, 1974; Drake, 1975).

REE abundances increase with increasing F.I. (Fig. 5.10) up to the tristanites (F.I. ~65) after which all except Lu exhibit a slight decrease to the peralkaline trachyte stage (F.I. ~88). Lu appears to increase slightly over this compositional range and then in common with the other REE exhibits trends of both enrichment and depletion in the rhyolitic rocks. Although not shown, the variation trends of Tb and Yb with F.I. for the series are very similar to those exhibited by the LREE. One intrusive comendite (49164) exhibits extreme enrichment in LREE with respect to the extrusive comendites and alkali rhyolites. However, the most obvious difference between the intrusive and extrusive rhyolitic rocks is the relative depletion of HREE in the latter.

The inflection points in all of the REE versus F.I. plots at F.I. ~65, broadly coincides with the first appearance of apatite as a phenocryst phase in the most evolved trachyandesites and tristanites. The REE are strongly partitioned into this phase as indicated by the high partition coefficients ($D_{REE}^{Ap/liq}$ = 4 to 11, see Table 7.4). The increase in concentration in the rhyolitic rocks exhibited by most of the REE also coincides quite closely with the disappearance of apatite as a phenocryst phase. Eu is the only REE which is consistently depleted in the most evolved rocks and this can be correlated with the appearance in these rocks of alkali feldspar as a phenocryst phase into which Eu is strongly partitioned ($D_{Eu}^{Kfsp/liq} = 1.5$) relative to the other REE ($D_{REE}^{Kfsp/liq} < 0.06$, see Table 7.4).

REE data for the Nandewar rocks were normalized to chondritic abundances using the values of Taylor and Gorton (1977) (i.e. concentration in the Leedey meteorite divided by 1.20), and plotted (Fig. 5.13) following the procedure of Coryell *et al.* (1963). Such plots are useful for indicating the extent of enrichment of the REE relative to chondritic abundances and for observing relative enrichment or depletion of LREE, HREE and Eu throughout a consanguinous rock series.

The Nandewar hawaiites, trachyandesites and tristanites typically have relatively flat, parallel chondrite-normalized REE patterns, although the groundmass fractions of two porphyritic trachyandesites (i.e. 49002 and 49010, Table 5.2) exhibit slight positive Eu anomalies. Plots of several samples also indicate a slight Tb depletion which may be due to analytical inaccuracy. However, concomitantly determined values on two international standard rocks are in close agreement with recommended values (see Appendix I), suggesting that these fluctuations are real.

Over the compositional range hawaiite to tristanite the total REE concentrations are considerably enriched (100 to 190 times chondritic abundances for La) with little or no change in the ratio of LREE to HREE as depicted in Fig. 5.12 by the constant La/Yb ratios.

The mafic trachytes (Table 5.2, Nos. 49083 and 49084) and a monzonite inclusion from an alkali rhyolite (Table 5.2, No. 49074) are characterized by slight positive Eu anomalies. Total REE abundances are variable with respect to the trachyandesites and tristanites. Two of the mafic trachytes (49083 and 49084, Table 5.2) have enrichment factors significantly less than 3 of the 6 analyzed trachyandesites and tristanites (i.e. 49008, 49012 and 49076, Table 5.2) at least for the LREE, whereas the remaining mafic trachyte (49088) and a groundmass separate from peralkaline trachyte 49098 both exhibit considerable enrichment in all REE relative to the less evolved rock types. The first evidence for the relative depletion of Eu is apparent in the peralkaline trachyte groundmass (49098G).

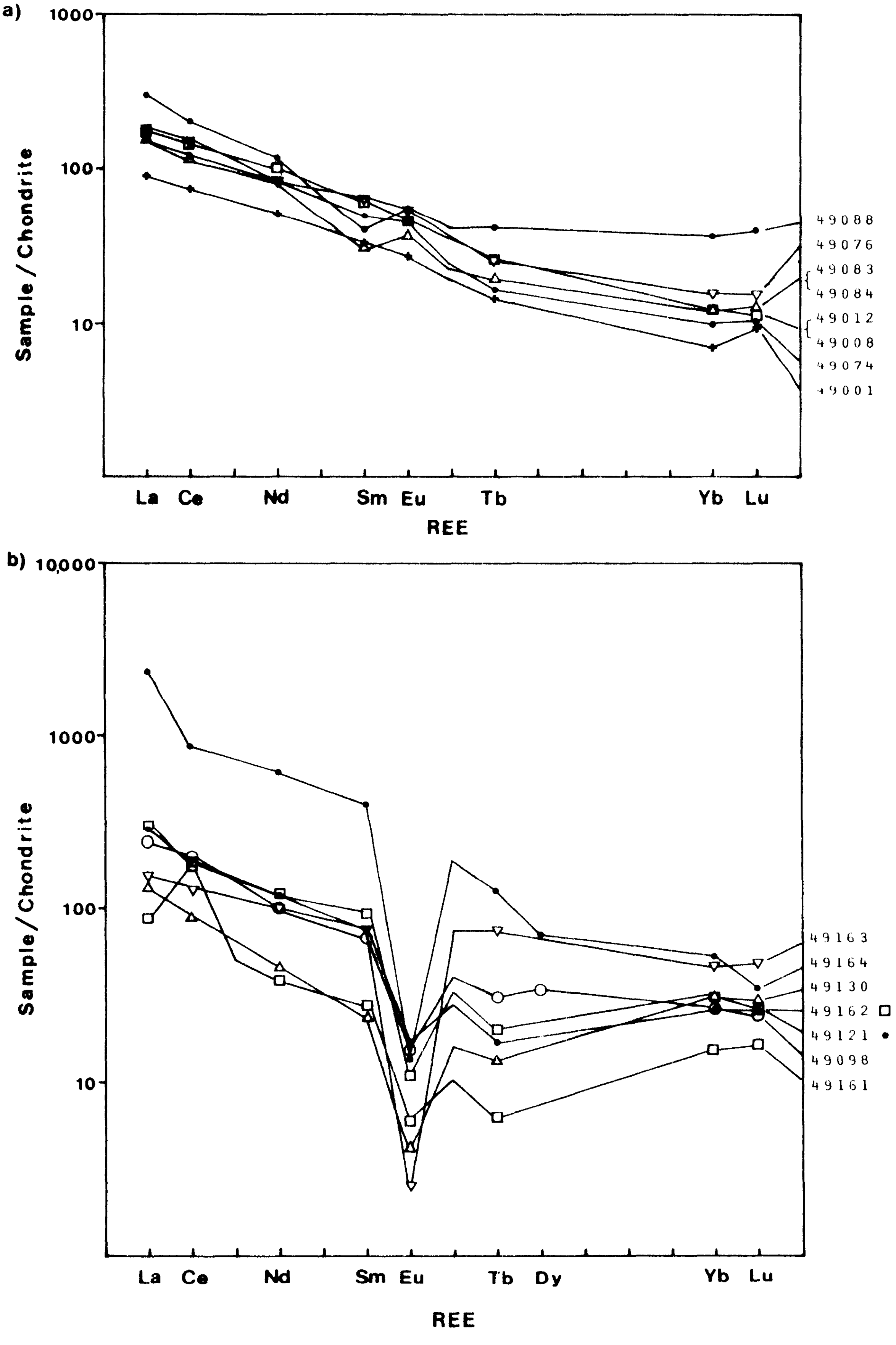


Fig. 5.13: Chondrite-normalized REE plots for

a) hawaiites, trachyandesites, tristanite and

b) mafic and peralkaline trachytes, alkali rhyolites and comendites.

Chondrite-normalized plots of the comendites and alkali rhyolites reflect the varied behaviour of the REE in these rocks. Most of the rhyolitic rocks are enriched in HREE with respect to less evolved rock types, whereas enrichment in LREE is much more variable. Several comendites (e.g. 49164) and alkali rhyolites (e.g. 49129) show relatively strong enrichment of LREE while others (e.g. 49130 and 49161) are more depleted in LREE than several of the trachyandesites. One consistent feature of the chondrite-normalized plots for the rhyolitic rocks is the presence of distinctive negative Eu anomalies or coupled depletion of Eu and HREE. The progressive relative depletion of Eu in the transition from the peralkaline trachytes to the comendites is reflected in the Sm/Eu ratios which increase sharply in the F.I. range 88 to 96 (Fig. 5.12).

A unique feature of the chondrite-normalized plot of comendite 49161 is the presence of a significant positive Ce anomaly. It is most unlikely that this anomaly is a result of analytical error since there was close agreement between La, Ce and Nd values determined by XRF and INAA techniques. Anomalous behaviour of Ce (indicated by negative Ce anomalies) has been noted in calc-alkaline rocks from New Guinea (Heming and Rankin 1979) and has been attributed to selective fractionation of Ce following oxidation of Ce^{3+} to Ce^{4+} during specific magmatic processes (Haskin *et al.*, 1968). However, experimental studies on synthetic Ca-Mg-Al silicate glasses with various admixtures of Fe_2O_3 and CeO_2 (Schreiber *et al.*, 1980), showed that Ce^{4+} is stoichiometrically reduced by Fe^{2+} in the melt to produce Fe^{3+} and Ce^{3+}. Consequently, it seems that Ce anomalies cannot be ascribed to stabilization of Ce^{4+} in magmas and an alternative explanation is required.

ISOTOPIC DATA

Strontium Isotopes

Rb, Sr and Sr isotopic compositions of representative extrusive and intrusive members of the Nandewar suite are presented in Table 5.3. The Sr isotope data have been plotted on a conventional isochron diagram (Fig. 5.14) and have been analyzed using the regression method of McIntyre *et al.* (1966). The best fit regression for all points excluding the older alkali rhyolite (49121), indicate an age of 19.9 ± 0.5 Ma

TABLE 5.3

Rb and Sr isotopic data for selected Nandewar specimens

Sample	Rb (μg/g)	Sr (μg/g)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ (measured)	$^{87}Sr/^{86}Sr$ † (initial)	Age* (Ma)	ε_{Sr}
Hawaiite (49001)	20.9	617.5	0.097	0.70395	0.70392	-	-12
Trachyandesite (49008)	41.6	851.8	0.141	0.70417	0.70413	-	-10
Trachyandesite (49011)	45.2	628.1	0.208	0.70425	0.70419	-	- 8
Trachyandesite (49012)	49.4	763.4	0.187	0.70408	0.70403	-	-11
Tristanite (49076)	62.2	515.8	0.348	0.70415	0.70405	-	-10
Syenite (49070)	65.5	473.4	0.400	0.70420	0.70409	-	-10
Microsyenite xenolith (49074)	52.7	391.4	0.389	0.70421	0.70410	-	-10
Mafic trachyte (49082)	80.0	273.8	0.843	0.70426	0.70402	18.3	-11
Peralkaline trachyte (49102)	108.2	24.6	12.696	0.70749	0.70389	19.4	- 9
Peralkaline trachyte (49098)	106.9	4.89	63.26	0.72259	0.70478	20.7	-
Comendite (49108)	174.7	6.64	76.13	0.72612	0.70473	20.5	-
Comendite (49163)	289.2	5.02	167.0	0.75164	0.70530	20.1	-
Alkali rhyolite (49121)	127.6	10.67	34.56	0.71493	0.70516	22.3	-
Alkali rhyolite (49130)	180.7	2.55	205.4	0.76082	0.70412	19.5	-

† Calculated assuming an age of 20 Ma

* Calculated assuming initial $^{87}Sr/^{86}Sr = 0.7040$

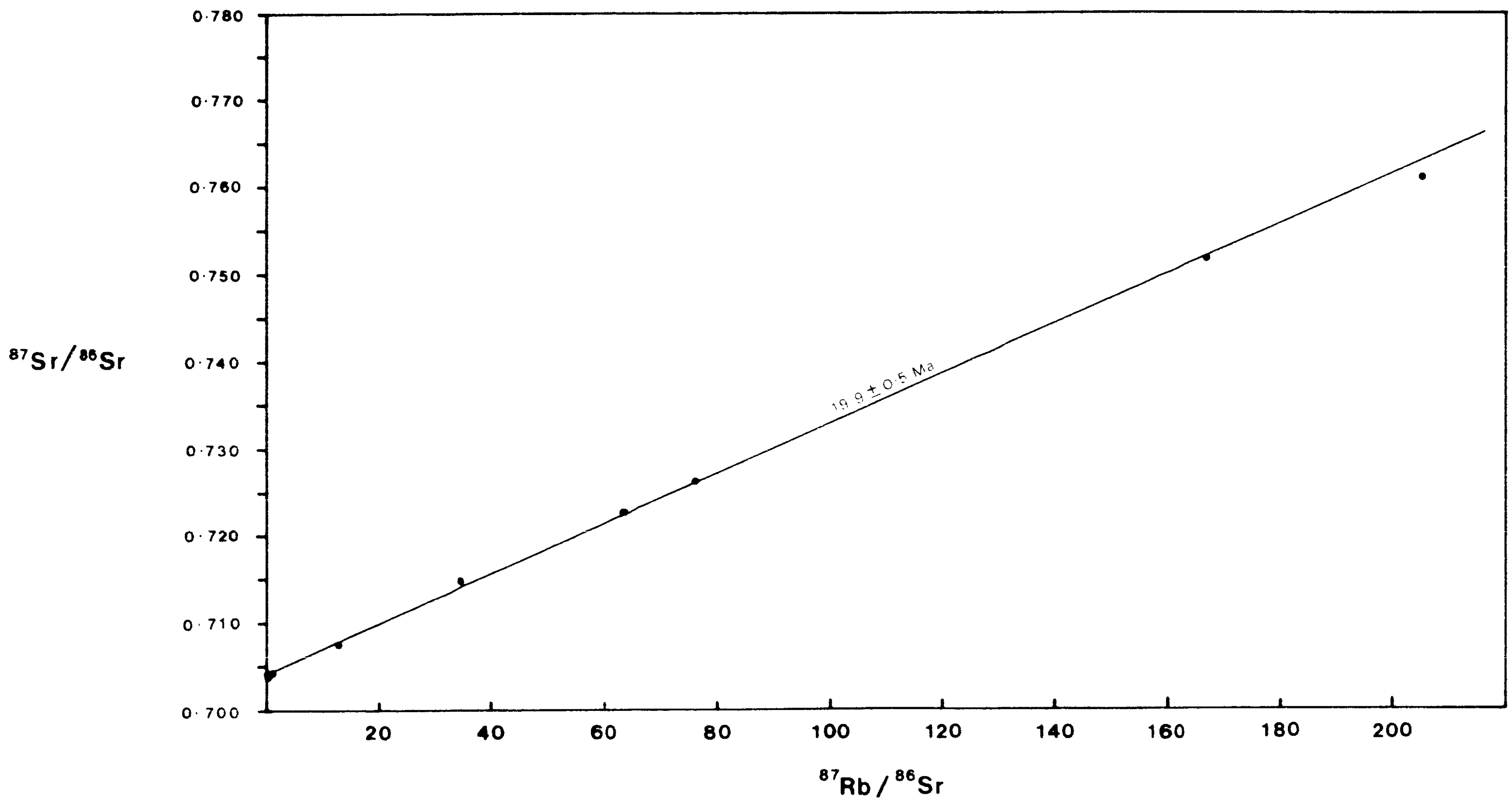


Fig. 5.14: $^{87}Sr/^{86}Sr$ (measured) versus $^{87}Rb/^{86}Sr$ isochron for the Nandewar volcanics.

with an initial $^{87}Sr/^{86}Sr$ ratio of 0.70406 ± 0.00008. The older alkali rhyolite specimen (49121) exhibits significant departure from the line of best fit which may be due to a real age difference, or alternatively the higher $^{87}Sr/^{86}Sr$ ratio could be due to contamination by radiogenic crustal Sr, or some other process capable of causing isotope fractionation (e.g. thermogravitational diffusion; Hildreth, 1981).

Ages calculated assuming a constant initial $^{87}Sr/^{86}Sr$ ratio of 0.7040 (Table 5.3) range from 18.3 to 22.3 Ma and are consistently 1 to 2 Ma older than K/Ar ages determined on similar rock types (Stipp and McDougall, 1968; Wellman *et al.*, 1969; Wellman and McDougall, 1974b), even after recalculation of the original K/Ar data using the new decay constants recommended by Steiger and Jäger (1977). Price and Compston (1973) noted similar discrepancies between Rb/Sr and K/Ar ages determined for the Dunedin Volcano, New Zealand.

The calculated age for the older alkali rhyolite (49121), assuming an initial $^{87}Sr/^{86}Sr$ ratio of 0.7040, is 22.3 Ma which is approximately 2 to 4 Ma older than rhyolitic and trachytic plugs which intrude the main shield-forming lavas. This older age is consistent with a K/Ar age of 20.7 Ma (recalculated from data of Stipp and McDougall, 1968) for a trachyte from the northern part of the Volcano which is considered to be amongst the earliest eruptives on the basis of field relations. The younger ages indicated for another alkali rhyolite (49130) and a peralkaline trachyte (49102), 19.5 and 19.4 Ma respectively, are consistent with their emplacement late in the development of the Volcano indicated by field relationships.

Initial $^{87}Sr/^{86}Sr$ ratios calculated assuming an age of 20 Ma (Table 5.3) display a moderately restricted range (0.70392 to 0.7053) which lies within the range of uncontaminated oceanic basalts compiled by Peterman and Hedge (1971). The initial ratios for the comendites, peralkaline trachyte (49098) and the older alkali rhyolite (49121) are slightly higher than those of the mafic variants. The higher value for the alkali rhyolite may be partly explicable by its older age, although contamination may also be partly responsible, as noted above. The higher values for peralkaline trachyte (49098) and the comendites contrast with the low values for the other peralkaline trachyte (49102) and alkali rhyolite (49130). These apparently random variations suggest that the specimens with the higher initial ratios may have been slightly contaminated by crustal material enriched in radiogenic Sr. The Carboniferous silicic calc-alkaline volcanics which form part of the basement to the Nandewar Volcano are potential contaminants. However, isotopic data are not available for these rocks to test this hypothesis.

Neodymium Isotopes

Neodymium isotope data are available for only one Nandewar specimen (Table 5.4), but when used in conjunction with the Sr isotopic data serve to illustrate the isotopic character of the source region.

TABLE 5.4

Neodymium and samarium isotope data for hawaiite 49001

	Sm (μg/g)	Nd (μg/g)	$^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$	$^{147}\mathrm{Sm}/^{144}\mathrm{Nd}$	$\varepsilon_{\mathrm{Nd}}$
49001	6.11	23.38	0.512015 ± 7	0.1302	3.7

The Nd and Sr isotopic ratios are reported in the ε notation (De Paolo and Wasserburg, 1976,1977) which represent the deviations of initial Nd and Sr isotopes in parts in 10^4 from the proposed value in a chondritic uniform reservoir (CHUR). These are given by:

$$\varepsilon_{\mathrm{Nd}} = \left[(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})^{T}_{\mathrm{Init.}} / (^{143}\mathrm{Nd}/^{144}\mathrm{Nd})^{T}_{\mathrm{CHUR}} - 1 \right] 10^4$$

and

$$\varepsilon_{\mathrm{Sr}} = \left[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{T}_{\mathrm{Init.}} / (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{T}_{\mathrm{UR}} - 1 \right] 10^4$$

where

$$(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})^{T}_{\mathrm{CHUR}} = (^{143}\mathrm{Nd}/^{144}\mathrm{Nd})^{o}_{\mathrm{CHUR}} - (^{147}\mathrm{Sm}/^{144}\mathrm{Nd})^{o}_{\mathrm{CHUR}} (e^{\lambda_{\mathrm{Sm}}T} - 1)$$

$$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{T}_{\mathrm{UR}} = (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{o}_{\mathrm{UR}} - (^{87}\mathrm{Rb}/^{86}\mathrm{Sr})^{o}_{\mathrm{UR}} (e^{\lambda_{\mathrm{Rb}}T} - 1)$$

and:

$(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})^{T}_{\mathrm{Init.}}$ and $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{T}_{\mathrm{Init.}}$ are the measured ratios in the rock corrected for decay since the time of crystallization T.

Present day reference values are:

$$(^{143}\text{Nd}/^{144}\text{Nd})^{o}_{\text{CHUR}} = 0.51264$$

$$(^{147}\text{Sm}/^{144}\text{Nd})^{o}_{\text{CHUR}} = 0.1967$$

$$\lambda_{\text{Sm}} = 6.54 \times 10^{-12}\text{yr}^{-1}$$

$$(^{87}\text{Sr}/^{86}\text{Sr})^{o}_{\text{UR}} = 0.7048$$

$$(^{87}\text{Rb}/^{86}\text{Sr})^{o}_{\text{UR}} = 0.085$$

$$\lambda_{\text{Rb}} = 1.42 \times 10^{-11}\text{yr}^{-1}$$

The initial Nd and Sr isotopic ratios have been plotted in terms of ε_{Nd} and ε_{Sr} and compared with data for volcanic suites from oceanic (Fig. 5.15a) and continental (Fig. 5.15b) settings respectively. The strong negative correlation between ε_{Nd} and ε_{Sr} exhibited by oceanic lavas is interpreted as indicating coherent fractionation of Rb/Sr and Sm/Nd during the evolution of the sub-oceanic mantle (O'Nions *et al.*, 1979). The Nandewar specimens plot near the field for Bouvetoya specimens in the oceanic plot and this indicates their derivation from a source which was depleted in LREE and Rb relative to chondrite for a substantial period of time. The source region for the Nandewar lavas was less depleted than the Ascension Island and MORB sources, or alternatively, has been depleted for a shorter period.

The depletion events producing the isotopic heterogeneity in the mantle are generally considered to be due to separation of a silicate melt fraction enriched in LREE and Rb relative to the source (De Paolo and Wasserburg, 1976; O'Nions *et al.*, 1977). The time at which this depletion occurred is not closely constrained. However, the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the source and the time of fractionation are related by the expression:

$$(^{147}\text{Sm}/^{144}\text{Nd})_{\text{Source}} = (\varepsilon_{\text{Nd}}/K_{\text{Nd}}\ T_s) + (^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}$$

where $K_{\text{Nd}} = 0.128\ \text{Ma}^{-1}$, $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$ and T_s is the time at which the source was fractionated from an initially chondritic Sm/Nd ratio (McCulloch and Perfit, 1981). Assuming a simple two-stage model in which the Rb/Sr and Sm/Nd are regarded as unfractionated up to the estimated age and then fractionated to values appropriate to a depleted

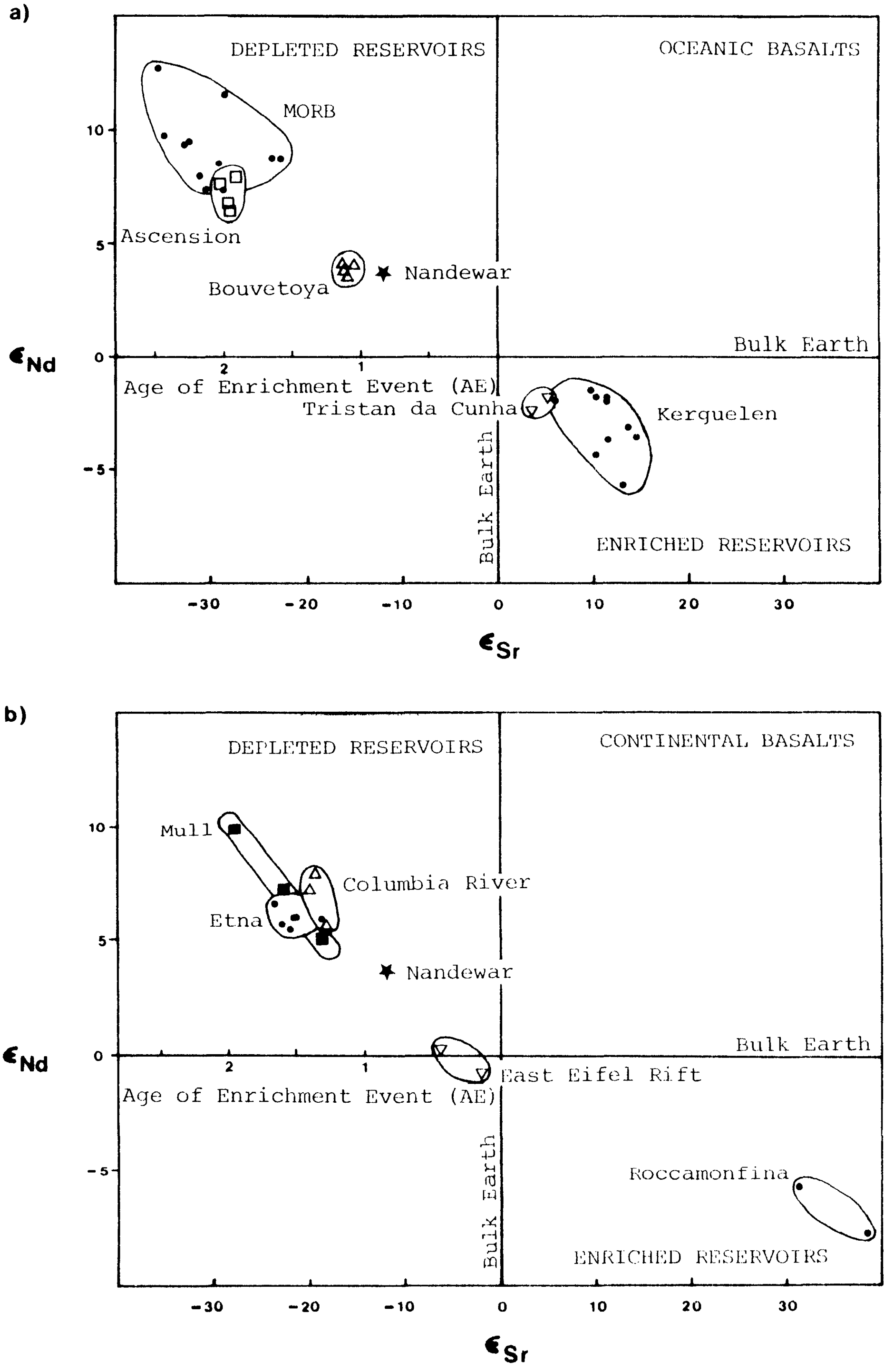


Fig. 5.15: Plots of ε_{Nd} versus ε_{Sr} for Nandewar hawaiite 49001 with

(a) oceanic volcanics and

(b) continental alkaline volcanics

source (i.e. $^{147}Sm/^{144}Nd$ ~0.23, cf. McCulloch and Perfit, 1981; Anderson, 1982), fractionation of the Nandewar source probably occurred in the region of 0.8 AE ago.

While most oceanic lavas have evidently been derived from sources characterized by ancient depletion events, the Kerguelen lavas (Dosso and Murthy, 1980) are products of a mantle reservoir characterized by an ancient enrichment event. This is reflected in their negative ε_{Nd} and positive ε_{Sr} values (see Fig. 5.15a) which indicate that the source region maintained higher Rb/Sr and lower Sm/Nd ratios than chondrite for a substantial period of time. Suites such as Tristan da Cunha (O'Nions and Pankhurst, 1974; O'Nions *et al.*, 1977) which have close to bulk Earth ε_{Nd} and ε_{Sr} values are considered to be derivatives of a mantle reservoir that has remained essentially unmodified since formation of the Earth (De Paolo and Wasserburg, 1976). Continental alkali lavas and flood basalts also exhibit a range of ε_{Nd} and ε_{Sr} values characteristic of bulk Earth, enriched and depleted reservoirs (see Fig. 5.15b).

The implications regarding the genesis of alkali basalts from depleted mantle reservoirs are discussed in the following chapter.

SUMMARY

The major and trace element chemistry of the Nandewar rocks strongly reflects their alkaline affinities. In particular the high concentrations of the 'residual' trace elements in the more evolved rock types are typical of many transitional alkaline volcanic suites. The chemical and mineralogical characteristics of transitional alkaline rock series similar to the Nandewar suite are reviewed in the following chapter.

The reasonably smooth and progressive variation of most elements with F.I., at least in the range F.I. 30 to 85, may be interpreted as evidence for the operation of the process of fractional crystallization in the genesis of the various members of the series. However, many of these trends may have alternative explanations, the diversity of which will be explored in Chapter 7. An explanation is also required for the variable behaviour of many of the trace elements in the most evolved rock types, particularly the tendency of the comendites to be enriched in certain 'residual' trace elements and alkalis relative to the commonly vesicular alkali rhyolites of similar F.I.

The Sr isotope data indicate that all compositional variants of the suite were derived from an isotopically similar source of upper mantle/lower crustal character, hence providing strong evidence for their cogenesis.

CHAPTER 6

COMPARATIVE REVIEW OF TRANSITIONAL ALKALINE ASSOCIATIONS FROM CONTINENTAL AND OCEANIC ENVIRONMENTS

The close spatial and temporal association of transitional alkali basalts and oversaturated peralkaline salic eruptives was first recognized by Coombs (1963) to be genetically significant and the association has now been recognized in a large number of oceanic and continental volcanic centres. The salic members have generally been interpreted as the final products of low-pressure fractional crystallization of transitional 'basaltic' melts.

In this chapter it is intended to examine volcanic associations from oceanic and continental settings and similar to the Nandewar suite to ascertain to what extent their observed volumetric relations and mineralogical and chemical characteristics are consistent with fractionation models. These are generally based on closed-system fractional crystallization of parental 'basaltic' melts as the prime genetic control on the more 'evolved' members. The review also examines the extent to which the chemical characteristics of alleged derivative melts may be explicable by alternative genetic models.

Tables 6.1 and 6.2 summarize the more important mineralogical and chemical characters of the members of specific oceanic and continental suites. These were selected because they have come to be regarded as classic examples of transitional alkaline series and/or have been subjected to detailed mineralogical and chemical investigation. The suites on Pantelleria, Oki, Dôgo and Mayor Island have been included with the continental associations because of their close proximity to continents and the possibility that the compositions of some of the eruptives may have been modified as the result of contamination by continental crust.

RELATIVE VOLUMETRIC PROPORTIONS

An appreciation of the relative volumes of the various volcanic rock types in specific centres is important because closed-system crystal fractionation models dictate that progressively more 'evolved' rock types should occur in successively smaller volumes. Nevertheless a

TABLE 6.1

Characteristics of transitional alkaline series from oceanic islands

Oceanic Island	Maximum* 100*an*/(*ab*+*an*)	Maximum* $100Mg/(Mg+Fe^{2+})$	Alkali relations of series	Most evolved members of series	High-pressure megacrysts	Cognate cumulates, inclusions	Main References
Gough	47.5	63.4	moderately potassic	trachyte	-	gabbro	LeMaitre (1962, 1965), Zielinski and Frey (1970)
Bouvetoya	48.8	45.6	sodic	comendite	plagioclase?	-	Imsland *et al.* (1977), Prestvik (1982)
Ascension	45.5	41.5	sodic	comendite	-	wehrlite, gabbro, syenite, alkali granite	Daly (1925)
Gran Canaria (Canary Islands)	-	-	sodic and moderately potassic	pantellerite/ comendite	-	cpx-kaersutite, syenite	Frisch and Schmincke (1969), Schmincke (1969, 1973), Arana *et al.* (1973)
Terceira (Azores Islands)	52.8	66.2	sodic and moderately potassic	pantellerite/ comendite	-	gabbro, syenite, amphibolite, dunite	Schmincke and Weibel (1972), Self and Gunn (1976), White *et al.* (1979)
Easter	58.0	59.2	sodic	comendite	-	-	Baker *et al.* (1974)
Socorro	46.2	53.6	sodic	pantellerite/ comendite	-	-	Bryan (1970, 1976)
Reunion	66.0	57.6	sodic	trachyte	-	gabbro, dunite	Upton and Wadsworth (1972), Zielinski (1975), Ludden (1978a, b)

* Denotes highest *M* number or 100*an*/*ab*+*an* ratio for aphyric or slightly porphyritic rock types

TABLE 6.2

Characteristics of transitional alkaline series from continental volcanic provinces

Province Centre	Maximum* 100*an*/*ab*+*an*	Maximum* 100Mg/Mg+Fe^{2+}	Alkali relations of series	Most evolved members of series	High-pressure megacrysts	Cognate cumulates, inclusions	Main References
EAST AFRICA							
Boina	58.8	65.2	sodic	pantellerite	-	-	Barberi *et al.* (1975) Bizouard *et al.* (1980)
Erta'Ale	53.7	63.6	sodic	comendite	-	-	Barberi and Varet (1970), Barberi *et al.* (1974), Bizouard *et al.* (1980)
Fantale	40.4	39.9	sodic	pantellerite	-	-	Gibson (1972)
Paka	52.2	61.5	sodic	peralkaline trachyte	-	-	Sceal and Weaver (1971)
Silali	56.7	51.0	sodic to moderately potassic	comendite	-	gabbro, syenite	McCall and Hornung (1972)
Gregory Rift	58.3	55.8	sodic to moderately potassic	peralkaline trachyte	-	-	Baker *et al.* (1977)
Chabbi	-	-	sodic	pantellerite	-	-	MacDonald and Gibson (1969)
GULF OF ADEN							
Aden	52.2	57.7	sodic to moderately potassic	comendite	-	-	Cox *et al.* (1970)
Little Aden	51.9	63.1	sodic to moderately potassic	comendite	-	-	Cox *et al.* (1970)
Jebel Khariz	61.9	65.6	sodic	comendite/pantellerite	-	gabbro, syenite	Gass and Mallick (1968)
Jebel al Abyad	57.7	64.8	sodic	comendite	-	rare gabbro	Baker *et al.* (1973)
EASTERN AUSTRALIA							
Nandewar	49.2	65.2	moderately potassic	comendite	plag.,Fe-Ti oxides, opx,cpx,apatite	rare microgabbro, syenite	Abbott (1969), this study
Canobolas	37.1	51.6	moderately potassic	comendite	-	microsyenite	Middlemost (1981)
Comboyne	40.9	48.6	sodic to moderately potassic	comendite/pantellerite	plag.,olivine, cpx,opx,Fe-Ti oxides,apatite	gabbro	Knutson (1975), Knutson and Green (1975)
SCOTLAND							
Skye	56.4	61.5	sodic	trachyte	-	-	Thompson *et al.* (1972, 1980)
NEW ZEALAND							
Banks Peninsula	50.8	60.5	sodic	comendite	-	-	Price and Taylor (1980)
Mayor Island	-	-	sodic	pantellerite	-	mugearite, basalt	Ewart *et al.* (1968), Rutherford (1978)
WESTERN U.S.A.							
Black Mountain	44.2	49.7	sodic to moderately potassic	comendite/pantellerite	-	-	Noble (1965), Ekren *et al.* (1971) Noble and Parker (1974)
PANTELLERIA	43.7	52.3	sodic	pantellerite	-	coarse-grained equivalents of lavas	Villari (1974)
OKI DOGO	58.6	65.8	sodic to moderately potassic	comendite/pantellerite	-	gabbro, peridotite	Uchimizu (1966), Nagasawa (1973)

* Denotes highest *M* number or 100*an*/*ab*+*an* ratio for aphyric or slightly porphyritic rock types

feature of many alkaline volcanic provinces is a distinctly bimodal distribution of mafic and felsic rocks and their predominance over eruptives with intermediate compositions.

The existence of a compositional hiatus in the frequency of analyses of alkaline volcanic rocks from the oceanic islands was clearly demonstrated by Chayes (1963). This observation and the implication that the rhyolitic and trachytic rocks were not necessarily derived by fractional crystallization of the associated basic rocks initiated a vigorous debate on the genesis of the salic eruptives. It was argued (Harris, 1963; Baker, 1968; Cann, 1968; Ridley, 1970) that the felsic lavas had been oversampled because of their distinctive appearance and their common occurrence as erosion-resistant intrusive domes and plugs. Nevertheless, field observations by Le Maitre (1962) on Gough Island, Bryan (1964) on Socorro Island and Self and Gunn (1976) on Terceira Island (Azores) provided estimates of the relative volumetric proportions of mafic and felsic lavas which in essence supported Chayes' (1963) findings. Trachytic rocks outcrop over approximately 50 percent of the exposed area of Gough Island and oversaturated felsic types comprise greater than 90 percent of the volume of Socorro Island. On Terceira Island the volumetric ratio of felsic to mafic rocks is approximately 70:30 for the exposed portion of the island. However, Self and Gunn (1976) suggest, on rather limited data, that *all* of the felsic rocks are exposed and that these in fact only comprise 4 to 5 percent of the total volcanic pile when the submerged section is taken into account. For most of the remaining oceanic islands discussed herein mafic rocks predominante, felsic rocks generally being volumetrically insignificant. On Gran Canaria mafic and felsic rocks are both more abundant than intermediate types (Baker, 1974).

High volume ratios of felsic to mafic rocks have long been recognized in continental alkaline volcanic provinces and these relationships are particularly evident in the East African Rift provinces. Williams (1972) estimated that the ratio of mafic to felsic lavas in Kenya is 1.3:1 for a total volume of 144,000 km^3. Similarly, Mohr (1968) estimated a ratio of 6:1 for mafic and felsic lavas of Ethiopia comprising a total volume of 345,000 km^3, and Vincent (1970) gives an estimate of 61:37 for the Tibesti Province in Chad. Within these provinces examination of specific volcanic centres indicates wide variations in the ratio of mafic to felsic eruptives. For example at Boina (Barberi *et al.*, 1975) and Erta Ale (Barberi and Varet, 1970) in Ethiopia, basaltic rocks are apparently most abundant and the more evolved types occur in successively smaller volumes. In contradistinction the volcanoes of Chabbi, Ethiopia (Macdonald and Gibson, 1969) and Menengai, Kenya (Williams, 1972) are composed entirely of felsic eruptives. A similar situation exists on Mayor Island, New Zealand (Ewart *et al.*, 1968). The Kenyan volcanic centres of Paka (Sceal and Weaver, 1971), Eburru (Weaver *et al.*, 1972) and Silali (McCall and Hornung, 1972), together with Fantale in Ethiopia (Gibson, 1972), are all characterized by a preponderance of acid lava types over basic and intermediate variants.

In the eastern highlands of Australia the relative volumes of felsic and mafic lavas also varies considerably between individual provinces. Several volcanic centres in New South Wales including Comboyne (Knutson, 1975), Canobolas (Middlemost, 1981), and Nandewar as well as the Glass Houses in south-east Queensland (Stevens, 1971) are characterized by felsic lavas dominanting the associated mafic and intermediate types. Stevens (1970) estimated the ratio of mafic to felsic lavas in the Main Range province of south-east Queensland to be 8:1 with a complete lack of volcanics with SiO_2 = 52 to 66 percent. In contrast, the Victorian Newer Volcanics (Irving and Green, 1976) and Tasmanian (Sutherland, 1969) provinces are dominated by basaltic lavas and intermediate to felsic types are exceedingly rare.

Occurrences of silicic peralkaline volcanic rocks in most centres of the western United States are accompanied by mafic lavas, although these are generally subordinate in volume (Noble and Parker, 1974). The volcanic centres of Aden and Little Aden (Cox *et al.*, 1970) provide an interesting example where rocks intermediate in composition between basalt and trachyte are rare in the cone-building series but are abundant in the post-caldera sequence. Other volcanic centres such as Jebel al Abyad in Saudi Arabia (Baker *et al.*, 1973), the Isle of Skye, Scotland (Thompson *et al.*, 1972) and the Banks Peninsula, South Island, New Zealand (Price and Taylor, 1980) are all characterized by mafic and intermediate lavas in excess of felsic types.

CHEMICAL CHARACTERISTICS OF TRANSITIONAL ALKALINE SERIES

Representative analyses of mafic and felsic rocks from oceanic and continental transitional alkaline suites are listed in Table 6.3, 6.4, 6.5 and 6.6. The main sources for these data are given in Tables 6.1 and 6.2 and for the sake of brevity are not quoted during the discussion of the chemical variation of rocks within each suite. Supplementary references, however, are mentioned where appropriate. Careful examination of published analytical data for suites from continental and oceanic island settings has not revealed any persistent chemical differences between suites from these contrasting settings except perhaps for the comendites (cf. Bailey and Macdonald, 1970). The continental and oceanic suites are therefore grouped together for the purpose of discussion of their important chemical characteristics.

Characteristics of the Mafic Associates

Some confusion in nomenclature is apparent when the mafic members of this association are described. Adopting the classification scheme of Coombs and Wilkinson (1969) many of the lavas described as trachybasalt by Le Maitre (1962) from Gough Island, and Bryan (1964) from Socorro Island would be termed trachyandesite and mugearite respectively. It thus becomes important to examine the degree of 'evolution' displayed by the most mafic variants in many of the volcanic provinces under consideration.

In columns 1 and 2 of Tables 6.1 and 6.2 are presented the C.I.P.W. normative plagioclase compositions (100*an/ab+an*) and *M* numbers ($100\text{Mg}/\text{Mg}+\text{Fe}^{2+}$, calculated with $\text{Fe}_2\text{O}_3/\text{FeO} = 0.2$) of the most mafic aphyric or mildly porphyritic rocks in each province. Inspection of the normative plagioclase compositions indicates that basalts *s.s.* (with 100*an/ab+an* > 50) are present in many provinces, notable exceptions including Gough, Bouvetoya, Ascension, Socorro Nandewar, Canobolas, Comboyne, and Jebel um Birka, where the most mafic member is usually hawaiite or trachyandesite (100*an/ab+an* < 50). Analysed mafic volcanics from Gough, Bouvetoya and Ascension, although they may be classified as basalts on the basis of normative plagioclase compositions, are also invariably porphyritic in plagioclase and/or olivine and hence the analyses may not represent true liquid compositions. Although basaltic rocks are apparently present on

TABLE 6.3

Representative analyses and C.I.P.W. norms of transitional alkaline mafic rocks from the oceanic islands

Analysis Number	1	2	3	4	5	6	7	8	9
SiO_2	47.85	49.86	48.64	42.30	47.75	47.79	46.96	45.99	46.99
TiO_2	3.40	3.51	3.52	3.29	2.47	2.97	3.07	2.18	2.65
Al_2O_3	15.05	14.80	15.54	12.49	14.75	15.88	13.53	15.65	14.55
Fe_2O_3	3.44	5.97	5.31	4.79	2.05	3.14	6.44	5.95	1.77
FeO	7.23	6.90	7.73	8.06	9.56	8.49	7.28	6.50	8.90
MnO	0.10	0.19	0.17	0.20	0.19	0.08	0.18	0.16	0.13
MgO	8.51	4.23	4.96	9.26	6.56	7.79	7.14	7.66	8.18
CaO	8.00	9.02	9.03	11.75	10.17	9.96	9.06	12.60	8.97
Na_2O	2.90	3.48	3.60	3.16	3.70	2.92	3.09	2.39	2.80
K_2O	1.97	1.24	1.24	1.03	1.20	0.73	1.18	0.71	1.43
P_2O_5	0.29	0.49	0.64	0.96	0.71	0.19	0.85	0.32	0.47
H_2O^+	0.59	0.59	0.16	2.36	0.06	0.22	0.43	0.12	2.03
H_2O^-	0.47	-	0.18		-	0.06	0.11	-	0.83
Total	99.80	100.28	100.72	99.65	99.17	100.22	99.32	100.23	99.70
ΣFe as FeO	10.33	12.27	12.51	12.37	11.40	11.32	13.07	11.85	10.49
$100Mg/(Mg+Fe^{2+})^*$	63.4	42.0	45.5	61.2	54.7	59.2	53.5	57.6	62.1
Na_2O/K_2O	1.47	2.81	2.90	3.07	3.08	4.00	2.62	3.37	1.96
C.I.P.W. Norms*									
or	11.64	7.33	7.33	6.09	7.09	4.31	6.97	4.20	8.45
ab	24.54	29.45	30.46	8.35	24.57	24.71	26.15	15.42	23.69
an	22.23	21.10	22.58	16.85	20.09	28.07	19.56	29.88	22.91
ne				9.96	3.65			2.60	
di	12.55	16.99	14.91	28.53	21.09	16.36	16.27	24.98	15.01
hy	1.32	12.52	3.36			3.39	4.26		2.92
ol	16.63	1.12	10.18	15.73	13.47	14.32	14.14	14.85	15.16
mt	2.54	3.02	3.07	3.04	2.80	2.78	3.21	2.91	2.58
il	6.46	6.67	6.69	6.25	4.69	5.64	5.83	4.14	5.03
ap	0.67	1.14	1.48	2.22	1.65	0.44	1.97	0.74	1.09
Rest	1.06	0.59	0.34	2.36	0.06	0.28	0.54	0.12	2.86
100 *an*/(*ab*+*an*)	47.5	41.7	42.6	66.9	45.0	53.2	42.8	66.0	49.2
D.I.	36.2	36.8	37.8	24.4	35.3	29.0	33.1	22.2	32.1
Trace Elements μg/g									
V	90	193	-	-	300	-	-	340	205
Cr	220	23	-	-	172	-	-	110	176
Ni	100	13	-	-	68	126	-	120	126
Cu	-	64	-	-	-	55	-	270	50
Zn	-	140	-	-	-	91	-	65	95
Rb	100	26	-	-	27	9	-	10	26
Sr	650	368	-	-	502	347	511	390	659
Y	12	31	-	-	-	32	-	22	20
Zr	125	217	-	-	-	213	237	125	178
Nb	-	-	-	-	-	26	43	-	44
Ba	650	274	-	-	530	179	356	310	297
La	24.0	26.8	-	-	39	-	34	16.7	33
Ce	37.8	65	-	-	98	-	81	36.5	63
Nd	32.3	-	-	-	50	-	-	20.6	32

1. Trachyandesite, Gough Island (Le Maitre, 1962, tables 10 and 11, No. G13; Zielinski and Frey, 1970, table 1, No. G-13).
2. Hawaiite, Bouvetoya Island (Imsland *et al.*, 1977, tables 4 and 6, No. 9; Prestvik, 1982, table 1, No. Bov 9).
3. Hawaiite, Ascension Island (Daly, 1925, table IX, No. 2).
4. Basalt, Gran Canaria (Borley, 1974, table 3A, No. 4, quoted from Fuster *et al.*, 1968).
5. Hawaiite, Terceira (Azores) (White *et al.*, 1979, tables 2, 3 and 4, No. T-21).
6. Olivine tholeiite, Easter Island (Baker *et al.*, 1974, table 1, No. 5).
7. Hawaiite, Socorro Island (Bryan, 1976, tables 1 and 2, No. S-144).
8. Olivine basalt, Reunion Island (Upton and Wadsworth, 1972, table 3, No. Re512G; Zielinski, 1975, table 4, No. 512G).
9. Trachyandesite, Nandewar Volcano (this study, No. 49000).

* Calculated with $Fe_2O_3/FeO = 0.20$, - = not determined.

TABLE 6.4

Representative analyses and C.I.P.W. norms of salic rocks associated
with transitional alkaline mafic rocks from the oceanic islands

Analysis Number	1	2	3	4	5	6	7*	8	9	10	11
SiO_2	62.45	69.09	71.88	70.76	68.5	67.03	66.22	72.70	68.91	61.02	72.82
TiO_2	0.38	0.27	0.25	0.43	1.0	0.40	0.54	0.20	0.40	0.90	0.14
Al_2O_3	17.92	13.10	12.85	14.37	9.6	14.97	10.61	12.87	10.83	15.20	12.95
Fe_2O_3	2.06	1.05	3.60	0.86	7.5	2.96	9.41	0.86	2.91	3.65	2.35
FeO	3.11	3.38	0.05	1.33	0.1	2.15	-	2.06	4.56	3.05	0.85
MnO	0.16	0.11	0.29	0.18	0.45	0.16	0.35	0.07	0.25	0.19	0.03
MgO	0.09	0.02	0.18	0.72	0.1	0.15	0.44	0.01	0.22	1.08	0.03
CaO	1.17	0.72	0.60	0.43	0.5	0.69	0.80	0.62	0.24	2.38	0.19
Na_2O	6.47	5.84	5.32	5.40	5.2	6.47	7.01	5.76	6.96	6.39	5.32
K_2O	6.14	4.77	4.78	5.45	4.5	4.60	4.60	3.89	4.46	4.31	4.37
P_2O_5	0.09	0.08	-	0.06	0.10	0.02	0.02	0.01	0.02	0.11	0.02
H_2O^+	0.16	0.20	0.18	-	1.7	0.28	-	0.27	0.26	1.07	0.27
H_2O^-	0.27	-	0.17	-	-	-	-	-	0.10	-	0.47
CO_2	-	0.28	-	-	-	-	-	-	-	0.67	-
Total	100.47	98.91	100.15	99.99	99.3	99.88	100.00	99.32	100.12	100.02	99.81
ΣFe as FeO	4.96	4.32	3.29	2.10	6.85	4.81	8.47	2.83	7.18	6.33	2.96
Agpaitic Index	0.96	1.13	1.08	1.03	1.40	1.04	1.56	1.06	1.50	1.00	1.04
C.I.P.W. Norms											
Q		17.20	23.00	16.67	24.98	10.73	15.68	23.45	19.85	3.60	25.50
or	36.28	28.19	28.25	32.21	26.58	27.18	27.44	22.99	26.36	25.47	25.82
ab	51.57	40.82	39.48	43.57	24.31	51.39	29.24	44.54	30.87	54.07	42.28
an	1.72									0.06	
ne	1.72										
ac		3.04	4.87	1.87	17.33	2.96	12.37	2.49	8.42		2.41
ns		1.20					3.86	0.32	4.30		
di	3.08	1.14	0.97	1.45	0.39	2.86	3.38	2.68	0.93	5.51	0.40
hy		5.41		2.96	0.07	0.87	6.94	2.19	8.24	1.46	
ol	1.75										
mt	2.99		0.38	0.31		2.81				5.29	2.20
il	0.72	0.51	0.47	0.82	1.17	0.76	1.04	0.38	0.76	1.71	0.27
hm			1.65		1.54						
ap	0.21	0.19		0.14	0.24	0.05	0.05	0.02	0.05	0.25	0.05
Rest	0.43	0.84	1.07		2.64	0.28		0.27	0.36	2.59	0.88
Σ femics	8.75	11.49	9.06	7.55	21.68	10.31	27.64	8.08	22.70	12.51	5.47
D.I.	89.6	86.6	90.7	92.5	75.9	89.3	72.4	91.0	77.1	83.1	93.6
Trace Elements µg/g											
Cr	-	4	-	-	-	1.9	-	-	-	12	1
Ni	3	n.d.	-	-	-	n.d.	-	6	-	10	12
Cu	-	n.d.	-	8	-	-	-	11	-	10	7
Zn	-	39	-	-	-	-	-	246	-	195	260
Rb	300	127	-	100	-	103	192	85	-	130	294
Sr	-	28	-	82	-	12	11	28	n.d.	110	1
Y	20	164	-	-	-	-	-	156	-	100	130
Zr	1000	1420	-	1116	-	-	-	1049	1535	850	1245
Nb	-	-	-	-	-	-	-	126	206	-	282
Ba	n.d.	183	-	847	-	576	-	364	33	532	4
La	135	100	-	122	-	113	-	-	140	63	55
Ce	164	228	-	-	-	255	-	-	299	161	103
Nd	130	-	-	-	-	104	-	-	-	75	50

1. Trachyte, Gough Island (Le Maitre, 1962, tables 10 & 11, No. G149; Zielinski and Frey, 1970, table 1, No.G-149).
2. Comendite Obsidian, Bouvetoya (Imsland *et al.*, 1977, tables 5 & 6, No. 30; Prestvik, 1982, table 1, No. Bov 30).
3. Comendite, Ascension Island (Daly, 1925, table X, No. 6).
4. Comendite, Gran Canaria (Arana *et al.*, 1973, tables 1 & 4, No. 1R).
5. Pantellerite, Gran Canaria (Schmincke and Swanson, 1967, table 3, No. 2).
6. Comendite, Terceira (Azores) (White *et al.*, 1979, tables 2, 3 & 4, No. T-13).
7. Pantellerite, Pico Alto Volcano, Terceira (Azores) (Self and Gunn, 1976, Appendix, No. T-0052).
8. Comendite Obsidian, Rano Kau Volcano, Easter Island (Baker *et al.*, 1974, table 1, No. 16).
9. Pantellerite, Socorro Island (Bryan, 1976, tables 1 & 2, No. S-138).
10. Trachyte, Reunion Island (Upton and Wadsworth, 1972, table 3, No. Re364; Zielinski, 1975, table 4, No. 364).
11. Comendite, Nandewar Volcano (this study, No. 49163).

\- = not determined   n.d. = not detected

* no FeO determined, norm calculated with $Fe_2O_3/FeO = 1.0$, remaining norms calculated with measured Fe_2O_3/FeO ratios.

TABLE 6.5

Representative analyses and C.I.P.W. norms of transitional alkaline mafic rocks from continental volcanic provinces

Analysis Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	46.75	48.78	47.11	47.68	46.80	45.21	47.9	46.99	51.38	51.04	45.08	44.18	48.7	48.0	46.8	48.13
TiO_2	2.30	1.73	3.24	2.02	3.00	3.28	1.69	2.65	2.36	2.70	2.15	2.98	1.95	2.2	3.39	1.93
Al_2O_3	13.93	14.55	13.65	15.55	13.71	15.63	16.5	14.55	14.76	16.05	14.14	13.26	19.5	16.5	14.40	14.32
Fe_2O_3	3.20	4.17	5.08	2.87	5.10	6.47	1.39	1.77	2.27	3.31	1.50	4.47	2.3	4.5	5.62	2.60
FeO	8.08	6.48	10.95	8.62	7.35	7.86	9.01	8.90	9.18	8.19	10.93	8.61	6.6	7.0	7.52	9.70
MnO	0.19	0.20	0.22	0.20	0.17	0.21	0.17	0.13	0.15	0.18	0.19	0.18	0.15	0.19	0.15	0.19
MgO	9.75	8.50	4.89	6.73	7.75	5.29	9.00	8.18	5.69	3.85	10.29	9.18	5.5	5.2	6.55	11.03
CaO	10.08	12.29	9.20	12.69	10.28	9.48	10.7	8.97	7.63	7.19	8.54	10.68	10.8	8.5	10.16	8.87
Na_2O	2.70	2.19	3.73	2.64	2.54	2.98	3.26	2.80	3.80	4.10	3.16	3.25	3.2	4.0	3.30	2.24
K_2O	0.80	0.25	1.00	0.65	0.87	0.75	0.54	1.43	1.45	1.76	0.52	0.94	0.6	1.8	0.96	0.75
P_2O_5	0.35	0.17	-	0.35	0.42	0.34	0.30	0.47	0.59	0.59	0.26	0.65	0.4	0.9	0.71	0.13
H_2O^+	0.78	0.33	0.04	-	1.38	1.44	0.44	2.03	0.45	0.87	3.49	0.54	0.3	0.7	0.83	0.36
H_2O^-	0.33	0.07	0.07	-	0.36	0.83	0.09	0.83	0.47		-	0.27	-	-	-	0.30
CO_2	-	-	-	-	0.08	0.23	-	-	-	-	-	0.21	-	-	-	-
Total	99.24	99.71	99.18	100.00	99.81	100.00	100.99	99.70	100.18	99.83	100.25	99.40	100.0	99.49	100.39	100.55
ΣFe as FeO	10.96	10.23	15.52	11.20	11.94	13.68	10.26	10.49	11.22	11.17	12.28	12.63	8.67	11.05	12.58	12.04
100Mg/Mg+Fe^{2+}	65.2	63.6	39.9	55.8	57.7	44.8	64.8	62.1	51.6	42.0	63.8	60.5	57.2	49.7	52.3	65.8
Na_2O/K_2O	3.38	8.76	3.73	4.06	2.92	3.97	6.04	1.96	2.62	2.33	6.08	3.46	5.33	2.22	3.44	2.99
							C.I.P.W. Norms*									
or	4.73	1.48	5.91	3.84	5.14	4.43	3.19	8.45	8.57	10.40	3.07	5.55	3.55	10.64	5.67	4.43
ab	22.78	18.53	25.86	20.46	21.49	25.22	22.68	23.69	32.15	34.69	22.74	15.33	27.08	27.42	25.84	18.95
an	23.53	29.13	17.55	28.66	23.44	27.06	28.79	22.91	18.93	17.46	22.86	18.82	37.07	21.75	21.64	26.80
ne	0.03		3.09	1.02			2.66				2.16	6.59		3.48	1.13	
di	19.58	24.97	23.51	26.25	19.82	13.52	18.11	15.01	12.41	11.96	14.45	23.25	11.35	12.01	19.78	13.26
hy		12.74			7.85	3.18		2.92	13.68	10.52			3.90			14.16
ol	19.47	6.03	12.94	12.27	10.24	13.01	18.64	15.16	4.89	3.54	23.82	18.07	9.91	14.26	13.97	15.33
mt	2.69	2.51	3.81	2.75	2.93	3.36	2.52	2.58	2.76	2.74	3.02	3.10	2.13	2.72	3.09	2.96
il	4.37	3.29	6.15	3.84	5.70	6.23	3.21	5.03	4.48	5.13	4.08	5.66	3.70	4.18	6.44	3.61
ap	0.81	0.39		0.81	0.97	0.79	0.70	1.09	1.37	1.37	0.60	1.51	0.93	2.09	1.65	0.30
Rest	1.11	0.40	0.11		1.92	2.79	0.53	2.86	0.92	0.87	3.49	1.29	0.30	0.70	0.83	0.66
100 *an/ab+an*	50.8	61.1	40.4	58.3	52.2	51.8	55.9	49.2	37.1	33.5	50.1	55.1	57.8	44.2	45.6	58.6
D.I.	27.5	20.0	34.9	25.3	26.6	29.6	28.5	32.1	40.7	45.1	28.0	27.5	30.6	41.5	32.6	23.4
							Trace Elements µg/g									
V	-	-	-	-	-	-	-	205	-	100	-	220	-	-	-	-
Cr	370	-	-	124	-	-	-	176	-	42	-	420	-	-	75	-
Ni	75	102	-	72	-	26	-	126	-	23	-	245	-	-	-	-
Cu	25	110	-	-	-	103	-	50	-	37	-	125	-	-	78	-
Zn	55	74	-	-	-	92	-	95	-	81	-	-	-	-	100	-
Rb	18	-	16	8	-	13	10	26	-	24	9	-	9	-	15	-
Sr	382	-	522	486	-	608	408	659	-	577	313	-	400	-	480	375
Y	-	-	-	25	-	18	18	20	-	26	25	23	-	-	-	-
Zr	121	-	169	88	-	145	125	178	-	284	128	240	-	-	n.d.	-
Nb	-	-	37	26	-	27	14	44	-	-	6	64	-	-	-	-
Ba	250	-	474	380	-	375	167	297	-	369	235	360	150	-	n.d.	373
La	19.6	-	34	19.8	-	-	-	33	-	-	-	40	13	-	24	-
Ce	35.9	-	89	30	-	-	-	63	-	-	25	89	27	-	44	42
Nd	21.8	-	-	-	-	-	-	32	-	-	18	37	17	-	-	26

1. Basalt, Boina Volcanic Centre, Ethiopia (Barberi *et al.*, 1975, tables 1 & 2, no. G495).
2. Basalt, Erta'Ale Range, Ethiopia (Barberi *et al.*, 1974, table 1, no. CH48a; Treuil *et al.*, 1971, table 1, no. CH48a).
3. Hawaiite, Fantale Volcano, Ethiopia (Weaver *et al.*, 1972, table 1, no. Y802).
4. Basalt, southern Gregory Rift (Baker *et al.*, 1977, table 1, no. KLR-32).
5. Basalt, Aden Volcanic Centre (Cox *et al.*, 1970, table 3, no. A803).
6. Basalt, Jebel Khariz, Southern Arabia (Gass and Mallick, 1968, table 2, no. 87).
7. Basalt, Jebel al Abyad, Western Saudi Arabia (Baker *et al.*, 1973, table 2, no. 5).
8. Trachyandesite, Nandewar Volcano, N.S.W. (this study, no. 49000).
9. Hawaiite, Canobolas Volcano, N.S.W. (Middlemost, 1981, table 1, no. 3).
10. Hawaiite, Comboyne Volcanic Centre, N.S.W. (Knutson, 1975, tables 41 & A-3, Appendix III, no. 6570).
11. Basalt, Isle of Skye, Scotland (Thompson *et al.*, 1972, table 1, no. 918; Thompson *et al.*, 1980, table 1, no. 918).
12. Basalt, Banks Peninsula, New Zealand (Price and Taylor, 1980, tables 1 & 3, no. 104).
13. Porphyritic basalt inclusion, Mayor Island, New Zealand (Rutherford, 1978, tables 1 & 2).
14. Average hawaiite, Black Mountain Volcanic Centre, Nevada (Ekren *et al.*, 1971, table 14, no. 1).
15. Hawaiite, Pantelleria (Villari, 1974, tables 2, 3 & 4, no. 83V).
16. Basalt, Oki-Dogo Island, Japan (Uchimizu, 1966, table 15, no. 3; Nagasawa, 1973, table 1, no. 1).

* Calculated with $Fe_2O_3/FeO = 0.20$

\- = not determined

n.d. = not detected

TABLE 6.6

Representative analyses and C.I.P.W. norms of salic rocks associated with transitional alkaline mafic rocks from continental volcanic provinces

Analysis Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	70.85	71.60	69.56	63.65	69.54	72.0	71.5	72.82	68.18	73.79	60.66	69.43	74.7	69.25	68.00	72.73
TiO_2	0.36	0.42	0.49	0.94	0.33	0.51	0.14	0.14	0.20	0.15	0.89	0.24	0.22	0.25	0.35	0.24
Al_2O_3	9.78	11.50	9.62	14.12	12.77	9.0	11.8	12.95	15.59	10.74	15.87	13.65	10.1	9.10	8.73	9.57
Fe_2O_3	3.03	1.30	2.16	2.01	4.03	7.17	2.51	2.35	2.26	3.87	2.50	2.51	1.93	3.70	5.60	3.86
FeO	3.76	2.45	5.45	6.03	0.99	1.57	1.17	0.85	0.90	1.11	2.43	1.35	2.45	2.61	3.19	3.24
MnO	0.16	0.16	0.17	0.27	0.17	0.29	0.10	0.03	0.04	0.06	0.13	0.08	0.10	0.19	0.19	0.13
MgO	<0.01	0.42	0.02	0.04	0.13	0.00	<0.1	0.03	0.20	0.04	1.26	0.11	<0.01	0.01	0.38	0.26
CaO	0.30	1.44	0.47	1.31	0.62	0.90	0.28	0.19	0.27	0.22	2.04	0.38	0.20	0.06	0.60	0.07
Na_2O	5.93	6.10	6.66	6.34	5.48	5.05	6.03	5.32	6.30	5.16	5.65	5.80	5.60	7.00	6.74	4.71
K_2O	4.46	3.15	4.39	5.22	4.96	3.14	4.16	4.37	4.97	4.24	5.59	4.92	4.25	4.29	4.82	4.37
P_2O_5	0.04	0.08	-	0.07	0.04	0.04	0.12	0.02	0.40	0.02	0.53	0.07	0.01	0.01	0.13	0.00
H_2O^+	0.40	1.01	0.13	-	0.13	0.92	1.29	0.27	0.87	0.51	1.11	0.19	0.29	0.14	0.46	0.16
H_2O^-	0.39	0.00	0.08	-	0.44	0.24	0.14	0.47			-	0.15	-	0.01	0.06	0.12
CO_2	-	-	-	-	-	-	-	-	-		-	0.22	0.05	-	-	-
Total	99.47	99.63	99.20	100.00	99.63	100.83	99.34	99.81	100.18	99.91	98.66	99.10	99.90	99.62[1]	99.25	99.46
ΣFe as FeO	6.49	3.62	7.39	7.84	4.62	8.02	3.43	2.96	2.93	4.59	4.68	3.61	4.19	5.94	8.23	6.71
Agpaitic Index	1.49	1.17	1.63	1.14	1.13	1.30	1.22	1.04	1.01	1.22	0.97	1.09	1.37	1.78	1.87	1.30
C.I.P.W. Norms																
Q	26.75	24.40	24.66	4.38	19.63	32.82	24.31	25.50	12.17	29.25	2.25	17.34	32.53	27.34	22.76	29.72
or	26.36	18.61	25.94	30.85	29.31	18.56	24.58	25.82	29.37	25.06	33.03	29.07	25.12	25.30	28.48	25.82
ab	25.47	41.61	25.04	43.57	38.07	28.81	37.53	42.28	52.52	31.64	47.81	42.82	28.29	22.95	18.07	24.89
ac	8.77	3.76	6.25	5.82	7.31	12.26	7.26	2.41	0.69	10.59		5.51	5.58	11.04	16.20	11.17
ns	3.43	1.33	5.64	0.81			1.22						2.97	1.77	4.79	0.53
di	1.09	5.71	2.08	5.38	1.35	0.30	0.54	0.40	0.84	0.84	4.20	0.03	0.54		1.86	0.30
hy	6.03	2.20	8.46	7.26			1.82		0.11	1.39	2.29	1.99	4.03	4.76	5.62	6.28
mt					2.18	4.25		2.20	2.45	0.30	3.62	0.88				
il	0.68	0.80	0.93	1.79	0.63	0.97	0.27	0.27	0.38	0.28	1.69	0.46	0.42	0.47	0.66	0.46
ap	0.09	0.19		0.16	0.09	0.09	0.28	0.05	0.09	0.05	1.23	0.16	0.02	0.03	0.30	
Rest	0.79	1.01	0.21		0.57	2.78	1.43	0.88	0.87	0.51	1.11	0.84	0.40	2.66	0.52	0.28
Σ femics	20.09	13.99	23.36	21.22	11.56	19.49	11.39	5.47	4.56	13.45	13.03	9.03	13.56	18.07	29.43	18.74
D.I.	78.6	84.6	75.6	78.8	87.0	80.2	86.4	93.6	94.1	85.9	83.1	89.2	85.9	75.6	69.3	80.4
Trace Elements µg/g																
Cr	86	-	n.d.	-	n.d.	-	400	1	-	n.d.	-	-	n.d.	n.d.	n.d.	-
Ni	0.3	9	n.d.	-	-	-	-	12	-	16	-	-	n.d.	n.d.	6	-
Cu	-	7.5	-	-	3	-	-	7	-	7	-	-	6	3	9	-
Zn	120	113	260	-	-	192	-	260	-	237	-	-	-	-	410	-
Rb	148	77	120	115	220	39	228	294	-	416	79	-	134	900	200	-
Sr	2	96	12	10	15	48	8	1	-	5	271	-	0.3	1.5	18	-
Y	-	-	130	93	120	-	173	130	-	95	34	80	145	500	-	-
Zr	1175	-	1050	764	>1000	296	2212	1245	-	2848	388	1100	1100	6530	2920	-
Nb	-	-	155	207	360	121	273	282	-	-	22	175	69	680	-	-
Ba	n.d.	-	700	160	210	757	9	4	-	2	2289	54	9	5	n.d.	-
La	151	-	120	152	220	-	-	55	-	-	-	133	95	-	251	-
Ce	269	-	270	185	-	-	-	103	-	-	203	225	150	-	408	-
Nd	119	-	-	91	-	-	-	50	-	-	89	87	89	-	-	-

1. Pantellerite, Boina, Volcanic Centre, Ethiopia (Barberi *et al.*, 1975, tables 1 & 2, no. D227).
2. Comendite, Erta' Ale Range, Ethiopia (Barberi *et al.*, 1974, table 1, no. CH20; Treuil *et al.*, 1971, table 1, no. CH20).
3. Pantellerite, Fantale Volcano, Ethiopia (Gibson, 1972, table 1, no. Y346).
4. Peralkaline trachyte, southern Gregory Rift (Baker *et al.*, 1977, table 1, no. KLR-54).
5. Comendite, Aden Volcanic Centre (Cox *et al.*, 1970, tables 3 & 6, no. A843).
6. Pantellerite, Jebel Khariz, South Arabia (Gass and Mallick, 1968, table 2, no. 105).
7. Comendite, Jebel al Abyad, Western Saudi Arabia (Baker *et al.*, 1973, table 2, no. 26).
8. Comendite, Nandewar Volcano, N.S.W. (this study, no. 49163).
9. Comendite, Canobolas Volcano, N.S.W. (Middlemost, 1981, table 5, no. 26).
10. Pantellerite, Comboyne Volcanic Centre, N.S.W. (Knutson, 1975, tables 4.1 & A-3, Appendix III, no. 6641).
11. Trachyte, Isle of Skye, Scotland (Thompson *et al.*, 1972, table 1, no. 208; Thompson *et al.*, 1980, table 1, no. 208).
12. Comendite, Banks Peninsula, New Zealand (Price and Taylor, 1980, tables 1 & 3, no. 93).
13. Pantellerite, Mayor Island, New Zealand (Ewart *et al.*, 1968, tables 4 & 5, no. 5).
14. Pantellerite, Gold Flat Member of the Thirsty Canyon Tuff, Western U.S.A. (Noble, 1965, table 1, no. 1; Noble and Parker, 1974, table 1, no. 7).
15. Pantellerite, Pantelleria (Villari, 1974, tables 2, 3 & 4, no. 137V).
16. Pantellerite, Oki-Dogo Island, Japan (Uchimizu, 1966, table 15, no. 38).

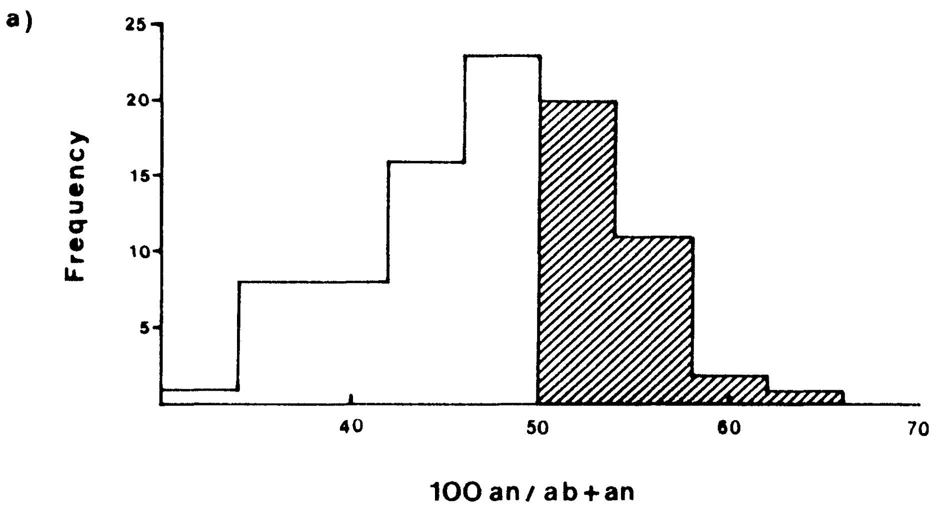
- = not determined n.d. = not detected

[1] Includes 0.78% Cl, 1.30% F, 0.78% ZrO_2, 0.08% SO_3, 0.62% other, 0.16% rare alkalis, less 0.72% O≡F, Cl.

Easter Island, the most abundant mafic type is hawaiite (Baker *et al.*, 1974). The abundance of trachyandesites and hawaiites relative to basalts is clearly illustrated by the frequency histograms of 100*an/ab+an* ratios (Fig. 6.1) for predominantly aphyric or mildly porphyritic rocks with 100*an/ab+an* > 30. Although the number of analyses is to some extent limited by the selection criteria, analyses of rocks with 100*an/ab+an* = 30 to 50 are evidently significantly more common than those with 100*an/ab+an* ⩾ 50 in both oceanic island and continental environments.

A more obvious characteristic of the mafic rocks is provided by the *M* numbers of the most mafic rocks in each province (column 2, Tables 6.1 and 6.2), and the frequency histograms of *M* numbers of eruptives with $M > 40$ (Fig. 6.2). It is clear from these data, and also from other more generalized studies of mafic alkaline rocks (e.g. Schwarzer and Rogers, 1974), that the great majority of mafic rocks in these volcanic provinces have *M*-values significantly less than 66. According to many workers (e.g. Irving and Green, 1976; Frey *et al.*, 1978), these aphyric volcanics with $M < 66$ would not be primary mantle-derived partial melts because liquids with such compositions would not be in equilibrium with residual upper mantle peridotites of 'pyrolite' type with $M = 90 \pm 2$. If this is so, the scarcity of 'primary' melts ($M = 66$ to 75) in these volcanic provinces implies significant fractionation of a Mg-rich phase (olivine or orthopyroxene) from these melts prior to their eruption at the surface.

There is significant variation in the degree of silica saturation or undersaturation displayed by the mafic rocks from the various provinces. The Bouvetoya and Easter Island suites have variants that are *qz*-normative and clearly subalkaline associated with *hy+ol*-normative types which range from alkaline to subalkaline using the discriminant function proposed by Chayes (1966). Some of the mafic rock types from the Canobolas, Comboyne and Oki Dôgo provinces (Table 6.5, analyses 9, 10 and 16 respectively) are also *hy+ol*-normative and subalkaline in character. Most other provinces exhibit a range of mafic rock compositions between mildly undersaturated *ne*-normative and *hy+ol*-normative types with alkaline affinities.



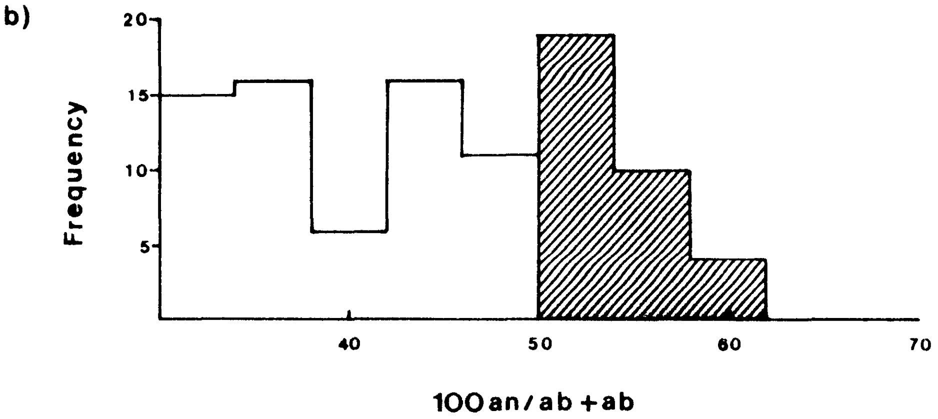
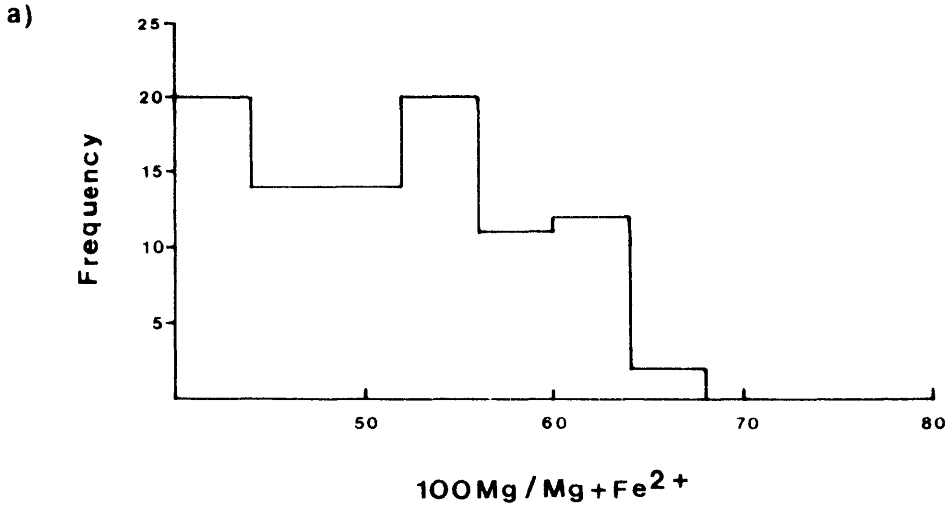


Fig. 6.1: Frequency histograms for 100*an/ab+an* ratios of mafic volcanics associated with trachytes and peralkaline rhyolites from a) oceanic island, and b) continental volcanic provinces.



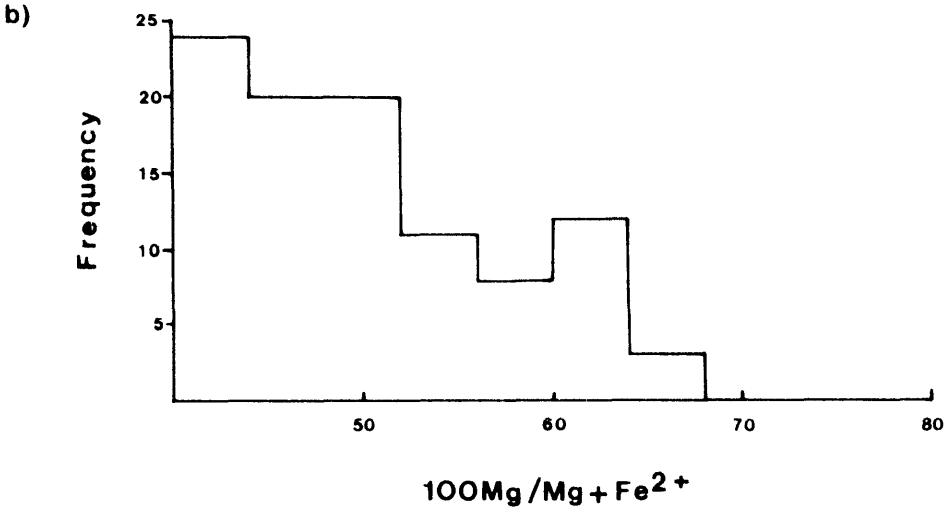


Fig. 6.2: Frequency histograms for 100Mg/Mg+Fe^{2+} (*M*) ratios of mafic volcanics associated with trachytes and peralkaline rhyolites from a) oceanic islands, and b) continental volcanic provinces.

Range of Rock Types in the Suites

Although many of the suites examined are devoid of mafic rocks which would generally be regarded as 'primary' mantle-derived basalts, most suites exhibit a reasonably continuous range of compositions between the most mafic types (typically hawaiites or trachyandesites) and the most 'evolved' variants which are either trachytic or rhyolitic. A list of the most evolved rock types in each province (column 5, Tables 6.1 and 6.2) indicates that comendites and/or pantellerites are the most common felsic associates of transitional alkaline mafic rocks in continental and oceanic island settings. Chayes (1970) noted that the characteristic silicic volcanic rocks on the oceanic islands are comendites, whereas pantellerites are more common in continental alkaline volcanic provinces. However, the occurrence of comendites and pantellerites in both environments suggests that their conditions of formation are not specific to a particular crustal regime. Pantellerites and comendites are field associates in a number of suites, whereas in others either pantellerites or comendites are the most 'evolved' types. Several suites, including Skye, Gough, Réunion, Paka and southern Gregory Rift are characterized by peraluminous or peralkaline trachytes as the most 'evolved' representatives.

Chemical Variation Within and Between Suites

Major Elements

All transitional alkaline suites with a moderately wide range of rock compositions exhibit an increase in SiO_2 content from the mafic to the felsic members. The highly silicic rhyolites characteristic of the majority of suites have 10 to 35 percent *qz* in the norm. A comparison of pantellerite and comendite analyses indicates that pantellerites typically have lower SiO_2 contents (66 to 72 wt. percent) than comendites (70 to 75 wt. percent). However, pantellerites from several suites including Chabbi and Mayor Island have considerably higher SiO_2 contents (73 to 75 wt. percent) than comendites from other suites (e.g. Banks Peninsula and Aden, 67 to 70 wt. percent). In other chemical characteristics these high SiO_2 pantellerites appear to be transitional to comendites and have relatively low total Fe contents (total Fe as FeO = 3 to 6 wt. percent) compared to typical pantellerites from Pantelleria (total Fe as FeO = 5 to 9 wt. percent, cf. Table 6.6, analysis 15). The compositional differences between continental and oceanic island comendites noted by Bailey and Macdonald (1970) relate principally to the higher SiO_2 contents of some continental types, although this is not universal.

The mafic members of the various suites exhibit limited variation in Al_2O_3 content. High-Al (i.e. > 16 wt. percent) aphyric or mildly porphyritic mafic types are represented in the Jebel al Abyad and Comboyne suites although many specimens from the latter are quite 'evolved' hawaiites (cf. Table 6.5, analysis 10). The mafic rocks from the remaining suites are characterized by moderately low Al_2O_3 contents (13.0 to 15.5 wt. percent). Variation of Al_2O_3 content with Fractionation Index (F.I.) does not follow a single trend for all suites. Several, including Boina and Erta Ale, exhibit strong depletion of Al_2O_3 in some intermediate members of the series (minimum of 9.07 wt. percent Al_2O_3 in a ferrobasalt from Erta Ale; Barberi *et al.*, 1974, Table 1, analysis F12), followed by a trend of Al_2O_3 enrichment in the more'evolved' trachytes. The Boina suite exhibits an additional trend of Al_2O_3 depletion in the transition from the trachytes to the pantellerites. This trend does not occur in the Erta Ale series and comendites from this suite are characterized by similar or higher Al_2O_3 contents, compared with intermediate members of the suite. The suites from Bouvetoya, Terceira, Easter, Socorro, Pantelleria, Oki Dôgo and Jebel Khariz also exhibit a trend of decreasing Al_2O_3 with increasing F.I., but it is gradual and continuous from the mafic to the felsic types. A contrasting trend of Al_2O_3 variation with increasing F.I. is shown by the suites from Réunion, Aden and Little Aden, Paka, Silali, Canobolas, Comboyne and to a lesser extent Gough Island. In these suites Al_2O_3 increases initially with increasing F.I. and then decreases in the most 'evolved' associates.

There is considerable variation in the total Fe content of the mafic members of the various suites. This is partly attributable to varying D.I. and MgO contents of the most mafic representative in each suite. However, comparison of specimens with similar D.I. and MgO contents indicates that high-Fe (total Fe as FeO = 12 to 14 wt. percent) mafic rocks are represented in the Easter, Bouvetoya, Ascension, Socorro, Boina, Paka, southern Gregory Rift, Jebel Khariz, Skye, Banks Peninsula and Pantellerian suites, whereas the mafic members of the remaining suites are in general characterized by lower total Fe (i.e. total Fe as FeO < 12 wt. percent). Fe content varies antipathetically with Al_2O_3 content in the suites which exhibit strong Al_2O_3 depletion (e.g. Boina and Erta Ale). The intermediate members of these suites are characterized by a marked absolute enrichment of Fe (total Fe as FeO up to 23.3 wt. percent) in a dark trachyte from Erta Ale; Barberi *et al.*, 1974, Table 1, analysis F55), whereas the more evolved trachytes and comendites are rapidly depleted in Fe. Barberi *et al.* (1974) noted that this trend of absolute Fe enrichment closely parallels the trend displayed by tholeiitic lavas from Thingmuli, Iceland (Carmichael, 1964). A further trend of Fe enrichment is evident for the Boina suite in the transition from the trachytes (total Fe as FeO = 5 wt. percent) to the pantellerites (total Fe as FeO up to 7 wt. percent).

The variation of total Fe in the low-Fe suites and the remaining high-Fe suites generally follows a trend of gradual depletion with increasing F.I. except for the suites which have pantellerites as their most evolved members, and these typically exhibit late Fe-enrichment. The total Fe contents of the mafic members of a suite apparently has no direct bearing on the Fe content of the associated felsic rocks, because pantellerites (high-Fe) and comendites (low-Fe) display no preferential association with either high-Fe or low-Fe mafic volcanics.

In all suites MgO and CaO exhibit trends of gradual depletion with increasing F.I. Depletion in MgO tends to be more rapid than CaO in the mafic and intermediate rocks and the rate of decrease of MgO also decreases with increasing F.I. CaO displays remarkably linear variation trends with F.I. for most suites. Comendites and pantellerites from the majority of suites are extremely depleted in MgO (usually << 0.3 wt. percent MgO) and to a lesser extent CaO (usually < 0.7 wt. percent CaO). Pantellerites from Pantelleria (0.15 to 0.91 wt. percent MgO), Gran Canaria (0.2 to 1.15 wt. percent MgO) and comendites from Erta Ale (0.42 to 0.67 wt. percent MgO) exhibit relatively high MgO contents by comparison. Unusually high CaO contents (0.6 to 2.2 wt. percent CaO) are also a feature of the comendites from Bouvetoya, Erta Ale and Aden, and pantellerites from Jebel Khariz and Pantelleria.

The alkali relations for the suites, indicated in column 4 of Tables 6.1 and 6.2, vary from strongly sodic (Na_2O/K_2O >> 2) to moderately potassic (Na_2O/K_2O < 2). The suites from Erta Ale, Jebel Khariz, Jebel al Abyad, Skye and Easter Island are strongly sodic with $Na_2O/K_2O = 4$ to 8.8 for the more mafic variants. Mafic rocks characterized by very high Na_2O/K_2O ratios typically have quite low K_2O (0.2 to 0.6 wt. percent K_2O). The distinctly sodic character of the mafic types in these suites is also clearly apparent in the more 'evolved' variants, whereas suites with mafic members which are only mildly sodic often have intermediate members with moderately potassic affinities (e.g. Silali, Aden, Comboyne, Gran Canaria, Terceira, Oki Dôgo and Black Mountain). The most potassic transitional alkaline series described to date is from Gough Island. The mafic members of this suite have $Na_2O/K_2O = 1.5$ and several trachytes have $Na_2O/K_2O < 1$.

In general, pantellerites are characterized by higher Na_2O/K_2O ratios and agpaitic indices (molecular Na_2O+K_2O/Al_2O_3) than comendites (MacDonald and Bailey, 1973), but comendites from the strongly sodic suites noted above have higher Na_2O/K_2O ratios than many pantellerites (Fig. 6.3a). A plot of Na_2O/K_2O versus D.I. for mafic rocks associated predominantly with pantellerites and comendites (Fig. 6.3b) indicates that there is complete overlap of Na_2O/K_2O ratios of the mafic variants. In the light of these data it appears that the alkali relations of the mafic rocks in a specific suite have no bearing on the development of either pantellerite or comendite as the most evolved volcanic associate of that suite.

The concentration of TiO_2 varies moderately between the mafic members of the various suites. Mafic rocks with moderately high TiO_2 (> 3.0 wt. percent) are also typically high-Fe types, whereas low-Fe types usually have TiO_2 < 3.0 wt. percent. Variation of TiO_2 within the suites follows a trend of gradual depletion with increasing F.I., or alternatively, several suites (e.g. Boina and Erta Ale) display an initial slight increase in TiO_2 followed by a trend of depletion towards the more 'evolved' types. Pantellerites and comendites exhibit considerable overlap in their TiO_2 contents which are generally quite low (<0.5 wt. percent TiO_2).

Variation in the MnO content between the mafic rocks of the suites is small, even where there are significant differences in total Fe, TiO_2 and alkalies. In suites with comendites as the most 'evolved' represent-

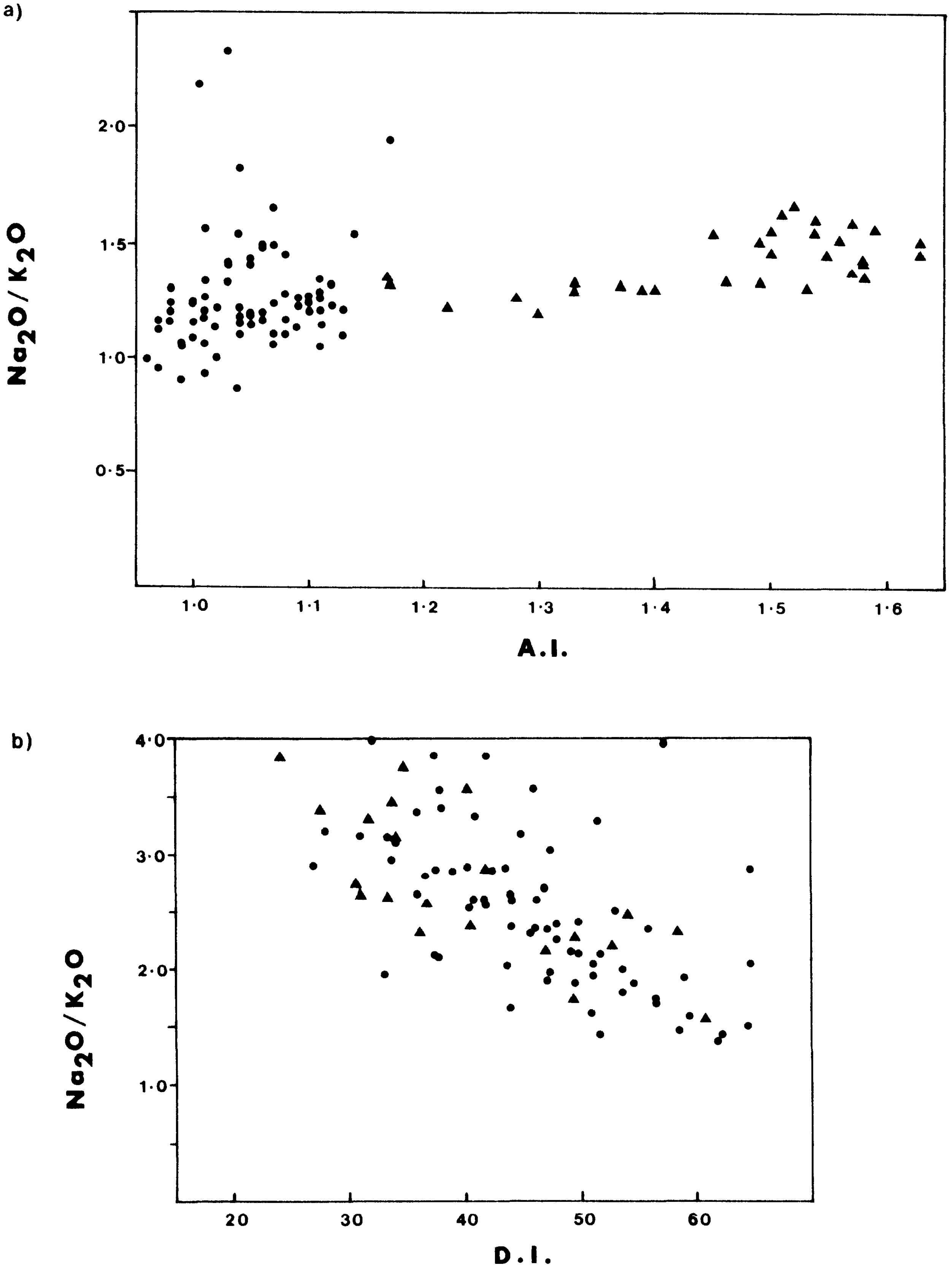


Fig. 6.3: a) Na_2O/K_2O versus Agpaitic Index for pantellerites (triangles) and comendites (dots) from all provinces.

b) Na_2O/K_2O versus D.I. for mafic to intermediate rocks associated predominantly with pantellerites (triangles) and comendites (dots).

ative MnO contents usually increase initially with increasing F.I. and are then strongly depleted in the highly-silicic members (< 0.10 wt. percent MnO). The Socorro, Erta Ale and Aden comendites have atypically high MnO concentrations (0.11 to 0.22 wt. percent). In contrast, pantellerites are characteristically enriched in MnO (0.10 to 0.33 wt. percent) compared to comendites, and those from Pantelleria, Boina, Jebel Khariz, Terceira and Socorro also exhibit absolute enrichment of MnO over associated mafic rocks.

P_2O_5 concentrations vary considerably between the mafic members of the various suites. Low P_2O_5 levels (0.08 to 0.40 wt. percent) typify the mafic rocks from the Skye, Erta Ale, Oki Dôgo and Gough Island, whereas the mafic rocks from most other suites have P_2O_5 = 0.3 to 1.0 wt. percent. All suites display an initial enrichment in P_2O_5 content with increasing F.I. followed by a strong depletion. Uniformly low P_2O_5 values (< 0.1 wt. percent) are characteristic of comendites and pantellerites from most suites, although a comendite from Oki Dôgo (Uchimizu, 1966, Table 15, analysis 30) and a pantellerite from Jebel Khariz (Gass and Mallick, 1968, Table 2, analysis 90) have what appear to be extraordinarily high P_2O_5 contents (0.75 and 0.64 wt. respectively).

Trace Elements

Available trace element data for representative mafic and felsic rocks from oceanic and continental provinces are listed in Tables 6.3, 6.4, 6.5 and 6.6.

The transition elements V, Cr and Ni display a wide range of concentrations in the mafic members of the suites. Part of this variation is possibly due to variations in M values of the most mafic members in each province, although, rocks with M = 61 to 66 from a number of provinces have 90 to 220 µg/g V, 220 to 420 µg/g Cr and 75 to 245 µg/g Ni. These values largely overlap with estimated ranges of trace element abundances in 'primary' (i.e. M = 66 to 75) alkali basalts from the Monaro volcanics, New South Wales (Kesson, 1973). The range of trace element abundances suggested by Kesson for 'primary' alkali basaltic melts are V = 115 to 170 µg/g, Cr = 165 to 310 µg/g and Ni = 115 to 235 µg/g. Suites in which the most mafic members have M < 60 (e.g. Bouvetoya, southern Gregory Rift, Comboyne and Mayor Island) typically have quite low Cr and Ni contents (e.g. 23 to 124 μg/g Cr and 7 to 85 μg/g Ni for those suites). V, Cr and Ni are usually depleted quite rapidly to very low levels (i.e. < 10 μg/g) in the intermediate members of most suites and generally remain at very low levels in the most 'evolved' members of each suite. Pantellerites from Boina and comendites from Jebel al Abyad are unusual in that they display exceptional enrichment of Cr (86 to 400 μg/g) over less evolved associates. Slight enrichment of Ni is also evident in the Comboyne and Erta Ale comendites and a pantellerite from Jebel Khariz (up to 36 μg/g Ni), compared with intermediate members of those suites.

Cu also exhibits a considerable range of concentrations within the mafic variants of the various suites. Mafic rocks with similar *M* values have Cu contents which range from 25 μg/g (Boina) up to 270 μg/g (Réunion). Zn contents are less variable in mafic rocks of similar *M* value and range from 55 μg/g (Boina) to 74 μg/g (Erta Ale). Cu either exhibits a trend of gradual depletion with increasing F.I., or alternatively, slight enrichment in the intermediate rocks followed by depletion to low levels (1 to 11 μg/g) in the most 'evolved' types. On the other hand, Zn displays variable behaviour within and between suites. It is commonly enriched in pantellerites (e.g. Pantelleria, up to 410 μg/g) and comendites (e.g. Comboyne, up to 811 μg/g), although in some suites Zn is depleted compared to associated mafic and intermediate types (e.g. Bouvetoya, 39 μg/g in comendite compared to 140 μg/g in mafic type). Enrichment of Zn in felsic rocks (with similar F.I.) from a single suite is also sometimes quite erratic (e.g. Comboyne comendites 237 to 811 μg/g).

Apart from being clearly more potassic than other transitional alkaline suites, the Gough Island suite is characterized by significantly higher concentrations of Rb, Sr and Ba. The Gough Island mafic rocks (100 μg/g Rb) have up to 100 times the Rb concentrations of mafic rocks with similar *M* values from other provinces. The Skye, Jebel Khariz and Easter Island mafic rocks are the most depleted in Rb (1 to 14 μg/g), whereas the mafic variants of most other suites have Rb values in the range 10 to 20 μg/g. The Skye and Easter Island mafic rocks also have somewhat lower concentrations of Ba (49 to 235 μg/g) compared to those from most other suites (170 to 690 μg/g) and Gough Island in particular (650 to 900 μg/g). Sr levels in the Gough Island mafic rocks (650 to 700 μg/g) are typically higher than those from other suites (304 to

711 µg/g). Ba and Sr are usually enriched in the intermediate rocks of most suites followed by depletion to low levels (< 50 µg/g) in the most 'evolved' types. A comendite from Jebel Khariz is exceptional in having higher Sr (612 µg/g) than associated mafic and intermediate variants. However, pantellerites and comendites sometimes display enrichment in Ba relative to intermediate and mafic associates. This is evident for the suites from Boina, Fantale, Bouvetoya, Pantelleria, Gran Canaria and Easter Island for which comendites and pantellerites have Ba in the range 183 to 1035 µg/g. Rb exhibits a trend of gradual enrichment with increasing F.I. in most suites, although like Zn, this enrichment is occasionally quite erratic amongst felsic rocks of similar F.I. from the same suite (e.g. Comboyne comendites, 197 to 904 µg/g Rb). An exception to the general trend of Rb enrichment in felsic rocks is provided by a pantellerite from Jebel Khariz which has an extraordinarily low concentration of Rb (39 µg/g) compared to several intermediate and mafic associates (up to 104 µg/g).

Zr and Nb display a restricted range of concentrations amongst the mafic members of many suites (typically 120 to 150 µg/g Zr and 20 to 40 µg/g Nb). In contrast the basaltic rocks from Skye exhibit a relatively broad range in Zr concentrations (84 to 176 µg/g) and have significantly lower Nb contents (4 - 10 µg/g) than the mafic rocks of all other suites for which data are available. On the other hand, unusually high Zr and Nb concentrations (160 to 240 µg/g Zr and 43 to 64 µg/g Nb) characterize the most mafic variants from the Banks Peninsula suite. All suites display trends of enrichment in Zr and Nb with increasing F.I. Enrichment, particularly of Zr in pantellerites and comendites, is sometimes to extreme levels (e.g. Pantelleria and Comboyne, up to 3040 and 5827 µg/g Zr in a pantellerite and comendite respectively), and is sometimes quite erratic amongst felsic members with similar F.I. from a particular suite (e.g. Comboyne, 815 to 5827 µg/g Zr). Available data do not indicate such extreme enrichment and fluctuations of Nb in the felsic members of the suites.

The LREE content of the mafic members of the suites is moderately restricted, compared with the variability of certain other trace elements. Most suites have mafic members with La = 20 to 30 µg/g, Ce = 36 to 60 µg/g and Nd = 20 to 30 µg/g, whereas Skye lavas with similar *M* values are characterized by considerably lower concentrations (La = 5 to 14 µg/g, Ce = 15 to 33 μg/g and Nd = 13 to 27 μg/g). Enrichment of the LREE with increasing F.I. is a feature of all suites, and in common with the behaviour of Zr and Zn, occasionally this enrichment is both erratic and extreme (e.g. Black Mountain pantellerites, La = 69 to 439 μg/g and Ce = 123 to 796 μg/g). It is evident in suites for which more complete REE analyses are available (i.e. Pantelleria, Skye, Oki Dôgo, Boina, Banks Peninsula, Gough, Bouvetoya and Terceira) that many quite 'evolved' rocks, including trachytes, benmoreites and tristanites, exhibit no relative depletion of Eu (commonly interpreted as indicative of plagioclase fractionation) in chondrite-normalized plots. On the other hand, pantellerites and comendites invariably display negative Eu anomalies.

Isotopes

The ranges of initial $^{87}Sr/^{86}Sr$ ratios and $^{206}Pb/^{204}Pb$ ratios in the suites for which data are available are listed in Table 6.7. The oceanic lavas generally exhibit a more restricted range of $^{87}Sr/^{86}Sr$ ratios than the continental lavas. Exceptions to this include, trachytic and rhyolitic lavas from Ascension, Gough (Gast *et al.*, 1964) and Easter Islands (Baker *et al.*, 1974) which have significantly higher $^{87}Sr/^{86}Sr$ ratios than their mafic associates. More recent data on Sr isotopes in Ascension lavas (O'Nions and Pankhurst, 1974) indicate a much more restricted range. It should be noted that the specimens analyzed by Gast *et al.* (1964) which were enriched in radiogenic Sr also had anomalously high $^{206}Pb/^{204}Pb$ ratios.

A plot of initial $^{87}Sr/^{86}Sr$ ratio vs F.I. for both continental and oceanic suites (Fig. 6.4) shows that the greater spread in $^{87}Sr/^{86}Sr$ ratios of the continental lavas is due to the generally higher values which characterize the more 'evolved' types. In contrast the Boina lavas (Barberi *et al.*, 1980) display a very restricted range of $^{87}Sr/^{86}Sr$ values.

Nd isotopic data are only available for several basalts and trachytes from Bouvetoya and Ascension (O'Nions *et al.*, 1977) and they have been plotted on a ε_{Nd} vs ε_{Sr} diagram (Fig. 5.15a) for comparison with a Nandewar hawaiite. Both suites have higher $^{143}Nd/^{144}Nd$ and lower $^{87}Sr/^{87}Sr$ ratios than postulated unmodified upper mantle (O'Nions *et al.*,

Table 6.7

Variation of initial $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ ratios in transitional alkaline suites from continental and oceanic island settings

Suite	Range $^{87}Sr/^{86}Sr$	Range $^{206}Pb/^{204}Pb$	References
Boina	0.7046 - 0.7074	-	Barberi *et al.* (1975)
	0.70368 - 0.70381	-	Barberi *et al.* (1980)
Erta Ale	0.7022 - 0.7048	-	Barberi *et al.* (1970)
	0.70354 - 0.70410	-	Barberi *et al.* (1980)
Fantale	0.7034 - 0.7091	-	Dickinson & Gibson (1972)
Jebel Khariz	0.7036 - 0.7069	-	Dickinson *et al.* (1969)
Aden	0.7038 - 0.7068	-	Dickinson *et al.* (1969)
Skye	0.70311 - 0.70571	-	Moorbath & Thompson (1980), Thompson *et al.* (1982)
		14.33 - 17.72	Dickin (1981)
Pantelleria	0.7023 - 0.7067	-	Barberi *et al.* (1969), Korringa & Noble (1972)
Gough	0.7039 - 0.7058	18.36 - 18.73	Gast *et al.* (1964)
Bouvetøya	0.70365 - 0.70376	-	O'Nions & Pankhurst (1974)
Ascension	0.7025 - 0.7072	19.43 - 19.78	Gast *et al.* (1964)
	0.70276 - 0.70287	-	O'Nions & Pankhurst (1974)
Terceira	0.70349 - 0.70370	-	O'Nions & Pankhurst (1974)
	0.70343 - 0.70373	-	White *et al.* (1979)
Easter	0.7025 - 0.7050	-	Baker *et al.* (1974)
		19.25 - 19.31	Tatsumoto (1966)
Réunion	0.7040 - 0.7046	- -	McDougall & Compston (1965), Ludden (1978a)
		18.68 - 18.78	Oversby (1972)

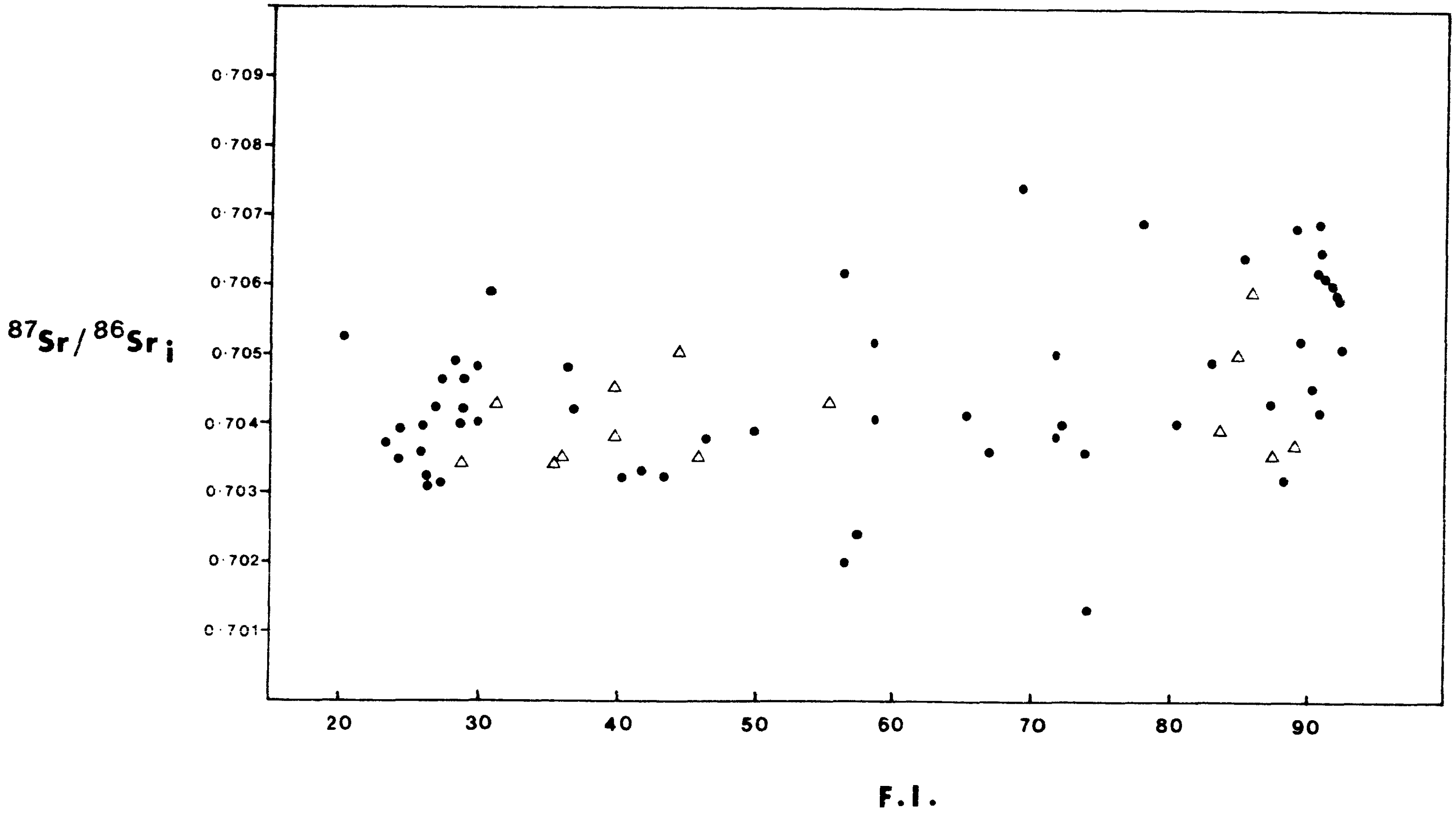


Fig. 6.4: Plot of initial $^{87}Sr/^{86}Sr$ ratio versus Fractionation Index for some volcanics from continental (circles) and oceanic island (triangles) provinces.

1977) indicating their derivation from a source region which was at some stage in its history depleted in LREE and Rb.

MODELS OF ORIGIN

The processes generally considered most important in the development of igneous rocks with contrasting compositions, and which may have operated singly or in association with others to produce the compositional variation observed in alkaline volcanic suites include:

1) Solid + Liquid (Fluid) Systems

   a) Closed-system fractional crystallization at high or low pressures
   b) Partial melting in the lower crust or upper mantle
   c) Metasomatism
   d) Contamination/hybridism/wall-rock reaction

2) Liquid + Vapour Systems

   Volatile transfer - closed-system or open-system (loss/addition)

3) Liquid Only Systems

   a) Magma mixing
   b) Liquid immiscibility
   c) Thermogravitational diffusion

High-Pressure Fractionation

A small but increasing number of relatively 'evolved' volcanic rocks are now interpreted as direct derivatives from high-pressure (> 9 to 10 kb) regimes. Lherzolite nodules occur in *ne*-normative hawaiites, mugearites and benmoreites from volcanic provinces in Victoria (Green *et al.*, 1974; Irving and Green, 1976; Ellis, 1976), south-eastern Queensland (Green *et al.*, 1974) and North Otago, New Zealand (Price and Green, 1972). Relatively 'evolved' lherzolite-bearing hosts with transitional chemistries include a trachyandesite from Taka-sima, North Kyusyu, Japan (Kuno, 1964) and a hawaiite from Kyogle, New South Wales (Wilkinson and Binns, 1969). Inclusions variously described as dunite or wehrlite and which may belong to the Al-augite group of Wilshire and

Shervais (1975) or Ti-augite group of Wilkinson (1975), have also been reported in mafic rocks from several provinces (e.g. Oki Dôgo, Ascension, Terceira and Réunion; see Tables 6.1 and 6.2, column 7). To date the most 'evolved' lherzolite-bearing hosts recognized include phonolites from Bokkos, Nigeria (M = 50.9, D.I. = 84.5; Wright, 1969; Irving and Price, 1974,1981), the McBride volcanic province, north-eastern Australia (M = 51.1; D.I. = 81.2) and Heldburg, Germany (M = 67.8, D.I. = 85.9; Irving and Price, 1981).

Cr-diopside lherzolite xenoliths are generally considered to represent either unmodified or very slightly modified lithospheric fragments accidently incorporated in their host magmas at depths greater than 20 to 30 km (Kleeman *et al.*, 1969; Nagasawa *et al.*, 1969; Frey and Green, 1974; Wilkinson, 1975; Hutchison *et al.*, 1975). Ultramafic xenoliths composed predominantly of tschermakitic pyroxenes commonly accompany lherzolite nodules and are interpreted either as magmatic precipitates at greater than 9 to 10 kb (Irving, 1974a,b; 1980; Ellis, 1976) or, for relatively Cr-rich clinopyroxenes, as samples of essentially unmodified layered upper mantle (Wilkinson, 1973). Various megacrysts often accompany both types of inclusions and there is considerable compositional and textural evidence (Binns *et al.*, 1970; Green and Hibberson, 1970; Knutson and Green, 1975) which suggests that they are cognate precipitates from their hosts at elevated pressures. However, variable megacryst compositions (Irving, 1974a; Stuckless and Irving, 1976) and apparent inconsistencies between megacryst assemblages and host basalt compositions in the Victorian volcanic province led Irving (1974a) to suggest that megacrysts may represent a random sample of phases precipitated from host and/or derivative and parental magmas, and hence they are of little use in deducing detailed fractionation trends in basaltic magmas.

Preservation of these high-pressure inclusions and precipitates which exhibit clear evidence of disequilibrium with their hosts at upper crustal P-T conditions, as well as considerations of necessary flow rates based on thermodynamic calculations (Maaløe, 1973) and viscosity measurements of natural liquids at elevated pressures (Kushiro *et al.*, 1976), provides strong evidence for rapid ascent and extrusion of these magmas from upper mantle pressure regimes.

Considerable field, chemical and experimental evidence indicates that intermediate to salic rocks, traditionally regarded as low-pressure fractionates of basaltic melts, may also be generated in the lower crust or upper mantle. Because of their low M values (M often << 66) these relatively 'evolved' melts are commonly interpreted as the products of fractional crystallization of 'primary' basaltic melts with M = 66 to 75 (Green *et al.*, 1974; Irving and Green, 1976; Irving and Price, 1981). Melts with $M < 66$ are not generally regarded as products of direct partial melting of the upper mantle (Green *et al.*, 1974; Irving and Green, 1976; Wass, 1980) because constraints imposed by the partitioning of Fe and Mg between olivine and liquid (Roeder and Emslie, 1970) indicate that such melts would not be in equilibrium with olivine ($Fo_{90 \pm 2}$) in 'pyrolite-type' model upper mantle compositions (Ringwood, 1966; Carter, 1970; Ringwood, 1975; Maaløe and Aoki, 1977; Green *et al.*, 1979).

Thompson (1972b) also suggested that certain 'andesitic' lavas (including tholeiitic andesites, hawaiites and trachyandesites) are largely produced by *in situ* closed-system high-pressure partial crystallization of bodies of basaltic magma. This proposal was based on the presence of a chemical discontinuity between basaltic and intermediate lavas from numerous anorogenic volcanic suites.

Several important criteria must be satisfied before an origin for the relatively 'evolved' lavas involving high-pressure fractionation can be accepted as viable. Firstly, if as suggested by Thompson (1972b) intermediate lavas formed in this manner are rapidly erupted with little further modification, then reasonable evidence in the form of high-pressure megacrysts and/or cognate cumulate inclusions should be observed if indeed high-pressure fractionation controls have been operative. Although such evidence is clearly present in the examples described above, it is commonly lacking in suites for which involvement of high-pressure fractionation processes have been advocated (cf. Thompson, 1972b). It is conceivable that evidence of high-pressure crystallization and derivation would be obliterated if the magmas were retained in subvolcanic magma chambers for extended periods. However, if the production of 'andesitic' melts by high-pressure fractionation is a widespread phenomenon, as appears to be required by the paucity of 'primary' ($M < 66$) liquids in many volcanic provinces, a reasonable proportion of these melts should be expected to ascend directly from the upper mantle with at least some evidence of their evolution at elevated pressures. An alternative model of polybaric fractionation of ascending magmas involving continuous plating of crystals on to conduit walls (Irving, 1980; Irving and Price, 1981) requires quite slow magma flow rates to permit production of relatively 'evolved' liquids. Slowly ascending magmas depositing crystals on conduit walls would obviously not contain ultramafic inclusions and megacrysts. Therefore, 'evolved' magmas such as the Bokkos phonolite (Nigeria) which carry high-pressure ultramafic inclusions belonging to the Cr-diopside xenolith suite (Wright, 1969; Irving and Price, 1981) and which have clearly been transported from upper mantle pressures to the surface in relatively short periods of time, would not in all likelihood have been produced by such a process.

It is also important when assessing the role of high-pressure fractionation in the genesis of the more 'evolved' members of volcanic suites ($M < 66$), that reasonable material balance be demonstrated between the alleged parent, its derivative and the crystal extracts controlling the fractionation process. Assuming that observed megacrysts in moderately 'evolved' lavas from the Victorian Newer Volcanics (Irving, 1974a; Irving and Green, 1976) represent high-pressure liquidus or near-liquidus precipitates from their hosts, Wilkinson (1977) modelled the hypothetical high-pressure fractionation trend basanite → nepheline hawaiite → nepheline mugearite. Semi-quantitative mass-balance calculations (Wilkinson, 1977) showed poor correlation for some elements (notably, CaO, Na_2O and K_2O) between the alleged derivatives and predicted compositions based on a crystal extract composed of olivine, clinopyroxene and kaersutite. Together with phlogopite, these were experimentally-determined liquidus or near-liquidus phases in a natural nepheline mugearite with 5 percent H_2O at 15 to 20 kb pressure (Irving and Green, 1972).

Irving and Price (1981) proposed that the Bokkos phonolite (Nigeria) was produced by high-pressure fractionation of a basanitic melt involving the removal of olivine, kaersutite, aluminous Ca-rich pyroxene, phlogopite, ulvöspinel and apatite. Major and trace element models for the transition from nepheline hawaiite to phonolite indicate reasonable agreement between predicted and observed compositions with the exception of Ba, Sr, Rb and possibly Cr. The 'parental' nepheline hawaiite (transitional to nepheline mugearite, *M* = 67.9, 100*an/ab+an* = 30.7) was evidently generated by prior high-pressure fractionation of a basanitic melt not presently represented in the volcanic pile. Megacrysts, which could be interpreted as evidence supporting the crystallization of the mugearitic and phonolitic melts at elevated pressures, are absent (or not mentioned) even though upper mantle lherzolite xenoliths were entrained.

Examples of relatively 'evolved' members of transitional alkaline suites with evidence of direct high-pressure derivation are comparatively rare (e.g. Taka-sima, Japan, Kuno, 1964; Kyogle, New South Wales, Wilkinson and Binns, 1969). The best documented example of a transitional suite with evidence of magmatic evolution at elevated pressures is the Comboyne suite, New South Wales (Knutson and Green, 1975). They demonstrated that mugearite is a potential derivative of transitional hawaiite via removal of approximately 27 percent of crystal extracts including olivine, clinopyroxene, orthopyroxene, plagioclase and minor ilmenite and apatite. The transitional hawaiite 'parent' (*M* = 45.9, D.I. = 51.9) has also allegedly been generated from a transitional basaltic melt by fractionation at elevated pressures. Experimental duplication of megacryst species and compositions observed in the hawaiite with 2 percent H_2O and at pressures of 6 to 8 kb, plus the absence of lherzolite xenoliths in the host and abundance of plagioclase in the megacryst population, indicates evolution of these magmas at significantly lower (crustal) pressures than the mugearitic and phonolitic magmas from eastern Australia and Nigeria.

Experimental phase relationships of a transitional alkali basalt (hawaiite, 100*an/ab+an* = 42.7, *M* = 66.2) from Auckland Island, New Zealand (Green and Hibberson, 1970) provide some constraints on the likely products of high-pressure fractionation of transitional basaltic melts. Orthopyroxene, clinopyroxene and minor olivine occur as megacrysts in the basalt and are also the experimentally-determined near-liquidus phases at 11 to 18 kb in melts with approximately 2 percent H_2O. Fractionation of orthopyroxene or orthopyroxene + clinopyroxene with minor olivine would rapidly decrease *M* values in derivative liquids. However, the resultant liquids would also be more silica undersaturated and a trend toward *ne*-normative compositions would be initiated. Therefore, if transitional hawaiites (with $M < 66$) are indeed products of high-pressure fractionation processes involving removal of orthopyroxene and clinopyroxene, it would follow that the proposed parents must be more *hy*-normative and approach subalkaline (tholeiitic) compositions.

It is clear from the preceding discussion that whilst there is ample evidence demonstrating that some relatively 'evolved' volcanics have their origin at high-pressures (>9 to 10 kb) in the upper mantle, the evidence regarding their formation by fractional crystallization of more mafic melts in this regime is more equivocal. An origin for these relatively 'evolved' lavas by high-pressure fractionation, particularly where they are the most mafic variants represented, is even more equivocal where there is no evidence of the alleged crystal extract.

Low-Pressure Fractionation

Disregarding the not insignificant problem posed by the absence or rarity of 'parental' magmas with appropriate compositions, genetic controls relevant to the production of the more evolved members of alkaline volcanic associations will now be considered. Closed-system fractional crystallization operating at low pressures has been proposed as the principal mechanism responsible for the development of rock types more evolved than 'basalt' in all except four of the volcanic provinces reviewed in this chapter. In several provinces (e.g. Canobolas, Middlemost, 1981; Mayor Island, Ewart *et al.*, 1968; Bouvetoya, Imsland *et al.*, 1977), open-system volatile transfer has been suggested as a subsidiary late-stage process.

To be internally consistent, fractionation models should satisfy the majority of constraints listed below:

a) volumetric relationships - successively more evolved differentiates should occur in successively smaller volumes.

b) chemical coherence and mass-balance - members of a cogenetic suite related by crystal fractionation controls should exhibit strong coherence on chemical variation diagrams and reasonable mass-balance should be demonstrated between the alleged parent, derivative and observed phenocryst compositions.

c) cognate cumulates - there should be reasonable evidence of cognate cumulates as inclusions within lavas especially if fractionation is considered to generate a wide spectrum of derivatives.

d) magma chamber models - the order of eruption of alleged derivatives should be consistent with realistic models of magma chambers.

e) intrusive complexes and vitric residua - fractionation trends should be consistent with demonstrable products of closed-system crystallization delineated by differentiated intrusions and vitric residua in lavas of similar composition.

Volumetric Relationships

It is clear from the earlier discussion of the relative volumetric proportions of the various lava types from transitional alkaline suites, that the more evolved types are commonly more abundant than their mafic or intermediate associates. Arguments advanced to explain these apparently anomalous volumetric relationships are commonly based on different physical characteristics of magmas of different composition, or the mechanics of crystallization. Le Maitre (1968) proposed that less-viscous acid and basic magmas may be extruded in preference to relatively more-viscous intermediate magmas. Limited support for this proposal is found in the eruptive centres of Aden, Little Aden and Jebel Khariz (Gass and Mallick, 1968), where trachyandesites feature prominently only in post-caldera formations. If caldera collapse had not occurred, trachyandesites would be poorly represented in the volcanic pile, compared with the mafic and felsic types. However, the proposal that intermediate magmas may be more viscous than mafic and felsic types, and therefore less readily erupted, gains little support from field relations in the Nandewar Volcano. The Nandewar trachyandesites occur typically as flows which are thinner and of greater areal extent than the associated trachytes.

It has also been argued (Gill, 1973,1974; Noble and Parker, 1974; Stolper and Walker, 1980) that the more mafic magmas types are effectively filtered by the upper crust because they have insufficient density contrast with surrounding crustal rocks to permit their ascent to the surface. Other controls on magma ascent, including volatile content of the melt, viscosity, volatile overpressure in the magma chamber and possible tectonic controls have probably been underestimated when the mode of extrusion of kimberlites and alkali basalts laden with ultramafic xenoliths is considered (cf. Wilkinson, 1982).

An alternative explanation for the development of bimodal magma associations was proposed by Wyllie (1963) and Mukherjee (1967). They argued that bimodality may be a result of the mechanics of crystallization, whereby steeper liquidus and solidus slopes in the basic and acid stages of crystallization enhance production of greater volumes of these lavas relative to intermediate types. Some support for this proposal is manifest in the presence of compositional gaps in small differentiated sills (Wilkinson, 1966). A bimodal distribution of mafic and felsic rock types is also a feature of transitional alkaline intrusive complexes from Morotu, Japan (Yagi, 1953), Carnarvon Range, Queensland (Bryan, 1969) and Tugtutoq, south Greenland (Blaxland and Upton, 1978; Blaxland, *et al.*, 1978; Upton and Thomas, 1980).

The volcanic provinces which provide the greatest difficulties for the crystal fractionation model are those characterised by massive volumes of felsic variants and only minor quantities of associated mafic types (e.g. Gregory Rift, McClenaghan *et al.*, 1971; Williams, 1972; Lippard, 1973; Baker *et al.*, 1977). Generation of these salic magmas by crustal fractionation, of necessity, requires probably 10 to 20 times as much mafic and cumulate material. A positive residual gravity anomaly along the Gregory Rift axis is generally interpreted as the remnants of a large unerupted basic batholith (Searle, 1970; Goles, 1976) at a high level (i.e. at depths less than 19 km) in the crust. Bailey (1978) argued that space considerations do not permit existence of the required volume of solidified mafic magma, and that the positive gravity anomalies are due to the presence of a relatively dense residue in the lower crust from an episode of partial melting. Geophysical data are apparently inconclusive regarding the nature of the crust and upper mantle beneath the East African Rift, and hence cannot be applied at present to elucidate the genesis of these massive volumes of salic lavas.

The possibility that volcanoes are inefficient in their sampling of available liquids and the advanced state of erosion in some older volcanic centres, may result in incorrect estimates of original volumetric relationships. The usefulness of estimated relative volumes of lava types in solving the problem of the genesis of these suites, is therefore somewhat diminished, and ideally this approach should be most relevant to youthful volcanic edifices.

Chemical Coherence and Mass-Balance

Reasonable coherence of chemical data when plotted on standard variation diagrams has often been regarded as evidence that a suite of lavas are cogenetic and related by crystal fractionation controls. Such trends may suggest a common parentage, but they are not of necessity the unique reflection of fractionation controls. More rigorous mathematical techniques (Bryan *et al.*, 1969; Wright and Doherty, 1970; Albarede and Provost, 1977) are now available for testing the viability of crystal fractionation controls in producing observed compositional variations in lava suites. Calculated fractionation models for a number of suites are presented in Table 6.8.

A fundamental constraint which should apply when modelling fractionation trends of lava suites in this way is the use only of observed phenocryst types and compositions in the calculations. This constraint was ignored in a number of modelling studies (e.g. Baker *et al.*, 1977; Price and Taylor, 1980; Middlemost, 1981) for which significant quantities of phases, not present as phenocrysts, were alleged to have been fractionated so as to provide satisfactory solutions for the calculations. It is not sufficient merely to obtain a satisfactory mathematical model to demonstrate the feasibility of fractional crystallization in the genesis of a suite of lavas. There must also be reasonable agreement between the relative proportions of phenocrysts present in the rocks and the proportions predicted from calculations. Such commonsense constraints are necessary, because, although models appear to be improved by addition of more components (i.e. sums of squares of residuals are reduced), this may only be an artifact of the calculation procedure (Wilcox, 1979) and as a consequence the solution may be meaningless.

In several suites (e.g. Bouvetoya, Imsland *et al.*, 1977; Canobolas, Middlemost, 1981; Socorro, Bryan, 1976) the mathematical models do not provide adequate solutions, particularly regarding the derivation of the

Table 6.8

Summary of mass balance requirements for several transitional alkaline suites

Suite	Fractionation Steps				References
Boina	Basalt → Ferrobasalt 60.6% extract; 6.1 ol, 34.5 plag., 19.0 cpx, 1.0 timt/ilm	Ferrobasalt → Dark trachyte 56.1% extract; 1.7 ol, 13.0 plag., 27.2 cpx, 14.2 timt/ilm	Dark trachyte → Alkali rhyolite(D232) 29.6% extract; 4.7 ol, 14.8 plag., 6.7 cpx, 2.0 timt/ilm, 1.4 apat.	Alkali rhyolite(D232) → Alkali rhyolite(D217) 16.8% extract; 2.7 ol, 5.8 plag., 7.8 cpx, 0.5 timt/ilm	Bizouard *et al.* (1980)
Erta Ale	Basalt → Andesine basalt 62.0% extract; 8.0 ol, 29.5 plag., 22.7 cpx, 1.8 timt/ilm	Andesine basalt → Dark trachyte 22.2% extract; 8.4 plag., 12.4 cpx, 1.4 timt/ilm	Dark trachyte → Rhyolite(D94) 42.6% extract; 4.4 ol, 10.3 plag., 13.6 cpx, 10.9 timt/ilm, 2.9 apat.	Dark trachyte → Rhyolite(CH20) 55.6% extract; 5.4 ol, 20.6 plag., 13.9 cpx, 12.6 timt/ilm, 3.1 apat.	Bizouard *et al.* (198)
Southern Gregory Rift	Basalt(32) → Ferrobasalt(38) 57.1% extract; 6.9 ol, 29.2 plag., 19.9 cpx, 0.9 timt, 0.9 apat.	Ferrobasalt(38) → Benmoreite(18) 75.0% extract; 4.5 ol, 31.2 plag., 28.8 cpx, 9.3 timt, 1.2 apat.	Benmoreite(18) → Trachyte(7) 44.6% extract; 0.5 ol, 10.8 plag., 12.8 cpx, 2.0 timt, 0.4 apat, 18.1 kfsp.	Trachyte(7) → Trachyte(54) 56.7% extract; 1.6 ol, 4.2 cpx, 2.4 timt, 0.4 apat., 48.1 kfsp.	Baker *et al.* (1977)
Canobolas	Hawaiite → Mugearite 15.7% extract; 2.0 ol, 12.0 cpx, 1.7 timt/ilm	Mugearite → Benmoreite 26.0% extract; 2.1 ol, 13.6 plag., 7.0 cpx, 3.3 timt/ilm	Benmoreite → Trachyte 36.7% extract; 27.3 plag., 4.6 cpx, 4.8 timt/ilm	Trachyte → Comendite 68.2% extract; 5.1 cpx, 3.0 timt, 60.1 kfsp	Middlemost (1981)
Banks Peninsula					
1) Lyttleton Area	Basalt(104) → Basalt (49) 15.7% extract; 5.5 ol, 4.8 cpx, 4.1 timt, 1.3 apat.	Basalt(49) → Benmoreite(48) 62.1% extract; 7.4 ol, 19.3 plag., 28.0 cpx, 6.2 timt, 1.2 apat.	Basalt(49) → Trachyte(93) 76.5% extract; 10.0 ol, 32.1 plag., 24.5 cpx, 8.4 timt, 1.5 apat.		Price and Taylor (1980)
2) Akaroa Area	Basalt(80) → Hawaiite(101) 22.8% extract; 5.5 ol, 4.1 plag., 10.2 cpx, 3.0 timt	Hawaiite(101) → Mugearite(102) 48.5% extract; 4.4 ol, 18.9 plag., 19.9 cpx, 5.3 timt	Hawaiite(101) → Trachyte(123) 71.0% extract; 7.2 ol, 33.0 plag., 18.6 cpx, 10.8 timt, 1.4 apat.		
Gough Island	Basalt → Trachybasalt 28.0% extract; 1.9 ol*, 11.4 plag., 14.3 cpx, 2.3 ilm	Trachybasalt → Trachyandesite 21.6% extract; 5.6 ol, 9.3 plag., 1.1 cpx, 3.6 ilm, 2.0 kfsp	Trachyandesite → Trachyte 26.2% extract; 2.3 ol*, 10.1 plag., 13.3 cpx, 2.8 ilm, 5.2 kfsp*	Trachyte → Trachyte(G16) 4.3 ol, 30.2 plag., 4.6 cpx, 2.4 ilm, 20.8 kfsp	Zielinski and Frey (1970)
Bouvetøya	Basalt(I) → Basalt (II) 35.1% extract	Basalt (II) → Icelandite 62.5% extract	Icelandite → Comendite 57.1% extract		Imsland *et al.* (1977)
Socorro Island	Basalt(10) → Trachybasalt(77) 55.6% extract; 8.5 ol, 32.3 plag., 9.4 cpx, 5.0 timt, 0.4 apat	Basalt(10) → Trachyte(5) 73.7% extract; 10.4 ol, 40.0 plag., 12.2 cpx, 9.2 timt, 1.9 apat	Basalt(133) → Pantellerite(138) 92.8% extract; 20.1 ol, 33.5 plag., 17.5 cpx, 5.8 ilm, 2.1 apat., 13.8 kfsp		Bryan (1976)
Réunion	Basalt(512G) → Hawaiite(415) 33.2% extract; 2.4 ol, 8.8 plag., 21.0 cpx, 1.0 timt	Hawaiite(332) → Mugearite(482) 42.4% extract; 5.7 ol, 23.2 plag., 8.2 cpx, 5.3 timt	Mugearite(482) → Benmoreite(356) 39.2% extract; 0.2 ol, 11.0 plag., 18.2 cpx, 9.8 timt	Benmoreite(356) → Trachyte(1) 13.5% extract; 0.9 ol*, 8.3 plag., 4.2 cpx, 1.0 timt	Zielinski (1975)

Abbreviations

ol - olivine
plag. - plagioclase
cpx - clinopyroxene
timt - titanomagnetite
ilm - ilmenite
apat - apatite
kfsp - alkali feldspar

* - component added in the transition

most 'evolved' representatives. In these examples appeal is generally made to the intervention of a volatile phase (of ill-defined composition) to account for the chemical imbalances which persist from calculations involving fractionation of observed phenocryst phases. In the Boina suite, although reasonable materials balance appears to have been demonstrated for the transitions from basalt to metaluminous rhyolites (see Table 6.8), calculations for the transition metaluminous rhyolite → pantellerite were not provided by Bizouard *et al.* (1980). The results of such calculations utilizing data from Barberi *et al.* (1975) and Bizouard *et al.* (1980) are presented in Table 6.9. They represent the best fits with lowest sums of squares of residuals from a number of attempts involving the removal of various combinations of phenocrysts. The calculations indicate that a satisfactory solution is not obtained, particularly for Al_2O_3, Na_2O and K_2O. The major difficulty in this transition is to reduce the Al_2O_3 content from 15.3 wt. percent in the metaluminous rhyolite to 9.9 wt. percent in the pantellerite without decreasing the alkali content. Fractionation of anorthoclase (the most Al-rich phenocryst phase present) is the most efficient method of reducing the Al_2O_3 content. Unfortunately it also contains considerably more Na_2O and K_2O than the liquid from which it is being removed, thereby depleting the derivative in these components.

Similarly, consideration of feldspar fractionation trends in the system Na_2O-K_2O-Al_2O_3-SiO_2 led Macdonald *et al.* (1970) to conclude that pantellerites from Eburru Volcano, Kenya could not have been produced by fractionation in a closed system of alkali feldspar from associated pantelleritic trachytes. Comparable arguments are relevant to the genesis of comendites and pantellerites from Bouvetoya (Imsland *et al.*, 1977), Canobolas (Middlemost, 1981) and Socorro Island (Bryan, 1976). In the latter example Bryan proposed that comendites and pantellerites were direct derivatives of basaltic magmas via crystal fractionation controls without the development of intermediate variants. Mass-balance calculations (see Table 6.8) indicate that the Socorro comendites and pantellerites could not have been derived from associated trachytes by fractionation of observed phenocrysts, whereas calculations are consistent with the direct production of pantellerite and comendite from associated 'basalt'. However, mathematical models covering such large compositional ranges are unrealistic because they also require the removal of unrealistically large quantities of phases with more-or-less constant compositions. Obviously, liquid compositions must change in response to removal of solid phases whose compositions differ from that of the liquid, and the compositions of subsequent precipitates will accordingly be different.

A further anomaly with fractionation models concerns the behaviour of P_2O_5 in the suites. P_2O_5 commonly decreases in the compositional range mugearite to trachyte, consistent with the appearance of apatite as a liquidus or near-liquidus phase. However, P_2O_5 depletion generally continues to very low levels in the most 'evolved' associates in which apatite is extremely rare or absent as a discernable phenocryst phase. The experimental data of Watson and Capobianco (1981) indicate that ~0.14 wt. percent P_2O_5 is soluble in peralkaline silicic melts and that fractional crystallization processes are incapable of reducing P_2O_5 contents below these levels. Loss of P_2O_5 in a volatile phase is also an inadequate explanation for some pantelleritic obsidians at least, as is discussed in a subsequent section on volatile transfer.

Demonstration of mass-balance for the major elements is fundamental and critical to any acceptance of the crystal fractionation model. Even further constraints are imposed on this model by trace element distribution patterns. The trace element contents of derivative magmas should be explicable in terms of parental liquid compositions, partitioning relations of the elements concerned, and proportions of fractionated phase derived from the major element mass-balance calculations. Unfortunately, trace element partition coefficients appropriate to specific volcanic suites are sparse, and hence quantitative modelling of trace element abundances generally is not possible. Use of partition coefficients deduced from phenocryst/groundmass data from other volcanic suites, or experimentally-determined values (e.g. Zielinski and Frey, 1970; Zielinski, 1975; Bryan, 1976; Baker *et al.*, 1977) provides at best a qualitative assessment of trace element behaviour during fractionation. Ion microprobe studies (Shimizu and le Roex, 1982) have shown that the clinopyroxene partition coefficients (at least for some trace elements) adopted by Zielinski and Frey (1970) to model the trace element contents of some Gough Island lavas, were inappropriate. Moreover, dependence of partition coefficients on temperature and liquid compositions (Sun *et al.*, 1974; Lindstrom and Weill, 1978; Takahashi, 1978; Irving, 1978; Watson and Green, 1981; Dunn and McCallum, 1982) requires extremely critical selection of D values in trace element modelling studies.

Although rigorous trace element modelling is not possible for most volcanic suites, using presently available data, variations in trace element abundances should at least be broadly compatible with predicted crystal extracts and known crystallochemical behaviour of the elements. Examples of lavas for which element abundances appear to be incompatible with predicted crystal extracts include the pantellerites from Jebel Khariz (Gass and Mallick, 1968) and Fantale (Gibson, 1972) which are characterized by high Ba contents. Removal of substantial amounts of alkali feldspar from presumably trachytic parent melts is required by an origin involving closed-system crystal fractionation. Alkali feldspar typically has relatively high crystal/liquid partition coefficients for Ba (5 to 6; cf. Berlin and Henderson, 1969; Philpotts and Schnetzler, 1970) and low Ba concentrations (typical of most comendites and pantellerites; cf. Macdonald and Bailey, 1973) should result from the removal of very significant amounts of this phase. The converse problem is evident in the Boina suite where Ba undergoes extreme depletion over the interval alkali rhyolite (736 μg/g Ba) → pantellerite (<10 μg/g Ba). This depletion cannot be explained by removal of the amounts of phenocrysts predicted for this transition (see Table 6.9) assuming a partition coefficient $D_{Ba}^{Kfsp/liq} = 5.5$, calculated from anorthoclase and whole-rock Ba contents (Barberi *et al.*, 1975; Tables 1 and 5). Very high Cr contents in the Boina pantellerites, and high Cr and Sr coupled with low Rb levels in Jebel Khariz pantellerites compared to intermediate associates, are also incompatible with closed-system crystal fractionation models.

Linear correlations between pairs of 'residual' trace elements (i.e. elements with $D^{Sol/liq} \ll 1$) have been recognized in a number of volcanic suites (Sceal and Weaver, 1971; Weaver *et al.*, 1972; Ferrara and Treuil, 1974; Allègre *et al.*, 1977) and these are generally attributed to closed-system fractionation. Indeed Barberi *et al.* (1975) claimed that such correlations are in fact diagnostic of the efficacy of crystal fractionation processes. Baker (1978), however, demonstrated that this was not necessarily the case. The only requirement for retaining a

TABLE 6.9

Boina trachyte D217 calculated as a linear combination of pantellerite D227, anorthoclase, augite, olivine and titanomagnetite

	D217 Estimated	D217 Observed*	D227 Observed*
SiO_2	66.86	66.87	71.81
TiO_2	0.40	0.37	0.36
Al_2O_3	14.86	15.30	9.91
Fe_2O_3	1.77	1.80	3.07
FeO	3.57	3.58	3.81
MnO	0.16	0.13	0.16
MgO	0.03	0.04	0.00
CaO	1.35	1.38	0.30
Na_2O	7.29	6.07	6.01
K_2O	3.70	4.42	4.52
P_2O_5	0.02	0.04	0.04

Solution Wt. Fraction	
D227	0.4330
Anorthoclase	0.5184
Augite	0.0293
Olivine	0.0091
Titanomagnetite	0.0101

Σ (residuals)^2 = 2.2093

			D227 Predicted
Ba (µg/g)	736	<10	363

* Data including mineral analyses taken from Barberi *et al.* (1975), Bizouard *et al.* (1980) and normalized to 100% anhydrous for the purpose of performing the calculations.

constant ratio between a pair of elements x and y in a melt, is that the solid/liquid and liquid/vapour bulk distribution coefficients D_x and D_y remain equal.

The residual trace elements are those with large ionic radii and high charges (e.g. Ta, Hf, U, Th, Nb, Y, Zr) which do not substitute readily in the common rock-forming minerals. In a crystallizing magma characterized by anhydrous liquidus or near-liquidus assemblages the volatile components H_2O, F and Cl also constitute 'residual' or incompatible constituents. Hydrous phenocryst phases are rare or absent in members of transitional alkaline suites and hence the volatile components should be concentrated to similar degrees as the other incompatible elements if the systems remain closed. Although F and Cl are usually enriched in silicic volcanic glasses relative to transitional basaltic glasses, H_2O is generally much lower in the silicic variants (Nicholls and Carmichael, 1969; Macdonald and Bailey, 1973; Bailey, 1978). Bailey (1978) demonstrated that differential loss of H_2O in a volatile phase from a crystallizing magma system was not a plausible explanation for the low H_2O contents in natural pantelleritic glasses. Dissociation of H_2O in the melt would also reduce the H_2O content, but this would result in increased oxyen fugacities (Hamilton and Anderson, 1967), which is at variance with the increasingly reduced nature of the more evolved members of these suites (cf. Bizouard *et al.*, 1980). The highly variable concentrations of 'residual' trace elements in comendites and pantellerites from a number of suites (e.g. Comboyne; Knutson, 1975) which exhibit only minor variations in major element chemistry, are also unlikely to be simple products of closed-system fractional crystallization.

Further inconsistencies with fractionation models are apparent in the REE distribution patterns displayed by many suites. As noted earlier, many relatively 'evolved' rock types (including trachytes from several suites) do not display relative depletion of Eu in chondrite-normalized plots. Mass-balance calculations (see Table 6.8) require the removal of large quantities of plagioclase (up to 20 wt. percent) even to produce hawaiites from a basaltic parent. Relatively low fO_2 conditions were deduced from Fe-Ti oxide compositions for transitional basaltic rocks of the Boina suite (Bizouard *et al.*, 1980) and such conditions should stabilize Eu in the divalent state (Weill and Drake, 1973; Sun *et al.*, 1974), thereby permitting its substitution in plagioclase. If plagioclase/liquid partition coefficients for divalent Eu are at least 3 to 10 times greater than those of the trivalent REE in this compositional range (Schnetzler and Philpotts, 1970), pronounced relative depletion of Eu should be a feature of hawaiites and all more evolved variants produced by extensive plagioclase fractionation of more 'basic' progenitors.

Zielinski (1975) argued that simultaneous fractionation of apatite, itself characterized by a negative Eu anomaly, would tend to counteract the effects of plagioclase fractionation on Eu abundances. However, the partition coefficients employed by Zielinski (1975) were derived from apatite/groundmass data for a dacite (Nagasawa, 1970). The few apatite/groundmass partitioning data available for alkaline rocks (Irving, 1978; this study, Table 7.4) indicate no preferential exclusion of Eu from apatite relative to the trivalent REE. Watson and Green (1981) argued that the apatite megacrysts used by Irving (1978) were xenocrystal because of the higher $D_{Eu}^{Ap/liq}$ value for apatite megacryst/host compared to their experimentally-determined partitioning relations for Eu, implied from the behaviour of Sr. In view of the differences in the partitioning behaviour of Eu and Sr for apatite/liquid in a Nandewar tristanite ($D_{Sr}^{Ap/liq} = 2.8$, $D_{Eu}^{Ap/liq} = 6.8$, Table 7.4), this conclusion is evidently unjustified. Thompson *et al.* (1980) argued that the lack of negative Eu anomalies in the relatively 'evolved' Skye lavas may be due to compositional effects of the type described by Morris and Haskin (1974) which include, increasing $X(Eu^{2+})$ in synthetic glasses with increasing $CaAl_2Si_2O_8$ and SiO_2 content of the glasses at constant T and fO_2. However, Sun *et al.* (1974) found that plagioclase concentrates Eu relative to the other REE under all conditions investigated, the effect being enhanced by reducing conditions. This problem can only be properly resolved by measurement of plagioclase/groundmass partition coefficients for the REE in specific volcanic suites.

Uniformly low $^{87}Sr/^{86}Sr$ ratios for the Boina lavas (see Table 6.7) provides strong evidence for their derivation from a common source inheriting 'mantle' characteristics. However, for most continental suites the isotopic data are inconclusive. Although the higher $^{87}Sr/^{86}Sr$

ratios which characterize the more evolved members of many suites may indicate their derivation from a discrete source region enriched in radiogenic Sr, these ratios are most commonly interpreted as reflecting contamination by radiogenic upper crustal rocks. The contamination model has been most effectively argued for the Skye lavas (Carter *et al.*, 1978b; Moorbath and Thompson, 1980; Thompson *et al.*, 1980,1982; Dickin, 1981) where systematic determination of the Sr, Pb and Nd isotope and trace element characteristics of lavas and basement rocks has enabled the variable and sometimes specific nature of the contaminants to be assessed. The variation of $^{87}Sr/^{86}Sr$ within the Fantale lavas (Ethiopia) is unlikely to be due to derivation from a separate source or crustal contamination and Dickinson and Gibson (1972) suggested that an increase of Rb/Sr ratios, and therefore $^{87}Sr/^{86}Sr$ ratios, in the upper part of a magma chamber was due principally to feldspar fractionation. An alternative mechanism (Hildreth, 1981) is that the isotopic zonation in the magma chamber resulted from the process of thermogravitational diffusion. The chemical features of magmas considered to have formed by this process are discussed in a subsequent section.

The higher $^{87}Sr/^{86}Sr$ ratios of the evolved lavas from Gough, Ascension and Easter Islands cannot be attributed to contamination by continental crust although interaction with seawater cannot be ruled out. Higher $^{206}Pb/^{204}Pb$ ratios in the more evolved Ascension and Gough lavas relative to their mafic associates (Gast *et al.*, 1964) provide additional support for derivation of some of these magmas from an isotopically distinct source and argue against simple closed-system fractionation controls in their genesis.

Cognate Cumulates

Mass-balance requirements of the crystal fractionation process (see Table 6.8) indicate that removal of 90 to 98 percent of crystal extracts from mafic 'parental' melts is required to produce the compositions of the felsic members of most volcanic suites. These calculations assume perfect separation of crystals from liquid and they ignore the role of any trapped intercumulus liquid, which may constitute up to 40 volume percent of the fractionated products of differentiated intrusions (Wager and Brown, 1968). The fractionation of this additional liquid apparently has no effect on the compositional trends of derivative liquids (Maaløe, 1976). It does, however, result in a reduction of the amount of residual liquids generated at any stage of fractionation. A similar effect would result from the extraction of melts at various stages of evolution of a fractionating magma chamber. Felsic lavas produced by crystal fractionation thus probably represent even smaller percentages of parental melts than previously suggested.

Wilkinson (1977) drew attention to the general paucity of inclusions in volcanic rocks which might be considered representative of the vast volumes of cognate cumulates that inevitably must be an obvious corollary of crystal fractionation models. Inclusion types described from transitional suites are summarized in column 7, Tables 6.1 and 6.2. Inclusions are apparently absent from many suites and where present are rarely abundant. It may be argued that cumulate phases settle to the bottom of a magma chamber and remain there following extraction of the fractionated melt. However, current interpretations of layered intrusions (McBirney and Noyes, 1979; Rice, 1981) minimize the role of crystal settling in their development. Evidence for this conclusion is provided by the plagioclase-rich zones of the Skaergaard intrusion. Density calculations (Bottinga and Weill, 1970) and experiments by Campbell *et al.* (1978) indicate that plagioclase should have floated in the relatively Fe-rich melts predicted for that stage of crystallization. McBirney and Noyes (1979) postulate that the plagioclase did not settle to its present position, but rather crystallized *in situ*. Crystal settling can be further inhibited if magmas behave as Bingham fluids (McBirney and Noyes, 1979), a state which may be induced by partial loss of volatiles (Sparks and Pinkerton, 1978). For such liquids, even crystals more dense than the liquid need to greatly increase in size to exceed the yield strength of the fluid (Rice, 1981).

Assuming 'normal' Newtonian behaviour of magmatic fluids, convection is likely to occur even in magma chambers composed of highly viscous siliceous melts (Shaw, 1965,1972; Bartlett, 1969), resulting in thorough mixing of the magma. Rice (1981) has argued from analogies in the glass industry that convection velocities are orders of magnitude greater than settling velocities inferred from Stokes' Law for both silicic and mafic magmas. Some support for this is found in the variable distribution of acid gneissic blocks in the Marginal Border Group rocks of the Skaergaard intrusion, which from relative solid/liquid density and viscosity considerations should have floated and been concentrated near the surface (Wager and Brown, 1968).

Magma Chamber Models

There is thus a small but growing body of evidence which minimizes the role of crystal settling in magma chambers as an aid to fractional crystallization processes. Solidification of a magma chamber on a front advancing from the floor, walls and roof (McBirney and Noyes, 1979) could, however, result in a series of progressively more 'evolved' liquids which potentially could be tapped periodically giving rise to an apparently consanguinous suite of lavas (cf. Thompson, 1972b). A requirement of this model is that the eruptive products be extruded in a particular order. Mafic types would have to be extracted first, followed by derivative intermediate melts and finally felsic types. Recharging of the magma chamber may interrupt the sequence, but the subsequent order of eruption of new derivative liquids should be the same following reestablishment of a homogeneous magma mixture (Huppert and Turner, 1981) and further crystallization.

Comparatively simplistic models of compositionally zoned magma chambers with basaltic melts at the base and mugearitic (Upton and Wadsworth, 1967) or pantelleritic (Bryan, 1976) melts at the top which have allegedly resulted from fractional crystallization are unrealistic from several view points. Firstly, consideration of the amount of crystallization of basaltic magma which is required to produce mugearitic or pantelleritic liquids (~60 to 90 percent) dictates that this range of liquid compositions would not coexist in a magma chamber undergoing closed-system fractional crystallization. Secondly, evidence discussed above supports active redistribution of early-formed crystals and homogenization of magmas by convection processes.

Intrusive Complexes and Vitric Residua

Perhaps the most convincing evidence for a cogenetic relationship between mafic and felsic rock types by fractional crystallization is provided by differentiated intrusions and compositional data on vitric residua in vitrophyric eruptives. Residual glasses in basanitic lavas are phonolitic (Wilkinson, 1966), whereas those in *qz*-normative tholeiitic types (Table 6.10, No.1) from north-eastern New South Wales (Wilkinson and Duggan, 1973; Duggan, 1974) are tholeiitic rhyolite in composition (Table 6.10, No.2). Examples of glassy residua from transitional basaltic lavas as yet appear to be undocumented, although it may be noted that felsic schlieren and pegmatoid segregations in olivine tholeiites (Table 6.10, No.5) from Picture Gorge, Oregon (Lindsley *et al.*, 1971) are trachyte to peralkaline trachyte in composition. The tholeiitic character of the parent lavas contrasts with the transitional chemistry of the normal associates of peralkaline melts. Compared to a typical transitional hawaiite from Pantelleria (Table 6.10, No.3), the Picture Gorge tholeiites are depleted in TiO_2, Na_2O, K_2O and P_2O_5, enriched in SiO_2 and Al_2O_3, and are strongly *hy*-normative.

The best examples of oversaturated salic rock types intimately associated with transitional alkaline mafic plutons are the intrusive complexes of the Morotu district, Japan (Yagi, 1953) and the Tugtutoq younger giant dyke complex, south Greenland (Blaxland and Upton, 1978; Blaxland *et al.*, 1978; Upton and Thomas, 1980). At Morotu, slightly *qz*-normative peralkaline syenites (Table 6.10, No.7) and metaluminous monzonites occur as schlieren in dolerite (Table 6.10, No.6) and comprise the central areas of zoned intrusions which apparently display gradational contacts to doleritic margins (Yagi, 1953).

The Tugtutoq younger giant dyke complex in southern Greenland (Upton and Thomas, 1980) consists of a mass of coalescing dykes which are mildly undersaturated olivine basalt or hawaiite in composition (Table 6.10, No.10). These dykes have associated cumulates and residual segregations, the most evolved of which are slightly *ne*- or *qz*-normative syenites (Table 6.10, No.9). Small segregations of alkali granite occur within quartz syenite intrusions indicating its localized derivation from the quartz syenite by fractional crystallization. The chemistry of the alkali granite segregations (Table 6.10, No.10) indicates their pantelleritic character, using the criteria of Macdonald and Bailey (1973), although they are not as strongly enriched in iron or depleted in Al_2O_3 as the type pantellerites from Pantelleria (cf. Table 6.10, No.4). It is worthy of note that although the granitic segregations derived by

TABLE 6.10

Representative analyses and C.I.P.W. norms of associated mafic and salic rocks from differentiated lavas and intrusions

Analysis No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	51.02	74.84	46.80	68.00	47.4	46.5	61.03	45.93	56.6	69.6	49.19	63.94	43.63	60.41
TiO_2	1.63	0.36	3.39	0.35	1.7	2.25	0.67	2.99	1.55	0.39	1.87	0.20	3.55	0.54
Al_2O_3	14.90	12.45	14.40	8.73	16.0	16.42	15.52	15.93	17.40	10.51	16.83	16.74	15.26	15.27
Fe_2O_3	2.27	-	5.62	5.60	3.3	4.05	5.08	2.92	2.72	2.86	1.72	2.67	4.22	2.90
FeO	8.90	1.57[1]	7.52	3.19	8.5	6.73	2.98	11.56	4.68	3.56	8.66	2.41	9.49	4.39
MnO	0.15	-	0.15	0.19	0.19	0.12	0.07	0.21	0.13	0.13	0.14	0.12	0.19	0.23
MgO	7.03	0.12	6.55	0.38	7.6	6.35	0.47	5.20	1.13	0.20	6.30	0.24	5.74	0.42
CaO	9.10	0.35	10.16	0.60	10.0	8.86	1.87	7.44	3.65	1.23	8.45	1.78	9.56	2.10
Na_2O	2.93	1.75	3.30	6.74	2.6	3.10	6.19	3.65	6.04	4.24	3.53	5.33	3.34	6.98
K_2O	0.33	5.79	0.96	4.82	0.4	1.54	5.15	1.65	3.90	4.37	1.16	5.33	0.88	3.77
P_2O_5	0.15	-	0.71	0.13	0.32	0.25	0.83	1.07	0.44	0.03	0.32	0.05	0.50	0.15
H_2O^+	0.80	-	0.83	0.46	2.4	3.40	0.39	0.91	1.13	0.56	1.45	0.26	2.17	0.53
H_2O^-	0.96	-		0.06		0.43	0.13	-	-	-	0.51	1.18	0.51	0.17
CO_2	-	-	-	-	-	-	-	-	0.14	0.72	-	-	0.36	1.57
Total	100.17	97.23	100.39	99.25	100.41	100.00	100.38	99.46	99.51	98.40	100.13	100.25	99.40	99.43
Σ Fe as FeO	10.94	1.57	12.58	8.23	11.47	10.37	7.55	14.19	7.13	6.13	10.21	4.81	13.29	7.00
$100Mg/Mg+Fe^{2+}$	57.5	12.0	52.3	17.5	58.2	56.3	21.9	43.5	30.1	9.1	56.5	15.1	47.6	11.2
Na_2O/K_2O	8.88	0.30	3.44	1.40	6.50	2.01	1.20	2.21	1.55	0.97	3.04	1.00	3.80	1.85
Agpaitic Index	0.35	0.73	0.45	1.87	0.29	0.41	1.02	0.49	0.81	1.11	0.42	0.87	0.42	1.02
C.I.P.W. Norms*														
Q	1.01	40.53		22.76			3.79			26.61		8.09		2.56
C		2.67												
or	1.95	34.22	5.67	28.48	2.36	9.10	30.43	9.75	23.05	25.82	6.85	31.50	5.20	22.28
ab	24.79	14.81	25.84	18.07	22.00	23.49	51.16	28.45	49.33	29.73	29.87	45.10	22.51	57.56
an	26.53	1.74	21.64		30.81	26.34		22.21	8.85		26.65	6.01	24.05	
ne			1.13			1.49		1.32	0.96				3.11	
ac				16.20			1.07			5.41				0.66
ns				4.79										
di	14.45		19.78	1.86	13.69	13.07	3.13	6.41	4.61	1.18	10.79	2.14	14.73	0.01
hy	23.50	2.59		5.62	11.99		0.26			5.19	4.09	1.60		6.61
ol			13.97		10.24	15.06		18.72	3.37		13.12		14.95	
mt	2.69		3.09		2.82	2.55	6.83	3.49	3.94	1.43	2.51	3.87	3.27	3.54
il	3.10	0.68	6.44	0.66	3.23	4.27	1.27	5.68	2.94	0.74	3.55	0.38	6.74	1.03
ap	0.35	-	1.65	0.30	0.74	0.58	1.92	2.48	1.02	0.07	0.74	0.12	1.16	0.35
Rest	1.76	-	0.83	0.52	2.40	3.83	0.52	0.91	1.45	2.20	1.96	1.44	3.50	4.09
100*an*/*ab*+*an*	51.7	10.5	45.6	0.0	58.3	52.9	0.0	43.8	15.2	0.0	47.2	11.8	51.6	0.0
D.I.	27.8	89.6	32.6	69.3	24.4	34.1	85.4	39.5	73.3	82.2	36.7	84.7	30.8	82.4

1. Olivine Tholeiite, Inverell, New South Wales (Wilkinson and Duggan, 1973, table 1, No. 4).
2. Microprobe analysis of residual glass from 1 above (Wilkinson and Duggan, 1973, table 1, No. 4G).
3. Olivine basalt, Pantelleria (Villari, 1974, table 2, No. 83V).
4. Pantellerite, Pantelleria (Villari, 1974, table 2, No. 137V).
5. Olivine Tholeiite, Picture Gorge, Oregon (Lindsley *et al.*, 1971, table 33).
6. Average of 4 dolerites from the Morotu district, Japan (Yagi, 1953, table 19, No. 1).
7. Syenite, Morotu district, Japan (Yagi, 1953, table 16, No. 1412).
8. Average of 4 chilled marginal dyke rocks Tugtutôq younger dyke complex, south Greenland (Upton and Thomas, 1980, table 6, No. 6).
9. Syenite residua, Tugtutôq younger dyke complex, south Greenland (Upton and Thomas, 1980, table 3, No. 9).
10. Peralkaline granite residua, Tugtutôq younger dyke complex, south Greenland (Upton and Thomas, 1980, table 3, No. 10).
11. Gabbro, Carnarvon Range, Queensland (Bryan, 1969, table 27, No. 1).
12. Microsyenite, Carnarvon Range, Queensland (Bryan, 1969, table 27, No. 2).
13. Onawe Gabbro, Banks Peninsula, New Zealand (Price and Taylor, 1980, table 2, No. 112).
14. Onawe Syenite, Banks Peninsula, New Zealand (Price and Taylor, 1980, table 2, No. 85).

* C.I.P.W. norms of mafic rocks calculated with $Fe_2O_3/Fe = 0.20$, remaining norms calculated with measured Fe_2O_3/FeO ratios.

\- = not determined

[1] = total iron as FeO

in situ fractionation comprise only a small volume of the syenite intrusives, alkali granites and syenites comprise about 80 percent of the total surface area of intrusive complexes in the Gardar province of south Greenland (Blaxland *et al.*, 1978).

Other examples of associated gabbro-syenite intrusions which occur in subvolcanic environments include those from the Carnarvon Range, Queensland (Bryan, 1969) and the Banks Peninsula, New Zealand (Price and Taylor, 1980) for which representative analyses of the mafic and felsic fractions are listed in Table 6.10. A common feature of the majority of these intrusive complexes is the bimodality of rock types with variants intermediate in composition between gabbro and *qz*- or *ne*-normative syenite being poorly represented or absent. Alkali granitic rocks of comenditic or pantelleritic affinity have not yet been described as residua intimately associated with mafic plutons. The absence of such a relationship weakens the proposal of Bryan (1976), that Socorro pantellerites resulted directly from fractional crystallization of basaltic magma without production of intermediate members.

Partial Melting in the Upper Mantle

Composition of the Upper Mantle

It is generally accepted by petrologists that the upper mantle has a peridotitic mineralogy. Lherzolite (olivine + orthopyroxene + clinopyroxene) with either plagioclase, spinel or garnet, depending on P-T conditions, is considered to be the most abundant upper mantle source rock since it is the dominant xenolith type in inclusion suites from alkali basalts, nephelinites and kimberlites (Ringwood, 1975). Studies of ultramafic inclusion suites (e.g. Carter, 1970; Hutchison *et al.*, 1975; Wilkinson and Binns, 1977) indicate considerable modal and chemical variation and this implies significant heterogeneity in the upper mantle. Xenoliths of eclogite, pyroxenite, wehrlite and harzburgite which often accompany inclusions of the Cr-diopside suite (Wilshire and Shervais, 1975) are regarded as relatively subordinate, although widespread components of the upper mantle, and many are members of the Al-augite or Ti-augite suite for which a high pressure cognate origin has been proposed. Phlogopite, amphibole, apatite, carbonates, ilmenite, rutile and zircon are accessory phases in some ultramafic inclusions (Dawson,

1981) and are considered to be important upper mantle storage reservoirs for volatiles (F, Cl, H_2O) and incompatible trace elements (e.g. P, K, Ti, Rb, Ba, Sr, Zr, Nb, U, Th, REE; Flower, 1971; Paul *et al.*, 1976; Smith, 1981; Smith *et al.*, 1981).

A number of estimates for the average major element composition of the upper mantle have been proposed. Most (e.g. Harris *et al.*, 1967; Carter, 1970; Maaløe and Aoki, 1977) are based on compositions of what appear to be the least refractory spinel or garnet lherzolite xenoliths from mafic alkaline rocks or kimberlites. Hypothetical 'pyrolite' compositions (Ringwood, 1966,1975) are combinations of refractory residua (dunite or harzburgite) and various natural basalt compositions in ratios considered to represent reasonable degrees of partial melting from cosmochemical and experimental considerations. Most calculated upper mantle compositions have *mg* = 87 to 90.

'Primary' Melt Compositions

A number of experimental studies have been undertaken to determine the near-solidus partial melt compositions of garnet lherzolite or 'pyrolite' under varying P_{H_2O}, P_{CO_2} and P-T conditions. Conflicting data from these experiments resulted in a controversial debate which centred on the depth (or pressure) at which early-formed liquids from the partial melting of model upper mantle compositions change from *qz*-normative to *ol*-normative. The outcome of this debate is critical from the point of view of establishing whether or not silica-oversaturated melts are potential derivatives of a lherzolitic upper mantle. Experimentalists who consider that dacitic to andesitic liquids are formed by small degrees of melting of garnet peridotite at 25 to 30 kb under water-saturated conditions (Kushiro, 1972; Kushiro *et al.*, 1972; Mysen and Boettcher, 1975; Boettcher *et al.*, 1975; Mysen and Kushiro, 1977), have based their claim primarily on the compositions of quenched liquids (glasses) from melting experiments. An alternative view point, that early-formed melts become *ol*-normative at pressures >10 kb is supported by similar experimental studies on synthetic and natural peridotite compositions (Nicholls and Ringwood, 1973; Green, 1973a,b,1976; Nicholls, 1974). Much of the controversy has apparently arisen due to modification of glass compositions in the charges because of quenching difficulties and Fe-loss during the experiments (Nehru and Wyllie, 1975; Green, 1976; Jaques and Green, 1979), although the relative importance of these uncertainties is still debated (Mysen and Kushiro, 1977).

On balance, the evidence from experimental studies favours the view that quartz-bearing (particularly rhyolitic) liquids are not formed by equilibrium partial melting of olivine-rich upper mantle material (Stern and Wyllie, 1973; Wyllie *et al.*, 1976). However, the proposal that some trachytes and phonolites may be generated by partial melting in the upper mantle (Wright, 1971) receives some support from isotopic studies of Nigerian specimens (Grant *et al.*, 1972) and natural interstitial partial melt (glass) compositions in spinel lherzolite xenoliths (Brooks and Printzlau, 1978; Stout and Johnston, 1980), and thus require further experimental investigation.

Experimental studies (Bultitude and Green, 1971; Green, 1972, 1973b) indicate an origin for basaltic melts (with $M > 66$) by variable degrees of partial melting of mantle peridotite in the presence of a H_2O- and CO_2-bearing vapour phase. Strongly silica-undersaturated alkaline rocks (e.g. kimberlites, olivine melilitites, olivine nephelinites) are considered to form by small degrees of partial fusion (i.e. <5 percent), whereas higher degrees of partial melting result in more silica-saturated basic liquids (Green, 1972,1973a). Olivine basalt compositions comparable to the transitional alkaline mafic rocks, are considered to form at ~15 kb by 20 to 25 percent melting of 'pyrolite' containing 0.1 to 0.2 percent H_2O. More recent experimental studies on the anhydrous melting behaviour of 'pyrolite' (Jaques and Green, 1980) confirmed the earlier results using a different technique for estimating melt compositions and degree of melting.

Extension of the range of 'primary' mantle-derived liquids has recently been proposed (Wilkinson and Binns, 1977; Wilkinson, 1977, 1980,1982) following the recognition of relatively Fe-rich lherzolite xenoliths (M ~80) considered to be representative of the least depleted portions of a heterogeneous upper mantle with M = 80 to 90. The prospect that portions of the upper mantle are more Fe-rich than 'pyrolite' unveils the potential for the direct generation of melts with $M > 58$ by partial fusion. This extended range of M values includes many lherzolite-bearing hawaiites, mugearites and benmoreites which have previously been regarded as the products of high-pressure crystal fractionation (cf. Green *et al.*, 1974; Irving and Green, 1976; Irving and Price, 1981). Direct derivation of relatively 'evolved' lavas by partial melting avoids the need to postulate large quantities of fractionated cumulate olivine and other phases, for which there is generally little evidence, and provides a reasonable explanation for the paucity of MORBs (Wilkinson, 1982) and transitional alkaline mafic lavas with $M > 66$ relative to those with M ~55 to 66. The apparent paucity of lherzolite xenoliths with $M < 88$ may simply reflect the pervasiveness of magma extraction events which have affected the regions of upper mantle sampled by common alkali basaltic magmas. Alternatively, relatively Fe-rich xenoliths, if incorporated in high temperature melts, may have experienced partial melting, mechanical disaggregation and accordingly lost their identity.

Frey *et al.* (1978) proposed that major and trace element characteristics of a Victorian olivine basalt (comparable to the mafic members of many transitional alkaline suites) are consistent with an origin by 13 to 17 percent partial melting of 'pyrolite' leaving a lherzolitic residue provided that the source 'pyrolite' was already enriched in strongly incompatible elements (Ba, Sr, Th, U, LREE) at x 6 to 9 chondritic abundances, and less enriched (x 2.5 to 3 chondrites) in moderately incompatible elements (Ti, Zr, Hf, Y, HREE) prior to the partial melting event. Frey *et al.* (1978) recognized the possibility that a similar range of melt compositions could be derived from a lherzolitic source with REE abundances x 2 to 5 chondrite (cf. Kay and Gast, 1973). However, this model requires extremely small degrees of partial melting for very undersaturated variants (0.4 percent for olivine nephelinite to 1 percent for basanite). Whether or not such small quantities of melt can be effectively separated from their source is debatable. Estimates of the degree of partial melting required to achieve permeability and magma segregation range from 0.1 percent (Walker *et al.*, 1978), 1 percent (Sleep, 1974) to >2 percent and probably in the order of 10 to 20 percent (Maaløe, 1981). The latter estimates are regarded as more realistic on the basis of textural features of natural interstitial melts in lherzolite xenoliths (Maaløe and Printzlau, 1979).

Mantle Heterogeneity

Regardless of the amount of partial melting involved in the genesis of basaltic magmas, all models appear to require that the source region is enriched to varying degrees in incompatible elements relative to chondrites. Other workers (e.g. Gast, 1968; Griffin and Murthy, 1969; Menzies and Murthy, 1980c) have also noted the depleted levels of K, Rb, Sr, Ba, Ti, P and REE in proposed mantle compositions and it has therefore become necessary to postulate enrichment of these elements in the source regions of alkaline magmas prior to partial melting events (cf. Sun and Hanson, 1975a; Mysen and Holloway, 1977; Frey *et al.*, 1978). The assumption that the upper mantle initially contained chondritic abundances of these elements is supported by near-chondritic REE abundances in some MORBs garnet peridotite xenoliths (Frey *et al.*, 1978) and ultramafic lavas (Sun and Nesbitt, 1978).

Further support for the existence of mantle enrichment events is provided by Sr isotopic data for alkali basalts from the oceanic islands (Sun and Hanson, 1975b). These basalts have an excess of Rb over that required to account for their ^{87}Sr contents which is interpreted as indicating enrichment of Rb in their source region. In contrast, some MORBs contain insufficient ^{87}Rb to account for their ^{87}Sr contents (Tatsumoto *et al.*, 1965). This isotopic imbalance is explained by depletion of Rb during evolution of the MORB source region, probably by partial melting events and subsequent development of the crust (O'Nions *et al.*, 1977,1978). Systematic Nd and Sr isotope studies have revealed a strong inverse correlation between ^{143}Nd/^{144}Nd and ^{87}Sr/^{86}Sr ratios indicating coherent fractionation of Rb/Sr and Sm/Nd during evolution of the sub-oceanic mantle (De Paolo and Wasserburg, 1976; O'Nions *et al.*, 1977). ε_{Nd} and ε_{Sr} values (see Chapter 5 for definition) are regarded as a measure of the deviation of initial ^{143}Nd/^{144}Nd and ^{87}Sr/^{86}Sr ratios from those predicted for a pristine unmodified upper mantle. Most MORBs and oceanic island basalts (including those from Bouvetoya and Ascension) have positive ε_{Nd} and negative ε_{Sr} values which indicate that their source region was depleted in Rb and LREE relative to model bulk Earth values (De Paolo and Wasserburg, 1976; O'Nions *et al.*, 1977,1980). On the other hand, the lavas from Tristan da Cunha (O'Nions *et al.*, 1977) have ε_{Nd} and ε_{Sr} values close to bulk Earth, suggesting that small amounts of essentially undifferentiated mantle have survived to recent times.

Available Nd and Sr isotopic data for continental basalts indicate ε_{Nd} and ε_{Sr} values close to bulk Earth or negative ε_{Nd} and either positive or negative ε_{Sr} values (e.g. Roccamonfina and Skye; Carter *et al.*, 1978a). It is difficult to ascertain if the inferred enrichment in radiogenic Sr and/or unradiogenic Nd in continental volcanics relative to bulk Earth is due to an ancient enrichment event in the mantle, resulting in increased Rb/Sr and decreased Sm/Nd, or whether it is due to selective crustal contamination, as has been claimed for the Tertiary plateau volcanics from north-west Scotland (Carter *et al.*, 1978b).

Although ε_{Nd} vs ε_{Sr} plots permit recognition of ancient enrichment or depletion events in magma source regions (particularly in the sub-oceanic mantle), they do not reveal very recent modifications (Carter *et al.*, 1978a). This resolves the apparent conflict in the isotopic character of the source regions for oceanic island basalts which are inferred to have been both depleted and enriched in Rb and LREE. Enrichment of Rb, LREE and other incompatible elements is thus considered to have occurred either shortly preceding, or during the anatectic event leading to 'basalt' generation.

Pb isotopic data for oceanic island basalts and MORBs also indicate long-lived heterogeneities in mantle source regions (Tatsumoto *et al.*, 1965; Gast, 1969; Oversby and Gast, 1970). However, the lack of correlations between Sr and Pb isotopic ratios for oceanic island basalts (Sun and Hanson, 1975b) reflects the more complex history of the U/Pb system which has led to a variety of alternative interpretations of these data (cf. Oversby and Gast, 1970; Sun, 1980; Chase, 1981; Anderson, 1982).

Upper Mantle Metasomatism

The mantle enrichment events, regarded as an essential ingredient of alkaline mafic magma genesis (Sun and Hanson, 1975a), are generally attributed to influx of a volatile-rich fluid or low-melting component into upper mantle lherzolite which has incompatible trace element contents less than or approaching chondritic abundances. Perhaps the most compelling evidence for the operation of such a process is provided by spinel lherzolite xenoliths from the west Eifel (Germany) in various stages of transition to mica clinopyroxenite (Lloyd and Bailey, 1975). These were interpreted as incompletely metasomatized anhydrous lherzolite to which significant Ti, Al, Fe, Mn, Ca, Na, K, H_2O, CO_2, Rb, Sr, Y, Zr, Nb, Ba and La had been added, and Si, Mg, Cr and Ni were reduced by dilution and/or removal. These chemical changes are considered to have resulted in crystallization of phlogopite, amphibole, more Fe-rich clinopyroxene, titanomagnetite, sphene, perovskite, apatite and calcite. Further studies of amphibole- and phlogopite-bearing lherzolite xenoliths (e.g. Varne, 1970; Varne and Graham, 1971; Frey and Green, 1974; Francis, 1976; Boettcher *et al.*, 1979; Boettcher and O'Neil, 1980; Erlank *et al.*, 1980; Menzies and Murthy, 1980a,b,c; Wass and Rogers, 1980; Wass *et al.*, 1980; Wilshire *et al.*, 1980; Jones *et al.*, 1982) have concluded that a similar array of elements were added to 'normal' upper mantle material by migrating silicate melts or supercritical fluids.

Experimentally-determined partition coefficients for the REE (and K; Ryabchikov and Boettcher, 1980) between aqueous (Mysen, 1979) or CO_2 fluids (Wendlandt and Harrison, 1979) and peridotite indicate that these elements (especially the LREE) are preferentially concentrated in the fluid phase at high pressures, and their solubility in the fluid increases with pressure. These studies demonstrate the potential mobility of these elements in a H_2O- or CO_2-rich fluid phase at elevated pressures. The decrease in SiO_2 which evidently accompanied metasomatism in xenoliths from south-west Uganda and west Eifel (Lloyd and Bailey, 1975) suggests that the metasomatizing medium was low in SiO_2 and probably volatile-rich fluids rather than actual silicate melts. These fluids most likely emanate from deeper in the mantle as a consequence of progressive Earth degassing (Bailey, 1980) and probably move primarily by fracture propagation (Spera, 1981). During their upward transit the solutions may scavenge alkalies, Fe and incompatible trace elements from surrounding rocks. On reaching depths beneath the continents appropriate to the upper stability limit of phlogopite (~150 to 200 km; Kushiro *et al.*, 1967; Modreski and Boettcher, 1972; Wendlandt and Eggler, 1980), and subsequently amphibole (~80-100 km; Kushiro, 1970; Holloway, 1973; Holloway and Ford, 1975), reaction occurs between the fluids and anhydrous peridotite resulting in partial or complete transformation of the 4-phase spinel or garnet peridotite to mica- and amphibole-rich assemblages.

A major area of uncertainty on upper mantle metasomatism is the extent of its effects. Examination of amphibole-rich veins in lherzolite xenoliths from California led Wilshire *et al.* (1980) to conclude that metasomatism is a local event rather than a precursor to alkali basalt generation. On the other hand, the dominance of amphibole- and mica-bearing xenoliths in alkalic lavas from south-west Uganda and west Eifel (Lloyd and Bailey, 1975) attests to the pervasive nature of the metasomatism in the source regions of these provinces. Experiments by Mysen *et al.* (1978) which demonstrate infiltration of aqueous fluids into crystalline peridotite at a rate of 2 to 3 mm hr^{-1} at 20 kb and $850^{\circ}C$, suggest that significant metasomatism could occur within geologically reasonable periods if infiltration of the fluids occurred via a closely spaced network of solution channels.

In addition to the compositional modifications induced by metasomatic fluids, it has also been argued (Bailey, 1982) that influx of solutions may actually initiate anatexis by lowering solidus temperatures and addition of heat. Some support for this proposal is provided by heat budget calculations (Bailey, 1970; Spera, 1981) which suggest that metasomatizing fluids will rise isothermally, thereby permitting upward transfer of heat.

Alternative Models

Alternative attempts to explain isotopic peculiarities and the LREE enriched and depleted character of alkali basalt and MORB respectively, are based on postulated disequilibrium melting (O'Nions and Pankhurst, 1974; Campbell and Gorton, 1980) or persistence of a refractory LREE-enriched phase (apatite) over extended melting intervals (Beswick and Carmichael, 1978). Consideration of likely diffusion rates in the upper mantle (Nelson and Dasch, 1976; Hofmann and Hart, 1978) indicates that disequilibrium between melt and residue is unlikely to persist for more than a million years, and hence disequilibrium melting is not generally considered to be the cause of isotopic heterogeneities in oceanic basalts. Persistence of residual apatite in upper mantle source rocks is not supported by its demonstrable high solubility in basaltic melts at elevated pressures (Watson, 1979b) and its general absence from xenoliths which are regarded as having lost only a small partial melt increment (Frey *et al.*, 1980).

Enrichment of incompatible elements in alkaline mafic melts has also been attributed to zone-refining (Harris, 1957,1974) or wall-rock reaction processes (Green and Ringwood, 1967). During ascent the magma is considered to continuously dissolve roof and wall-rock phases and reprecipitate them in the magma. Trace elements not partitioned into the major crystallizing phases will become progressively enriched in the melt fraction. The occurrence of the solution stoping process is supported by experimental work by Watson (1982) which showed that a melt may infiltrate the grain edges of forsterite 'rock' at a rate of 1 to 2 mm day^{-1}. However, the greater enrichment of incompatible elements in alkali basalts relative to many tholeiites is at variance with their inferred relative ascent rates indicated by the presence and general absence of lherzolite xenoliths, respectively.

Partial Melting in the Lower Crust

Estimated continental geotherms for moderate heat flows (Clark and Ringwood, 1964) suggest that temperatures in the lower part of the continental crust (20 to 40 km depth) range from 500 to 950°C with pressures in the range 7 to 12 kb. Typical liquidus temperatures of basalts and hawaiites for reasonable H_2O contents (Green and Hibberson, 1970; Knutson and Green, 1975) are in the range 1100 to 1250°C and these preclude their derivation by partial melting within the crust. Although the origin of peralkaline intermediate and silicic magmas has been generally attributed to fractional crystallization of basaltic magmas, a number of workers (e.g. Price and Compston, 1973; Barker *et al.*, 1975; Zielinski, 1975; Teng and Strong, 1976; Harris and Marriner, 1980; Taylor *et al.*, 1980; Radain *et al.*, 1981; Harris, 1982) have argued that some trachytes, syenites and peralkaline granites have originated by partial melting in the lower crust. Anhydrous liquidus temperatures for pantellerites and trachytes (Bailey *et al.*. 1974) span the range 820 to 1000°C, but these are reduced by 100 to 150°C in the presence of excess H_2O. The low H_2O contents of glassy peralkaline silicic volcanics suggest H_2O may only have a minor effect on liquidus temperatures. However F, which is commonly relatively abundant in these rocks, is equally effective in depressing liquidus temperatures (Wyllie and Tuttle, 1961; Glyuk and Trufanova, 1977; Manning *et al.*, 1980). Thus, production of peralkaline trachytes and rhyolites (and their intrusive equivalents) by partial fusion of suitable lower crustal source rocks in the presence of a H_2O- or F-rich volatile phase seems feasible and it obviously eliminates many of the problems inherent in crystal fractionation models.

The strongest advocates for the production of peralkaline silicic volcanics by partial melting in the crust, emphasizing the role of volatiles in this process, have been D.K. Bailey and co-workers (Bailey, 1964,1970,1972,1973,1974; Bailey and Macdonald, 1970,1975; Macdonald *et al.*, 1970,1971). In a comparison of continental and oceanic island comenditic obsidians Bailey and Macdonald (1970) found that the continental compositions showed close correspondence to the experimentally-determined quartz-feldspar minima in the system Na_2O-K_2O-Al_2O_3-SiO_2. In contrast, the majority of oceanic comendites display a trend ranging from trachyte to the quartz-feldspar cotectic zone, consistent with derivation through a trachyte stem involving crystal $\rightleftarrows$ liquid equilibria. They concluded from this that some continental comendites may have been produced by partial fusion of relatively quartz-rich crustal rocks.

Ringwood (1975) reviewed the evidence regarding the composition of the lower crust, and concluded on the basis of experimental and seismic data that the bulk composition is probably quartz dioritic, which under expected anhydrous conditions would most likely be represented by a heterogeneous mixture of acid, intermediate and basic granulites. Bailey (1974) argued that influx of a halogen- and alkali-bearing volatile phase into anhydrous granulitic rocks would initiate melting both by reduction of solidus temperatures and net addition of heat. Furthermore, addition of alkalis would promote peralkalinity in early formed melts. This model is appealing from several view points:

a) large volumes of peralkaline silicic volcanics occuring in continental regions (e.g. East African Rift) can be explained without the need to postulate the existence of even larger volumes of parental mafic rocks and cognate cumulates (necessary corollaries of crystal fractionation models), the evidence for which is generally lacking.

b) essentially anhydrous pantelleritic melts rich in halogens appear to be possible products of partial fusion in the presence of a H_2O-poor halogen-rich volatile phase, but are very difficult to explain as residual liquids produced by fractional crystallization of basaltic magmas.

c) aphyric glassy pantellerites with identical compositions erupted over a substantial period of time, such as those from Chabbi Volcano, Ethiopia (Macdonald and Gibson, 1969), could represent partial melts held at liquidus temperatures within the lower crust. However, if crystal fractionation was operative during their development, continuous removal of liquidus or near-liquidus phases should have modified the compositions of successive eruptives.

There are, however, a number of vagaries associated with this model, not the least of which is the nature of the all important and critical volatile phase. If volatile activity and metasomatism are widespread in the upper mantle source regions for alkaline magmas, persistence of this activity into the lower portions of stable continental regions appears plausible. In tectonic and oceanic regions, however, the presence of an interstitial melt phase, as suggested by the presence of low-velocity seismic zones in these areas (Ringwood, 1975), would be expected to halt the progress of upward migrating fluids by dissolving them. In the absence of well-documented examples of metasomatized lower crustal rocks, the composition of the fluid phase involved in this process may be assumed to have been analogous to those inferred to have been involved in mantle metasomatism. It was noted earlier that these fluids are generally considered to be enriched in alkalies and incompatible elements resulting in the crystallization of phlogopite, amphibole and apatite, the latter being an important repository for REE. Watson and Capobianco (1981) demonstrated that P_2O_5 has a relatively low and restricted solubility range in peralkaline silicic melts. Their data indicate that ~0.14 wt. percent P_2O_5 can be dissolved in granitic melts, and they argue that if a melt contains less than this amount any apatite present in the source rocks was necessarily consumed during melting. Thus, if peralkaline silicic melts are to be considered as the products of partial melting in the lower crust, their extremely low P_2O_5 abundances (i.e. generally < 0.02 wt. percent) indicate that their source rocks were essentially devoid of apatite, and if a fluid phase was involved, it also was low in P_2O_5. More importantly, these data preclude derivation of the series comendite/pantellerite to trachyte (characterized by increasing P_2O_5 contents) by progressive partial fusion of a single source because of the increasing P_2O_5 contents which would be required by progressive partial melting.

Presumably, if apatite is absent from the source rocks of peralkaline silicic melts interpreted as the products of partial melting, they have acquired their characteristically high ΣREE concentrations from other REE-rich accessory phases such as sphene, allanite, monazite and zircon. The behaviour of allanite and monazite during partial melting are as yet unknown. However, sphene apparently behaves as a residual phase during partial melting (Hellman and Green, 1979) and thus inhibits strong LREE enrichment of early-formed melts. Similarly, experimental determination of Zr saturation levels in peraluminous salic liquids (Watson, 1979c) indicates that Zr will remain in refractory zircon during partial melting, buffering the Zr content of the melt at low levels. However, addition of an alkali-bearing fluid phase may induce peralkalinity in early-formed melts. The increased solubility of Zr in peralkaline liquids (Watson, 1979c), together with possible contributions from the fluid phase, may enhance the Zr contents of these melts.

Isotopic evidence bearing on the origin of peralkaline rhyolites and trachytes by partial melting of lower crust is often inconclusive or ambiguous. For example, some continental transitional alkaline suites (e.g. Boina; Barberi *et al.*, 1980; see Table 6.7) exhibit a very narrow range of initial $^{87}Sr/^{86}Sr$ ratios, consistent with their derivation from a single source of 'mantle' character. On the other hand, the more silicic members of some suites (e.g. Jebel Khariz and Aden; Dickinson *et al.*, 1969; see Table 6.7) sometimes have higher initial $^{87}Sr/^{86}Sr$ ratios than their mafic associates, a feature usually attributed to contamination by crustal rocks enriched in radiogenic Sr or a previous fractionation event (Dickinson *et al.*, 1969; Carter and Norry, 1976). Alternatively, the higher initial $^{87}Sr/^{86}Sr$ ratios may simply reflect their derivation from a different source. Unfortunately, the very high

Rb/Sr ratios which characterize peralkaline rhyolites render them very susceptible to contamination by radiogenic Sr and this ambiguity of interpretation is not easily resolved.

Some oceanic comendites also exhibit higher initial $^{87}Sr/^{86}Sr$ ratios than mafic associates (e.g. Ascension Island, Gast *et al.*, 1964; Easter Island, Baker *et al.*, 1974; see Table 6.7). Baker and McReath (1972) proposed that this distinctive isotopic character was a result of their formation by remobilization of acid rocks erupted earlier in the volcanic sequence. Whilst thermal constraints probably limit the possibility of refusion of rocks within the volcanic pile, evidence supporting the origin of Ascension comendites and peralkaline granites by partial fusion of syenites was presented by Harris and Bell (1982). The compositions of interstitial glasses in partially fused syenite blocks included in a trachybasalt flow, are comparable in many respects to comendite and peralkaline granite compositions. The relatively low Na_2O/K_2O ratios of the interstitial glasses may be explicable by loss of volatiles (and Na), as is indicated by their vesicular nature.

Obviously, since peralkaline silicic rocks occur in oceanic island and continental settings, the presence of continental crustal material is not critical to their development. Moreover, the chemical coherence and continuity of compositions displayed by some suites provides strong arguments for cogeneis and derivation from a single source. Since production of compositions ranging from hawaiite to peralkaline rhyolite is not possible by progressive partial melting within the crust, and most unlikely within the upper mantle (see discussion above), a separate origin for the rhyolitic members of at least some suites by partial fusion seems most unlikely. However, the inapplicability of crystal fractionation models to the genesis of some pantellerites (Macdonald *et al.*, 1970; Bailey and Macdonald, 1975) suggests that the production of other peralkaline silicic melts by partial fusion of crustal rocks cannot be discounted, and that they may indeed be polygenetic.

Contamination/Hybridism

The processes of contamination and hybridism are considered to have had a negligible effect on the development of transitional alkaline suites. The restricted range of compositional variants which characterize these suites could not be reproduced in different crustal environments by contamination or hybridism of basaltic magmas. Evidence of partially assimilated material which might reasonably be expected in intermittently erupted magmas is rarely described. Furthermore, Bowen (1928) demonstrated that mafic magmas do not possess sufficient superheat to assimilate more than small amounts of relatively cold crustal rocks.

The higher $^{87}Sr/^{86}Sr$ ratios of the acid members of many continental suites suggest some contamination by crustal material enriched in radiogenic Sr. However, since these acid magmas are typically peralkaline, they can only have assimilated minor amounts of characteristically peraluminous crustal rocks. Isotopic enrichment may also be selective and accompanied by only minor changes in major element chemistry as was demonstrated for some Skye basalts (Thompson *et al.*, 1982).

Volatile Transfer

The compositions of most volcanic rocks are probably affected to some degree by loss of volatiles. Addition of a volatile phase is also feasible, but more difficult to prove. The potential importance of these processes in modifying melt compositions is dependent on the amount of fluid or vapour involved, and the extent to which melt components are partitioned into the fluid or vapour phase. Transfer of volatile constituents will occur in a vapour phase at low pressures (i.e. probably less than 200 to 500 bars), and in the form of supercritical fluids at higher pressures (Holloway, 1981).

The most abundant volatile constituents of basaltic magmas are H_2O and CO_2 with lesser amounts of SO_2, H_2, H_2S, HCl, HF, CO, S_2 and CH_4 (Gerlach, 1979,1980; Holloway, 1981). Acid peralkaline melts are characterized by relatively higher concentrations of F and Cl than basic melts (Bailey, 1978; Carmichael, 1979) and CO_2 may also be relatively important in the evolution of these melts (Bailey, 1978; Scott, 1982).

Volatile Loss

At a given set of P-T conditions, separation of a fluid phase from a melt will occur when the melt is saturated in that phase. Since the solubility of both H_2O and CO_2 increase with increasing pressure

(Khitarov and Kadik, 1973; Holloway *et al.*, 1976; Mysen *et al.*, 1976), exsolution of a fluid phase could be induced by a reduction in P_{total} during ascent of the magma if it is close to saturation point when formed. However, most transitional basaltic melts are probably strongly undersaturated at elevated pressures with respect to H_2O and CO_2, and these constituents therefore should remain dissolved in the melt.

Exhalative loss of vapour clearly occurs very close to the Earth's surface but it is difficult to assess the importance of this process. Estimates of Cl loss from basic melts summarized by Sigvaldason and Oskarsson (1976) vary widely (~10 to 70 percent of the original Cl content). This in part probably reflects the decreasing solubility of Cl in the melt with increasing temperature, and increased partitioning of Cl into the vapour phase with increasing H_2O and CO_2 content of the melt (Sigvaldason and Oskarsson, 1976).

Production of trachytic or rhyolitic melts by fractional crystallization of anhydrous phases from a basaltic melt should result in at least a 10 fold increase in the H_2O content of the derivative melts. The low H_2O contents which characterize peralkaline acid lavas therefore imply loss of large quantities of H_2O if they were formed in this way. Whilst there is evidence for loss of H_2O and F from some peralkaline granite intrusions (Macdonald *et al.*, 1973), experimental evidence which indicates that Cl is strongly partitioned into an aqueous phase in equilibrium with granitic melt (Kilinc and Burnham, 1972; Hards, 1976), suggests it is unlikely that virtually anhydrous pantelleritic obsidians (commonly enriched in Cl and F), ever contained more than a trace of H_2O. Enrichment of CO_2 should also be expected in trachytic and rhyolitic melts produced by crystal fractionation of basaltic magma. However, the rapidly decreasing solubility of CO_2 with increasing a_{SiO_2} of the melt (Mysen *et al.*, 1976) would necessitate expulsion of large quantities of CO_2 during formation by this process.

The nature of the material lost in a fluid phase can be inferred from metasomatic alteration zones surrounding peralkaline intrusive rocks (e.g. McKie, 1966; Woolley *et al.*, 1972; Macdonald *et al.*, 1973; Martin *et al.*, 1978; Taylor *et al.*, 1981; Strong, 1982). Macdonald *et al.* (1973) showed that loss of a H_2O- and F-bearing fluid phase from a crystallizing peralkaline granite in southern Greenland was accompanied by significant enrichment of K, Rb, Li, Zn, Zr, Y, Pb, Th, U and LREE in the adjacent gabbro. Similarly, fenitized quartzites adjacent to a pseudoleucite syenite in north-west Scotland (Woolley *et al.*, 1972; Martin *et al.*, 1978) display significant enrichment in Al, Na, Mg, K, Fe and REE, relative to barren quartzite.

Transportation of alkalies and the 'incompatible' trace elements (e.g. Zr, Nb, Ta, Th, U, REE) in a fluid phase has often been proposed to occur in the form of fluoride complexes (e.g. Beus, 1958; Bandurkin, 1961; Mineyev, 1963; Mineyev *et al.*, 1966; Buma *et al.*, 1971; Bowden and Whitley, 1974; Bailey and Macdonald, 1975; Fryer and Edgar, 1977). In addition, REE carbonate complexes have frequently been suggested to account for transportation of this group in CO_2-bearing fluids (Beus, 1958; Kosterin, 1959; Mitchell and Brunfelt, 1975; Wendlandt and Harrison, 1979; Harris, 1981). Fractionation of elements with very similar properties (e.g. REE, Nb and Ta), which evidently occurs in certain pegmatite deposits, has been attributed to the variable stability of these trace metal-volatile complexes with changing pH of the host solutions (Beus, 1959; Bandurkin, 1961; Mineyev, 1963).

While the field evidence for transportation (and hence loss) of significant quantities of alkalies and trace metals from peralkaline granitic melts is compelling, experimentally-determined partition coefficients for a wide range of elements between aqueous fluid and granitic melt indicate most elements (including Si, Al, F, Be, Li, Rb, Ba, Zr, Nb, Hf and REE) are concentrated in the melt phase (Cullers *et al.*, 1973; Hards, 1976; Flynn and Burnham, 1978; Webster and Holloway, 1980). In experiments conducted at 680 to 850^{o}C and up to 4 kb pressure (Hards, 1976), Cl and Mn were strongly partitioned into the vapour phase and Na, K and Sr display slight solubility in a Cl-bearing vapour phase. Pb and Zn (Webster and Holloway, 1980) and Fe dichlorides (Martin and Piwinskii, 1969; Whitney *et al.*, 1979) may also be abundant in an aqueous fluid separating from a granitic melt.

Flynn and Burnham (1978) found that relative to pure H_2O, the presence of Cl^- and F^- ions increased the partitioning of the REE (particularly the LREE) into the vapour phase. The concentrations of the trivalent REE in a Cl-bearing vapour phase varies in direct proportion to the cube of the vapour chloride molarity, and increases with decreasing pressure. While low concentrations of the carbonate ion and relatively low pressures (<4.0 kb) did not facilitate preferential partitioning of REE into a vapour phase (Flynn and Burnham, 1978), CO_2 vapour in equilibrium with immiscible carbonate and silicate melts at high pressures (5 to 20 kb) was enriched in REE relative to both melts (Wendlandt and Harrison, 1979).

Most of the partition coefficient data relevant to granitic systems appear to have been determined at liquidus or near-liquidus temperatures. Thus, it seems that while separation of a Cl-bearing fluid may occur at high temperatures, a F-rich fluid phase may not be expelled until quite late in the cooling history of the melt. This proposal is supported by experimental work (Kovalenko, 1977) which demonstrated a dramatic increase in the partitioning of Li and Rb into a F-bearing vapour phase in equilibrium with granitic melt as a result of either a drop in temperature of about $200^{o}C$, or an increase in F content of the melt. As a peralkaline granitic melt cools and crystallizes the interstitial liquid would become enriched in F and other volatiles, and if it eventually is saturated in these components a separate fluid phase will be generated. The fact that F-bearing granitic melts are only about 9 percent crystallized at $10^{o}C$ above the solidus (Bailey, 1977) indicates the high solubility of components in these melts. Thus, saturation concentrations of F in these melts will clearly only be approached at near-solidus temperatures.

It is concluded, therefore, that chemical modification of transitional basaltic melts by volatile loss is probably very minor. Loss of a Cl-bearing vapour phase at near-liquidus temperatures could affect some silicic peralkaline melts, although compositions of natural obsidians generally provide little support for this. Partially crystallized peralkaline silicic lavas may be affected to varying degrees by loss of an interstitial F-bearing fluid enriched in Na, K, Fe, Rb, Zr, Nb, Ta, Hf, Th, U and REE.

Volatile Addition

Modification of melt compositions by addition of a fluid phase is less commonly invoked than volatile loss. Macdonald *et al.* (1970) and Bailey and Macdonald (1975) showed that major and trace element characteristics of peralkaline trachyte and rhyolitic obsidians from Eburru Volcano

(Kenya Rift Valley) were not explicable by closed-system crystal $\rightleftarrows$ liquid interactions. They argued that if the lavas represented an evolutionary series resulting from progressive partial melting of a 'basaltic' source rock, then a separate fluid or vapour phase had contributed Na (and possibly Si and Fe), Zr, Rb and F to successive partial melts.

Their data require that in the transition, via progressive partial melting from pantellerite to peralkaline trachyte, Zr, Rb, and F are added in successively smaller amounts to successive melts to maintain a constant ratio with other trace elements, and that Na (and Fe?) are preferentially added to the peralkaline trachytic melts. A more irregular pattern of trace element enrichment might be expected to result from influx of a fugitive volatile phase into successive partial melt products. An alternative interpretation is that the data points below the inflection points in the plots shown in Fig. 3 (Bailey and Macdonald, 1975), represent a series of melts which were undersaturated with Cl, whereas those above the inflection points have suffered loss of an approximately constant amount of a Cl-bearing vapour or fluid with dissolved Na, Fe, Zn and Nb. All of these elements except Nb, partition to some extent into Cl-bearing fluids (see above). Unfortunately, the behaviour of Rb remains unexplained by this model and the system would still appear to require addition of Rb in decreasing amounts in successive partial melts.

Thus, modification of melt compositions by addition of a volatile-rich fluid phase is feasible, although equivocal in the example cited and probably not common in nature.

Magma Mixing

The process of magma mixing has recently acquired a measure of popularity as a mechanism for the genesis of intermediate members of the calc-alkaline series (Eichelberger, 1975,1978,1980; Anderson, 1976; Sakuyama, 1979,1981; Luhr and Carmichael, 1980; Huppert *et al.*, 1982) and mid-ocean ridge basalts or MORB (Donaldson and Brown, 1977; O'Hara, 1977; O'Hara and Mathews, 1981; Dungan and Rhodes, 1978; Dungan *et al.*, 1978; Huppert and Sparks, 1980a,b). Evidence has also been provided which supports the involvement of magma mixing in the genesis of some alkaline rocks (e.g. Brooks and Printzlau, 1978; Shimizu and le Roex, 1982).

The most convincing evidence for the operation of magma mixing is the presence of disequilibrium phenocryst assemblages in the resultant rocks. Shimizu and le Roex (1982) argued that zonation of Cr and Sc in augite microphenocrysts from Gough Island olivine basalts could only be explained by crystallization at different stages from magmas with distinctive trace element contents. Additional evidence of this type may become available from detailed ion microprobe studies. However, the paucity of petrographic or microprobe evidence indicating disequilibrium assemblages in transitional suites which have been subjected to detailed mineralogical investigations (e.g. southern Gregory Rift, Baker *et al.*, 1977; Boina and Erta Ale, Bizouard *et al.*, 1980) suggests that magma mixing, at most, plays a minor role in the genesis of the members of these suites.

Liquid Immiscibility

The process of liquid immiscibility, generally considered to be of little petrological significance following the work of Greig (1927) and Bowen (1928), has attracted renewed interest following the recognition of irrefuteable examples of natural coexisting immiscible silicate melts in the vitric residua of lunar (Roedder and Weiblen, 1970,1971) and terrestrial basalts (De, 1974; Philpotts, 1979). The immiscible granitic and ferropyroxenitic melts described by Roedder and Weiblen (1970) have closely analogous counterparts in the synthetic system K_2O-FeO-Al_2O_3-SiO_2 (Roedder, 1951; Watson, 1976). In addition, leucocratic ocelli which occur in a variety of mafic and ultramafic hosts (Philpotts and Hodgson, 1968; Philpotts, 1971,1972,1976; Ferguson and Currie, 1971,1972) are claimed to be the result of liquid immiscibility. Melting experiments conducted on a mixture of natural ocelli and matrix materials (Philpotts, 1971) demonstrated the presence of a pair of immiscible melts whose compositions closely approached those of the starting materials. Such experiments provide strong evidence for an immiscible relationship between host and ocelli.

Major element compositions of silicic glasses are comparable to those expected from fractional crystallization. However, experimentally-determined partition coefficients for a range of trace elements between immiscible potassic granite and ferropyroxenite liquids in the system K_2O-Al_2O_3-FeO-SiO_2 (Watson, 1976; Ryerson and Hess, 1978), suggest that trace element contents of the most silicic melt fraction resulting from immiscibility should be quite different from those produced by crystal fractionation controls. Watson (1976) found that of the trace elements Ta, Zr, Cr, Sr, Ba, Cs and the REE, all except Cs exhibited preference for the basic Fe-rich melt fraction. In contrast the incompatible trace elements (Ta,Zr,REE) are typically concentrated in residual silicic melts by fractional crystallization (Ferrara and Treuil, 1974; Barberi *et al.*, 1975). These partition coefficients were determined under anhydrous conditions, thereby ignoring possible effects resulting from depolymerization of the melts (Mysen *et al.*, 1980; Anfilogov *et al.*, 1979) and complex formation (Beus, 1958; Bandurkin, 1961; Mineyev, 1963; Fryer and Edgar, 1977) in the presence of volatiles such as H_2O, F and Cl. However, trace element data on ocelli-matrix pairs from Quebec (Eby, 1980) are consistent with the experimental data.

A recent review of the role of liquid immiscibility in igneous processes (Roedder, 1979) indicated that the most common compositional variants claimed to have been produced by this process were mafic or ultramafic and syenitic or rhyolitic types. In this regard the possible role of liquid immiscibility in the genesis of intimately associated gabbro-syenite complexes (e.g. Morotu, Yagi, 1953; Carnarvon Range, Bryan, 1969; Banks Peninsular, Price and Taylor, 1980) invites further investigation. Although volcanic provinces characterized by bimodal basalt-rhyolite volcanism are possible candidates for involvement of liquid immiscibility, suites exhibiting a continuous range of compositions from basalt or hawaiite to trachyte or rhyolite, are unlikely to have been produced by this process.

Liquid immiscibility may, however, play a somewhat lesser role in the late-stage evolution of peralkaline trachytic and rhyolitic melts. Roedder and Coombs (1967) described alkali granite blocks from a trachytic breccia on Ascension Island which exhibit evidence of at least two immiscible liquid fractions. One was a silicate-rich magma and the other a dense saline fluid containing 50 to 70 weight percent NaCl. Separation of a saline fluid possibly carrying complexed incompatible trace elements represents a potential mechanism for significant mass transfer in evolving silicic melts. The silicic melt fraction would be relatively depleted in volatile constituents, alkalies and incompatible trace elements. Such a process may provide an explanation for the highly variable trace element contents of comenditic and pantelleritic lavas from some volcanic provinces which cannot have resulted simply by closed-system fractional crystallization.

Thermogravitational Diffusion

Magmatic differentiation by diffusion of melt components in response to temperature gradients (i.e. the Soret effect) was generally regarded as implausible after Bowen (1928) demonstrated that diffusion rates are too slow to produce significant compositional variations within geologically reasonable periods. More recent determinations of diffusion rates for a variety of magmatic components in anhydrous basaltic and rhyolitic melts at 1 atmosphere pressure (Hofmann and Margaritz, 1977; Margaritz and Hofmann, 1978a,b) confirmed the relatively restricted mobility of ions in igneous melts. Watson (1979d,1981) showed that addition of H_2O greatly enhances diffusion rates at low pressures, and while increased pressure has an inhibiting effect on diffusion rates, this may be counteracted by the presence of only a small amount (~1 wt. percent) of dissolved H_2O. Nevertheless, diffusion processes alone do not seem capable of producing large volumes of magmas with contrasting compositions.

The combined effects of diffusion and convection were recognised as comprising a potentially important geological process by Wahl (1944) and the process of thermogravitational diffusion has recently been proposed as the principle mechanism responsible for compositional zoning in silicic ash-flow tuff units from the south-western U.S.A. and Mexico (Shaw *et al.*, 1976; Hildreth, 1979,1981; Smith, 1979; Crecraft *et al.*, 1981; Bacon *et al.*, 1981; Mahood, 1981a,b). The tuff units are claimed to have preserved in inverse order, original compositional layering in source magma chambers. However, Blake (1981) has argued that this view is too simplistic, requiring unrealistic flow patterns during magma extraction.

The Bishop Tuff, California (Hildreth, 1979,1981) comprises a high-silica calc-alkaline rhyolitic ash-flow tuff characterized by subtle vertical changes in major element chemistry and quite pronounced variations in temperature, isotopic ratios and trace element contents. The source magma chamber is inferred to have been upwardly depleted in Ca,Ti,Fe,K,Al,P,Mg,La,Ce,Nd,Eu,Sr,Ba,Zr,Cu,Ni,Co and V, whereas Si,Na, H_2O,Li,Be,B,Sc,Mn,Ga,Rb,Y,Nb,Mo,Sn,Cs,Ta,W,Pb,Th,U,Sm and the HREE were enriched in the roof zone relative to lower zones. Hildreth (1979) argued that this compositional zoning was inconsistent with fractional crystallization of observed phenocryst phases, partial fusion of likely crustal materials or liquid immiscibility processes. He concluded it had resulted from diffusion of metal ions or complexes through the melt, aided by convective circulation and driven by thermal and gravitational gradients within the magma chamber.

Hildreth (1981) suggested that zoned pantelleritic tuffs from Fantale, Ethiopia and Gran Canaria may have been produced in a similar manner, and that the extreme enrichment in Zr,Zn,Hf,Y,Nb,Ta,Na,Cl and REE which characterize these magmas may be due to more extensive complexing of highly-charged cations and alkalies by F and Cl. The Tala Tuff, Mexico (Mahood, 1981a,b) is apparently zoned from metaluminous rhyolite to mildly peralkaline rhyolite. If the analyzed hydrated glassy specimens are a reasonable reflection of pre-eruptive liquid compositions, the process of thermogravitational diffusion provides a viable alternative mechanism to fractional crystallization for the development of peralkalinity. Interpretation of the chemistry of hydrated glasses is, however, subject to uncertainties regarding the extent of post-eruptive alkali modification and halogen loss (Noble, 1967; Noble *et al.*, 1967). Hydrated glasses are generally depleted in Na and may be depleted or slightly enriched in K relative to non-hydrated equivalents. Therefore, the magma which produced the Tala Tuff was peralkaline in part at least, and may have been entirely peralkaline with a slightly greater molecular excess of alkalies over alumina in the upper part of the chamber. The apparent metaluminous character of the lower-most portions of the magma chamber may simply be an artifact of alkali (Na) loss.

Hildreth (1981) and Mahood (1981a) argued that the silicic melts producing these ash-flow tuffs are volatile-rich although undersaturated in volatiles, and are therefore unlikely to have coexisted with a separate volatile phase within the magma chamber. However, the pressure release accompanying ignimbritic eruptions results in the exsolution of large quantities of volatiles. Sparks (1978b) suggested that 70 to 85 percent of original H_2O dissolved in a silicate melt may be lost before and during eruption for initial H_2O contents of 0.7 to 6.0 wt. percent. The amount of material lost during eruption will obviously be dependent on the composition of the volatile phase and the extent of complexing of metal ions by anionic volatile constituents. It was noted in the section on volatile transfer that Mn is one of the few elements which displays a preference for a Cl-bearing vapour phase in equilibrium with a granitic melt (Hards, 1976). Since Mn was enriched in the early eruptives of the Bishop Tuff (presumably derived from the upper zones of the source magma chamber), it seems that eruption and quenching occurred very rapidly, preventing appreciable compositional modification by volatile loss.

The tendency for strong roofward enrichment of the highly-charged cations in the absence of significant major element variations lends strong support for the involvement of thermal-dependent diffusive processes in the development of the compositional zoning. This process may have been important in the production of highly variable trace element contents which characterize comendites and pantellerites from several transitional alkaline suites (e.g. Comboyne; Knutson, 1975; Jebel Khariz; Gass and Mallick, 1968).

Hildreth (1979) proposed that compositional variations resulting from thermogravitational diffusion may be restricted to the uppermost portions of magma chambers where convection is inhibited by the development of stable density gradients and progressive growth of an increasingly polymerized stagnant zone. The relatively restricted range in major element chemistry typical of most documented zoned eruptives (see Hildreth, 1981, p.10153) supports this proposal, and this mechanism seems incapable of producing a magma chamber zoned from basalt to trachyte or rhyolite. Zonation from trachyte to comendite may, however, be feasible (cf. Noble, 1965). Consideration of the relatively low viscosities typical of basaltic melts (usually $<10^6$ poise, Bottinga and Weill, 1972; Shaw, 1972; Kushiro *et al.*, 1976), and the turbulent convective flow predicted even for small magma volumes (Bartlett, 1969; Huppert *et al.*, 1982), suggests that any diffusive effects would be rapidly obliterated by thorough convective mixing of the melt.

Recent experimental investigations of fluid dynamics in magma chambers (Turner and Gustafson, 1978; Chen and Turner, 1980; McBirney, 1980; Turner, 1980) have resulted in more detailed models of the convective behaviour of magmas in response to thermal, density and compositional gradients in a chamber. Experiments on simple synthetic systems showed that when a fluid with a smooth vertical concentration gradient is subject to either a vertical or horizontal temperature gradient (or both), horizontal layers of uniform concentration and temperature will be generated by a process referred to as double-diffusive convection. Chen and Turner (1980) suggested that a concentration gradient might be initiated in a homogeneous magma body by crystallization of material (more dense than the liquid) on the side walls, thereby releasing less dense melt to rise along the boundary walls due to gravity and accumulate in the upper regions of the magma chamber. Cooling of this compositionally stratified melt is then considered to produce a series of well-mixed convecting layers with different compositions, density and temperature. Mahood (1981a) suggested that the presence of many thin tabular convection cells may aid further compositional zoning because mass transfer by diffusion need only occur at the boundaries between cells.

Although this model is appealing because of the potential to produce a compositionally stratified magma without large degrees of crystallization, the concept is somewhat nebulous in its geological applications and a more detailed understanding of the nature of the compositional stratification which may develop in complex magmatic systems is required before thermogravitational diffusion can be viewed as a viable control in the evolution of melts.

SUMMARY

In the preceding discussion it has been shown that the felsic members of transitional alkaline suites from both continental and oceanic regimes are often more voluminous than their mafic and intermediate associates. Although there is considerable overlap in the major and trace element compositions of the mafic members from many suites, some display significant variations in Fe contents, Na_2O/K_2O ratios and trace element contents which presumably reflect heterogeneities in their respective source regions. 'Basaltic' types (i.e. $100an/ab+an > 50$), well represented in some suites, are notably absent from others, and the most mafic variants in the majority of suites which have $M < 66$ would not generally be regarded as 'primary' mantle-derived melts.

Oversaturated peralkaline silicic volcanics of either comenditic or pantelleritic character are common associates of transitional mafic eruptives in most suites, and mafic or peralkaline trachytes may be the most 'evolved' representatives in a few. There is often considerable variation in trace element contents of the silicic members of particular suites which have similar major element compositions. These differences and the often inordinately large volumes of salic eruptives which occur in some provinces seem to be inconsistent with genetic models involving closed-system fractional crystallization.

Mass-balance calculations for major and trace elements, used to test the feasibility of producing the relatively 'evolved' compositions in a given suite from more mafic associates by crystal fractionation, generally require removal of very large quantities of crystal extracts for which there is little evidence as inclusions within the volcanic succession.

Progressive partial fusion of the more generally accepted upper mantle compositions does not seem capable of producing the spectrum of eruptives represented in these suites. The mafic members of most suites are considered to have been derived by partial melting in the upper mantle and may have been subsequently modified to unknown degrees by high-pressure fractional crystallization. However, the scarcity of high-pressure cognate cumulates in the volcanics suggests that effects due to this process at elevated pressures were minimal. Alternatively, the range of 'primary' mantle-derived melt compositions may be considerably extended to include the relatively 'evolved' mafic types characteristic of most suites by acceptance of a more Fe-rich pristine upper mantle composition.

Progressive partial fusion of lower crustal rocks is also precluded as a mechanism for producing entire suites because of the high liquidus temperatures of the mafic members. However, voluminous silicic volcanics unaccompanied by mafic types may well be products of partial fusion in the lower crust in the presence of an alkali-bearing fluid phase.

The processes of contamination, hybridism and magma mixing are accorded insignificant roles in the genesis of transitional alkaline suites due to the paucity of evidence of disequilibrium assemblages within the volcanics. In addition, trace element compositional data on the silicic variants are inconsistent with an origin involving liquid immiscibility, although separation of an immiscible saline-rich fluid phase may affect the alkali and trace element contents of some of the silicic peralkaline members.

Loss of a volatile phase from partly crystallized peralkaline silicic volcanics may also significantly affect their alkali, Fe and trace element contents, but this process is considered to have had little effect on superheated peralkaline silicic melts quenched to obsidians.

Some of the trace element variations evident in the 'evolved' members of many suites of similar major element composition, which do not seem explicable in terms of closed-system fractional crystallization models, may be attributable to some form of liquid-state differentiation such as thermogravitational diffusion. However, the mechanics of this process in natural magmatic systems are, as yet, poorly understood.